Microstructure and Mechanical Aspects of Multicrystalline Silicon Solar Cells

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VERA POPOVICH

Master of Materials Science, Technical University Hamburg-Harburg, Germany. Geboren te Vladivostok, Russia Dit proefschrift is goedgekeurd door de promotor: Prof. dr. ir. I.M. Richardson Copromotor: Dr.ir. M. Janssen

Samenstelling promotiecommissie:

Rector Magnificus,	voorzitter
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Microstructure and Mechanical Aspects of Multicrystalline Silicon Solar Cells

Ph.D. Thesis

VERA POPOVICH

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...to my Mom and Dad, whose encouragement and inspiration shaped who I am today

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CHAPTER 1

Introduction

"We need to invest dramatically in green energy, making solar panels so cheap that everybody wants them. Nobody wanted to buy a computer in 1950, but once they got cheap, everyone bought them".

Bjorn Lomborg

1.1 Research Background

In recent decades energy production has become a very important technological and political topic. The energy demand is increasing worldwide as a result of the population growth and also due to an increase of the energy consumption per capita [1]. Securing sources for this prospective increase in energy consumption is one of the biggest challenges faced by our generation [2].

Primary energy sources can be split into depleting and renewable sources [1]. Depleting energy sources, like fossil and nuclear, generate up to 78% of the total energy used. However, mankind is now facing the prospect of shortage of fossil fuels and also a trend of increasing environmental pollution has been observed over recent decades [3-5]. Renewable sources like, solar, geothermal and wind energy already contribute about 22% of the global energy supply [6]. Of the different renewable energy sources, only solar energy has the capacity to fill the demand gap. The energy supply from the sun to the surface of the earth is more than five orders of magnitude larger than the global energy consumption. Thus, less than 0.02% of the solar resources are sufficient to entirely replace fossil fuels and nuclear power as an energy source [7-8].

Currently, the world energy structure is undergoing a transition towards renewable energy resources (Figure 1.1). After fossil fuels peak, solar energy will most likely dominate as the main future energy source. Solar energy is projected to supply up to 30% of the world's energy demand by 2050 and it is also predicted to provide about 64% of the electricity supply in 2100, as indicated in Figure 1.1 [9].

Due to the growing demand for renewable energy sources, the production of solar cells has advanced dramatically in recent years. Between 2004 and 2009, grid-connected photovoltaic (PV) capacity increased at an annual average rate of 60%, making it the world's fastest-growing energy technology. Being one of its major players, the photovoltaic industry with crystalline silicon as a dominant segment, is expanding rapidly to meet growing energy demands all over the world [5].

An overview of commercially available photovoltaic technologies with their respective market shares is given in Figure 1.2 [10]. Wafer-based crystalline silicon, including multicrystalline silicon and monocrystalline silicon, is the dominant technology by far, with a market share of 86% in 2009. The abundance of the raw material, together with the high efficiency and longevity of silicon modules will continue to make crystalline silicon one of the most appropriate technologies for massive scale-up.



Figure 1.1 Share of global energy production. Solar will eventually provide for the largest share of energy in global production according to the German Advisory Council on Global Change, 2006 [9].

However, for crystalline silicon (c-Si) cells to satisfy future energy requirements, there is still a significant need for reductions in system costs and improvements in manufacturing to increase throughput and production yield. Thus, in the near future photovoltaic (PV) technology has to compete with other energy sources, both with respect to electricity generation capacity and investment costs. This can be achieved in two ways; by reducing production costs (and materials consumption) and/or by enhancing energy conversion efficiencies (cost / performance ratio). Swanson [11] believes that in the future, further cost reduction will continue to come from the a number of areas including new lower cost silicon production processes, improvement in slicing technologies that reduce kerf loss, thinner wafers, higher conversion efficiency, a higher level of automation, *etc.* [11]. Among these possible improvements, thinner wafers and lower cost of silicon production processes have a particularly large effect on cost reduction.

According to Luque and Hegedus [12], the major cost fraction in producing multicrystalline (mc) solar cell panels is the wafer (non-metallised silicon substrate) production, which accounts for 45% (Figure 1.3). One option for the cost reduction is to reduce the silicon content, thus to move to thinner wafers. However, thickness reduction leads to a high breakage risk of silicon solar cells (metallised silicon substrate). Therefore, a large research focus is currently being placed on the factors influencing the mechanical stability of crystalline silicon solar cells.



Figure 1.2 Different solar-cell technologies by total global market share in 2008 [12].

Figure 1.3 Cost distribution of the photovoltaic module. The wafer production costs take about 45% of the total module price [10].

One of the current technological problems is to identify and eliminate factors contributing to failure, such as thermo-elastic stresses and cracks, leading to the loss of wafer integrity and, ultimately, breakage of Si wafers and cells during the production process. These mechanical issues form the basis of this research.

1.2 Motivation and Specific Research Objectives

Crystalline silicon (c-Si) currently accounts for ~90% of the modules produced worldwide. To achieve grid parity, the point at which the cost of PV-generated electricity is equal to or cheaper than the power from the grid, the target module cost is ~1 dollar per watt. Since the costs of Si wafers alone is currently ~45% of a module [13], the module costs can be significantly reduced by producing high-efficiency solar cells using thinner and lower-cost silicon. Reduction of wafer thickness is a very critical step in reducing the wafer cost per module. In recent years, the thickness of silicon wafers has decreased to 180-200 μ m, which is about 40% thinner compared to the former standard wafer thickness of 300 μ m. However, this wafer-thickness reduction leads to a high breakage rate during the processing of solar cells [14]. The problem is

that the wafers contain defects created by processing steps and these defects reduce the strength significantly. Consequently, a higher breakage rate is unavoidable if thinner wafers are produced with identical fracture strength in combination with the same applied force during processing. In contrast, if identical displacements are applied to thinner wafers, the breakage will be decreased. To improve the wafer fracture strength, further knowledge is needed regarding the fracture behaviour, factors influencing fracture and suitable investigation techniques.

This research focuses on aspects related to the fracture strength of multicrystalline (mc) silicon solar wafers and cells. The aim is to determine which stages during the manufacturing process, from wafer to a complete cell, is critical with respect to the introduction of stresses or cell damage resulting in premature failure. Emphasis will be placed on fundamental understanding of microstructure, fracture strength and stress-state development from a solar wafer to a cell level, as well as the effect of processing conditions on these aspects.

The specific research objectives are addressed in the following six tasks:

- 1. Improve fundamental understanding of the aluminium and silver electrical contact formation and their properties;
- 2. Develop a fracture strength test suitable for thin silicon solar cell samples;
- 3. Investigate effects of various microstructural features on the strength of wafer-based crystalline silicon solar wafers and solar cells;
- 4. Quantify the impact of wafer and Al and Ag layer thicknesses on fracture strength and stress state;
- 5. Study the effect of solar cell processing conditions on fracture strength, solar cell bow and stresses in silicon wafers and solar cells;
- 6. Based on the results, provide indication on how to improve manufacturing, handling and inspection of thin crystalline silicon wafers and solar cells.

1.3 Thesis Outline

This thesis is divided into three main parts; a study of solar cell electrical contacts, investigation of solar wafer and solar cell fracture strength, stress characterization and the effect of processing conditions on these aspects.

Chapter 2 provides a description of silicon solar wafer and solar cell production steps. This chapter also includes particular issues related to solar cell production conditions. The main solar cell concepts and terminology are also introduced.

In chapter 3, aluminium and silver contact formation is discussed and a model is proposed. The chapter starts with a presentation of the state of the art of metallic contact formation mechanisms. This chapter addresses the effect of drying and firing conditions

as well as metallic paste types on properties of rear and front electrical contacts. Furthermore, the relationship between maximum cell bowing and microstructural features is discussed.

Chapters 4 and 5 address two fracture strength tests, which were especially designed for thin solar cell samples. Two experimental arrangements (4-point bending and ring-on-ring) were developed and a complex fracture strength calculation procedure was successfully employed in this research. Particular attention in these chapters is paid to the effect of silicon wafer crystallinity, processing defects, metallic contact firing conditions and layer thicknesses on fracture strength. Furthermore, the effect of silicon wafer surface treatment, including cutting, texturing and polishing is considered in detail. Interpretation of the results obtained in chapter 3 is used to discuss the data obtained in chapters 4 and 5.

Experimental results of residual and applied stress measurements in silicon solar wafers and solar cells are presented in chapter 6. The chapter addresses laboratory x-ray diffraction, synchrotron radiation and Raman spectroscopy stress determination tools, and presents stress characterizations performed on crystalline silicon wafers and solar cells. The results of this chapter are compared and correlated with behaviour reported in previous chapters.

Chapter 7 gives general conclusions of this research and recommendations for future work are discussed following the conclusions.

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CHAPTER 2

Basic Principles and Processing of Wafer-Based Crystalline Silicon Solar Cells

"The energy of the mind is the essence of life".

Aristotle

2.1 Introduction

Crystalline silicon solar cells have the highest efficiency and the most mature technologies of the commercially available solar cells. They offer the lowest cost in terms of dollar per watt. Two types of wafer-based crystalline silicon are used in industry; monocrystalline and multicrystalline silicon. Monocrystalline cells have a higher conversion efficiency than multicrystalline cells, but the costs of monocrystalline wafers are generally higher than those of multicrystalline wafers. Wafer-based crystalline silicon solar cells, with their mature and high efficiency technology are expected to be the dominant product in the solar cells market in years to come [1-3].

The overall goal in the solar cell industry for the next 5 years is to improve the fabrication techniques for low cost, high efficiency wafer-based crystalline solar cells. Thus, this project focuses on the wafer-based crystalline silicon solar cells.

It is well known that silicon is the most commonly used semiconductor material for microelectronic devices and solar cells. Mechanical properties of photovoltaic (PV) silicon wafers and solar cells can be affected by many factors, including distribution and interaction of intrinsic point defects, extrinsic impurities, structural defects, residual stresses induced by processing and the surface conditions. The necessity to improve wafer quality and manufacturing costs results in an on-going effort to develop silicon production technologies and equipment, as well as silicon wafer and solar cell processes. Solar cell processes, the relation between silicon wafer material characteristics and solar cell efficiency, as well as mechanical properties characterization, are areas of on-going research. The current steady reduction in wafer thickness causes larger wafer deformations and easier wafer fracture.

In this chapter, the basics of silicon solar cell as well as of crystalline solar cell processing steps will be introduced.

2.2 Materials and Processing of Silicon Solar Wafers

Although at least several hundred material systems, including combinations of semiconductors, metals, oxides, electrolyte solutions, organic molecules and polymers have been considered for solar cells, the vast majority of all commercial solar cells are made from silicon. The two dominant styles of photovoltaic cells on the market are the crystalline silicon cell design and the thin film silicon cell design [5-6]. The crystalline cell is by far the most developed of the two.

Silicon is an indirect semiconductor with a band gap of 1.124 eV. atoms from group III and V in the periodic table, usually boron and phosphorous, act as dopants in silicon. A phosphorous atom has an extra electron and is called a donor, while a boron atom with an excess hole is called an acceptor. Undoped intrinsic silicon has a resistivity of $\rho = 2.3 \times 10^3 \Omega m$ [2]. Doping increases the electrical conductivity of silicon. Doping concentrations are usually in the range of 10^{15} - 10^{16} cm⁻³, which corresponds to a resistivity between 0.01 and 0.1 Ωm [3].

Silicon cells can be single crystalline, multicrystalline, polycrystalline or amorphous. The key difference between these materials is the degree to which the semiconductor has a regular, ordered crystal structure, and therefore semiconductor material may be classified according to the size of the crystals making up the material [7]. In the beginning of solar cell technology, crystalline silicon solar cells were made exclusively from monocrystalline silicon material. These single crystals can be made by drawing an ingot from a melt of electronic grade silicon (the Czochralski process). The produced ingots are sawn into wafers, which form the basis for solar cell manufacturing. Drawback of this process is the low throughput, which is determined by the crystal growth rate. The low throughput results in high ingot costs [8].

Multicrystalline silicon (mc-Si, also called semicrystalline or polycrystalline silicon) is a cheaper wafer material for solar cells. Table 2.1 presents the various types of crystalline silicon.

Descriptor	Symbol	Grain size	Growth techniques
Single crystal	sc-Si	> 10 cm	Czochralski (cz) float zone
Multicrystalline	mc-Si	1 mm-10 cm	Cast, sheet, ribbon
Polycrystalline	pc-Si	1 μm-1 mm	Chemical-vapour deposition
Microcrystalline	μc-Si	< 1 µm	Plasma deposition

Table 2.1. Terminology for the various types of crystalline silicon (c-Si) [7].

2.2.1 Single Crystalline Silicon

Single crystalline wafers are typically more advantageous for usage in solar cells than multicrystalline wafers due to better electrical performance, but they are also more expensive. Crystalline silicon has a diamond-ordered crystal structure, with each atom ideally lying in a prescribed position. Crystalline silicon exhibits predictable and uniform behaviour, but because of the careful and slow manufacturing processes required, it is also the most expensive type of silicon. The regular arrangement of silicon atoms in single-crystalline silicon produces a well-defined band structure. Each silicon atom has four electrons in its outer shell. Pairs of electrons from neighbouring atoms are shared, so each atom shares four bonds with the neighbouring atoms (Figure 2.1) [7].

Single crystalline silicon is usually grown as a large cylindrical ingot producing circular or semi-square solar cells. The semi-square cell started out circular, but has had the edges cut off so that a number of cells can be more efficiently packed into a rectangular module. As in any crystalline material, the crystal orientation in crystalline silicon is defined by Miller indices. A particular crystal plane is denoted using parenthesis such as (100). Silicon crystals have a cube symmetry and so (100), (010), etc. are equivalent planes and collectively referred to using braces, {100} [9-11].

Similarly, the crystal directions are defined using square brackets, *e.g.* [100] and referred to collectively using triangular brackets, <100>.



Figure 2.1 Single crystalline silicon [7].

In solar cells the preferred orientation is <100> normal to the surface, as this can easily be textured to produce pyramids that reduce the surface reflectivity [12].

However, some crystal growth processes, such as dendritic web <111>, produce material with other orientations. To indicate the crystal directions, single crystal wafers often have a flat side to denote the orientation of the wafer and the doping used.

Single Crystal Silicon Processing

There are two single-crystal growth methods, float-zoning (FZ) and Czochralski growth (CZ). Figure 2.2 compares the characteristics of the FZ and CZ methods. In the Czochralski growth (CZ) method, electronic grade polycrystalline silicon is melted in a crucible (Figure 2.2) [13]. A small silicon seed crystal attached to the end of a spinning rod makes contact with the surface of the molten silicon and a crystal of silicon is then slowly pulled from the melt in a carefully controlled manner so as to maintain the diameter of the ingot and a stable growth front and to prevent spurious nucleation that would result in polycrystallinity.

The resultant round crystals are usually shaped into squares with rounded corners in order to obtain a better usage of the ingot area. The silicon melt reacts to a large extent with many materials. Only silica can be used as a crucible material, because its product of reaction with silicon, silicon monoxide, evaporates easily from the melt. Nevertheless, CZ-grown crystals contain 10^{17} – 10^{18} atoms/cm³ of mainly interstitial oxygen atoms [14].

An alternative crystal growth technique is the float-zone technique (Figure 2.2). A rod of solid highly purified but polycrystalline silicon is melted by induction heating and a single crystal is pulled from this molten zone. This material is of exceptional purity, because no crucible is needed, but it is more costly than CZ material. In particular, it has a very low oxygen contamination which cannot be avoided with the CZ material because of the quartz crucible [15]. However, the main technological disadvantage of the FZ method is the requirement for a uniform, crack-free cylindrical feed rod. A cost premium (100% or more) is associated with such poly rods. At the present time, float-zone technique (FZ) Si is used for premium high-efficiency cell applications and Czochralski growth (CZ) Si is used for higher-volume, lower-cost applications.

An interesting new development concerns tricrystals [16]. These are round crystals consisting of three single crystals arranged like pieces of a pie. They can be grown much faster and have a higher mechanical stability.



Figure 2.2 Single crystal growth techniques [13].

2.2.2 Multicrystalline Silicon

Multicrystalline (mc) Si wafers have a significant cost advantage over monocrystalline Si wafers, due to the more cost-effective crystallisation methods. They are produced by directional solidification of molten silicon. The solidification starts at certain nucleation points, from which small crystallites expand in the growth direction. The size of the crystallites that are formed and the composition and distribution of impurities in the wafers depend on the applied crystallisation technology.

Multicrystalline silicon (mc-Si) wafers consist of single crystalline grains having different crystallographic orientations separated by grain boundaries (Figure 2.3).

Grain boundaries introduce highly localized regions of carrier recombination due to the introduction of extra defect energy levels into the band gap, thus reducing the overall minority carrier lifetime from the material. In addition, grain boundaries reduce solar cell performance by blocking carrier flows and providing shunting paths for current flow across the p-n junction [17].

To avoid significant recombination losses at grain boundaries, grain sizes on the order of at least a few millimetres are required. This also allows single grains to extend from front to back of the cell, providing less resistance to carrier flow and generally decreasing the length of grain boundaries per unit of cell. Such multicrystalline material is widely used for commercial solar cell production.



Figure 2.3 a) At the boundary between two crystal grains, the bonds are strained, degrading the electronic properties. b) A 10×10 cm² multicrystalline wafer. The wafer has been etched, so that grains of different orientation show up as light and dark [7].

Multicrystalline Silicon Wafer Processing

Various techniques for the ingot-based crystallization process have been developed during the past 20 years. They all have the following process steps in common: ingot casting, ingot sizing, and wafer slicing. The dominant techniques are based on directional solidification. Figure 2.4 shows the principles of the Bridgman method, the heat-exchange method and the block-casting technology.



Figure 2.4 The principles of the Bridgman method, the heat-exchange method and block-casting technology to solidify a multi-crystalline silicon block [18].

Silicon is melted and poured into a square crucible. Liquid Si, which is kept in a (high purity) silicon nitride coated quartz crucible is thereby directionally solidified by slowly lowering the crucible from the heated casting frame (Bridgman method), or by extracting heat from the bottom of the crucible with the heat-exchange method. The upper zone of the crucible is kept at a temperature above the melting point of silicon. Thus, a solidification front moves from the bottom towards the top.

The main challenges of the crystallisation process are the maintenance of a planar solidification front, the control of the crystallisation velocity and the avoidance of extensive dislocation formation in the crystal. Because of the contact with the crucible, polycrystalline silicon has a higher impurity content and thus lower carrier lifetime and lower efficiency than monocrystalline silicon. To dates, little or no work has been done on the effect of impurities on mechanical strength of multicrystalline (mc) Si wafers.

A schematic flow chart of mc-Si wafer processes is shown in Figure 2.5 [19].



Figure 2.5 Process flow chart of the silicon-wafer fabrication [19].

After silicon-ingot processing, the top, bottom and side regions of the formed mc-Si ingot are cut away (contouring), and the ingot is then divided into several blocks with a desirable cross section, such as 125 mm \times 125 mm, 200 mm \times 200 mm, *etc.* (portioning). Each of the mc-Si bricks is wire-sawn into a number of mc-Si wafers with a certain thickness, such as 200 μ m.

For the purpose of sawing, blocks are glued to a substrate holder and placed in a multi-wire saw which slices them into the final wafers. Solar cell wafers are mainly cut by a wire that is moving in one direction, whereas wafers for the microelectronic industry are cut by oscillating wires. Cutting in one direction allows higher wire speed between 5 and 20 m/s, but yields less planar surfaces. Smoother and more even surfaces are obtained by oscillating sawing. The wire material is usually stainless steel [20-21].

Cutting is achieved by means of abrasive slurry which is supplied through nozzles over the wire web. The slurry usually consists of SiC hard grinding particles. Silicon is continuously removed through the interaction of the SiC particles below the moving wire and the silicon surface [22-23].

The interaction between the abrasive SiC particles and the crystal yields a distinct damage pattern. The surface structure of the sawn silicon consists of local indentations with a mean diameter of a few micrometers. Consequently, the saw damage consists of microcracks penetrating around 10 μ m deep into the wafer surface and / or a transformed and strained layer in the silicon crystal lattice [24-26].

As wafers become thinner, problems with increased breakage, especially during the sawing process, increase. At 20 wafers/cm and a wafer thickness > 300 μ m, breakage is on the order of 15%. This can rise to in the order of 40% when the wafer thickness is decreased to 200 μ m or up to 60% for a thickness of 180 μ m [24].

It is clear that, as wafers become thinner, a more detailed understanding of the breakage process becomes an important issue.

Defects Associated with Processing of Multicrystalline Silicon Ingots

Inherent to all forms of silicon block crystallization is the inhomogeneous distribution of the wafer characteristics, due to the batch-wise process with changing process conditions. One of the major reasons is the segregation of impurities, which are present because of the high solubility of most materials in the liquid silicon phase [27]. A positive effect of this is a cleaning of the silicon by segregation of impurities to the top of the block. The disadvantages of segregation, however, are the changing oxygen, carbon and doping concentrations in the wafers, which depend on the position of the wafers in the block. Additional contamination from the crucible also results in different wafer characteristics in the areas of the wafer in close contact with the crucible walls (bottom, sides). Together, these phenomena result in a location-dependent behaviour of the silicon wafers, leading to a broadening of the solar cell efficiency distribution, *e.g.* a variation in short circuit current of 5-10% depending on the position of the wafer in a block. No results are available yet on the influence of those defects on mechanical strength of silicon wafers.

As a rule of thumb, it is generally thought that dislocation densities below 10^5 cm⁻² are acceptable for solar cells. This is supported by results from experiments done on float-zone silicon wafers with varying dislocation densities. Below a dislocation density of 10^5 cm⁻², minority-carrier lifetime is high and dislocation-density independent. Between 10^5 cm⁻² and 10^6 cm⁻² there is a transition region, while above a dislocation density of 10^6 cm⁻² minority-carrier lifetime drops rapidly [28, 29]. In block-cast multi-crystalline silicon, dislocation density is typically in the range of or below 10^5 cm⁻². However areas with very high dislocation densities and resulting low minority-carrier lifetimes are also found. These areas normally occur in neighbouring

wafers at identical locations, which suggests that they grow with the solid-liquid interface vertically through the silicon block. Figure 2.6 represents a global defect model for photovoltaic silicon.

Some of the major cell-performance-limiting impurities are the transition metals like Fe, Cu, Ni, Cr and Au. A similarly important role is played by oxygen. Various oxygen or oxygen-containing defect clusters, showing strong recombination activity, may also form in mc-Si [29]. Especially the bottom part of an ingot is often contaminated with oxygen. Extended defects, such as grain boundaries and dislocations, might carry electrical charge and then act as efficient recombination centres. The electrical activity of these defect centres is largely influenced by their interaction with impurity atoms and usually increases with increasing impurity concentration [31]. Cast multicrystalline Si has been the topic of intense investigations in order to understand the microscopic nature of the defects and to find strategies for their suppression during crystal growth or for their removal during subsequent solar cell processing. Buonassisi [32], one of the leading researchers in the area of silicon defects, revealed the distribution and elemental identification of efficiency-limiting impurities in multicrystalline silicon solar cells (Figure 2.7).



Figure 2.6 Global defect model for photovoltaic silicon [30].

The effect of impurities on multicrystalline solar cells is complex. Impurities can preferentially segregate to grain boundaries and defects such as dislocations, where their electrical behaviour may be quite different than when dissolved in the interior of a grain. When the oxygen, nitrogen, or carbon levels exceed the solubility limits in solid silicon, they will precipitate to form a separate phase. These precipitates may also serve as sinks for impurities. The exact nature of the precipitation, redissolution, diffusion, outgassing, and interaction between a host of impurities and defects sometimes appears hopelessly complicated. There are clear instances where these effects can be exploited to expel harmful impurities from electronic devices or else sequester them as precipitates and grain boundaries where they do less harm to the solar cell.



Figure 2.7 Defect-etched mc-Si, revealing a plethora of structural defects [32].

Impurity gettering in integrated circuits is a well-established technique. In this case, oxygen precipitates are intentionally created in the bulk of the silicon in order to getter impurities away from the top surface region of the wafer [33]. Unfortunately, due to the relatively weak optical absorption of silicon, solar cells need to collect photogenerated charge carriers generated deep (> 100 μ m) in the silicon wafer. Thus, denuding a shallow surface region of impurities while increasing the impurities in the bulk of the wafer (as done in integrated circuits) is not an option for solar cells. From this perspective, it is perhaps fortunate that surfaces in the form of grain boundaries and precipitates exist throughout the bulk of a multicrystalline silicon solar cell, as they may be useful "sinks" for impurities in gettering processes.

Several techniques have been devised to remove impurities during solar cell processing. Mobile impurities can be pulled to the surface by phosphorus gettering [15], which occurs during emitter diffusion. Immobile point defects are deactivated by hydrogen passivation. Atomic hydrogen can diffuse into silicon even at relatively low temperatures. Processed wafers are exposed to atomic hydrogen produced in a plasma discharge. These methods will be discussed in more detail in the next subchapter.

The lifetime distribution of carriers in a multicrystalline silicon block presented in Figure 2.8, which shows that lower lifetime regions are to be found near the edges of the ingot [34]. It is obvious that the defective outer edge of the ingot is the result of interaction between the quartz crucible and the silicon melt during solidification. Prior to wafering, the edge regions are typically removed from the ingot which results in a lower process yield.



Figure 2.8 Lifetime distribution in silicon block cast. Picture is from application notes of Semilab equipment [34] (red colour corresponds to low level of lifetime, blue to high level).

In contrast to electrical properties, there is still a lack of knowledge regarding the effects of crystallinity, casting defects and impurities on mechanical properties of cast silicon wafers.

2.3 Production of Screen-Printed Multicrystalline Silicon Solar Cells

Currently, the industrial production of solar cells is dominated by the screenprinted solar cell technology. The success of this technology within the present solar industry stems from the fact that it can achieve reasonably good conversion efficiency through simple manufacturing processes that are applicable to both monocrystalline and the lower-cost multicrystalline silicon wafers. The screen-printed solar cell technology was first developed in the 1970s, but since then has improved significantly in terms of processing technology and final conversion efficiency. The wide availability of relatively cheap, standardised manufacturing equipment combined with mature understanding of the technology makes this technology highly suitable for large-scale production of solar cells.

Almost all screen-printed solar cells in commercial manufacturing use *p*-type single or multicrystalline Si wafers as substrates with thicknesses between 180 and 200 μ m. After chemical cleaning of the surface and random pyramid texturing, the Si-wafer

surface is subjected to thermal diffusion with *n*-type impurities, such as phosphorus, in a high temperature furnace to form the *p*-*n* junction. Following an edge-isolation process to remove excess phosphorus diffusion along the edges of the wafer, a silicon nitride (SiN_x) layer is deposited on the front surface of the solar cell for both surface passivation and anti-reflection coating. Finally, full-surface aluminium (Al) and silver (Ag) finger grid patterns are screen printed on the rear and front surface of the solar cell respectively, followed by a quick metal co-firing in a belt furnace to form a back surface field (BSF) and good ohmic contact between both metals and the Si. A schematic of the cross section of a typical screen-printed solar cell design is shown in Figure 2.9.



Figure 2.9 Schematic drawing of a solar cell with a silicon nitride antireflection coating and screen-printed silver front and aluminium rear contacts [34].

A solar cell consists of an n-type and a p-type region. A p-n junction is formed between the two semiconductor regions of opposite doping types. When light illuminates the solar cell, photons of energy higher than the band gap will excite electrons that flow from the n-type silicon to the p-type silicon through an external circuit.

Most conventional H-pattern screen-printed solar cells fabricated in the industry today use the process sequence summarized in Table 2.2 [35]. In the first step, the wafer is etched and cleaned to remove damage from sawing. Simultaneously, texture etching of the surface is performed to reduce the reflectivity of the surface. The second step involves phosphorus diffusion to form a p-n junction. In this step, also phosphorous gettering is performed at ~ 800 °C allowing metallic impurities to diffuse to the phosphorous layer where their solubility is increased. Then an antireflective coating, usually SiN_x, is deposited on the front side to absorb light more effectively. The

antireflective coatings usually also contain hydrogen that diffuses into the bulk and passivates defects and impurities in the cell during the firing step.

The last step is front side and rear side metallization. For a p-type solar cell, usually an Al paste is used for the rear side contact and an Ag paste for the front side. A short firing treatment allows the metal contacts on the front side to penetrate the antireflective coating.

In the following sections, the process and the most commonly used equipment for each process step will be summarized.

Table 2.2. Process sequence for screen-printed solar cells [35].

(1) Saw damage removal, texturing, and cleaning of <i>p</i> -type silicon wafer
(2) Phosphorus diffusion
(3) Plasma edge isolation
(4) Phosphorus glass removal (and single-side etching for edge isolation)
(5) Silicon-nitride deposition
(6) Ag screen printing of the front contact and drying
(7) Al/Ag screen printing of the rear busbars and drying
(8) Al screen printing of the rear and drying
(9) Co-firing of the front and rear contacts

2.3.1 Saw-Damage Removal, Texture, and Cleaning

After the casting, contouring and portioning, as already discussed in the previous section, silicon blocks are cut into very thin slices by a multi-wire saw (MWS).

After sawing the wafers are cleaned, rinsed and dried. Wire sawing induces small cracks penetrating around 10 μ m deep into the wafer surface, as shown in the cross-section image of Figure 2.10. Saw damage has to be removed from the wafer surface, because it reduces the mechanical strength of the wafer and increases recombination of electron-hole pairs in the surface region.



Figure 2.10 Cross-section image of a wafer after wire sawing [35].

Alkaline [36] or acidic [37] solutions as well as plasma etching can be used for saw-damage removal. In addition, this process step is normally used to form a surface texture that reduces the total reflection of the wafer. After etching, the wafer is cleaned to remove metal and organic contaminants that would cause an increase of surface and bulk recombination during the subsequent high-temperature process steps.

A solution of sodium hydroxide, NaOH, or potassium hydroxide, KOH, in water is normally used for alkaline saw-damage removal on multi- or monocrystalline silicon wafers. The etching reaction can be summarized as

$$\mathrm{Si} + 2\mathrm{H}_{2}\mathrm{O} + \mathrm{HO}^{-} \to \mathrm{HSiO_{3}^{-}} + \mathrm{H}_{2}$$

$$(2.1)$$

and takes place in three reaction steps: (i) oxidation of silicon; (ii) formation of a solvable salt, and (iii) dissolution of the salt in water.

Alkaline etching has different etching rates for different crystallographic orientations. For monocrystalline silicon wafers with a (100) surface orientation, this anisotropy results in the formation of small pyramids with square bases randomly distributed over the wafer surface [34].

Alkaline saw-damage removal, texturing, and cleaning are performed in batch processes. Wafers are held in cassettes that allow chemicals to wet the entire surface. These cassettes are moved automatically from one tank to the next filled with chemicals and water for etching, cleaning, rinsing, and drying. For process control, the loaded cassettes are weighed before and after etching to determine the etching depth from the difference in weight.

Alternatively, acidic texturing is an isotropic process. It is not dependent on the crystallographic orientation and it is therefore suited for saw-damage removal and texturing of multicrystalline silicon. A solution of HF, nitric acid (HNO₃), and water is introduced for saw-damage removal and texturing of multicrystalline silicon wafers [34]. The reaction takes place in two reaction steps:

(i) oxidation according to

$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 2H_2O + 4NO \text{ and}$$
 (2.2)

(ii) etching of silicon oxide according to

$$3\operatorname{SiO}_2 + 18\operatorname{HF} \to 3\operatorname{H}_2\operatorname{SiF}_6 + 6\operatorname{H}_2\operatorname{O}.$$
(2.3)

A typical process sequence is as follows: (i) saw-damage removal and texturing in H₂O, HNO₃, and HF, (ii) spray rinse, (iii) KOH to etch off porous silicon that was formed during acidic texturing, (iii) spray rinse, (iv) HCl clean, (v) spray rinse, and (vi) air drying.

Figure 2.11 shows SEM micrographs of an alkaline and acidic-textured multicrystalline silicon wafer.

The solar cell efficiency depends strongly on the etching depth of the acidic texture. If the etching depth is too shallow, crystal defects remain and the open-circuit voltage as well as the short-circuit current is reduced. If the etching depth is too deep,

the surface roughness increases decreasing the open-circuit voltage and short-circuit current (due to increased surface recombination). The best solar cell efficiency has been found for an etching depth between 4 and 5 μ m [38]. A solar cell efficiency improvement of 7% relative has been demonstrated if acidic-etched wafers were used instead of NaOH etched wafers [35].



Figure 2.11 a) Top view of a wafer after alkaline texture in KOH, IPA (isopropyl alcohol), and water forming random pyramids. b) SEM microscopic image of the surfaces of an acidic-textured multicrystalline silicon wafer [36].

2.3.2. Phosphorous-Diffusion

In the next step the n-type emitter layer is formed in the wafer, usually by way of diffusion of phosphorus atoms.

Most commonly used in the photovoltaic industry is a tube diffusion process. The wafers are placed vertically into a quartz boat. The boat moves into a quartz tube and is heated up to around 800 to 900 °C. Nitrogen flows as a carrier gas through a bubbler filled with liquid phosphorus oxychloride, POCl₃. The gaseous POCl₃ is mixed with O_2 and conducted directly into the heated quartz tube. Phosphorus oxide, P_2O_5 , is then deposited onto the wafer surfaces, while the released Cl_2 removes metal impurities. At the temperatures involved, phosphorus diffuses into the silicon forming a p-n junction with the p-type base.

2.3.3 Silicon-Nitride Deposition

As pointed out before, defects, impurities and grain boundaries in the silicon can reduce solar cell efficiencies by facilitating recombination of electrons and holes, generated in the semiconductor. Impurities can be inactivated by gettering. Grain boundaries and defects are usually inactivated by bulk passivation (also called hydrogen passivation). In this process hydrogen atoms created in a plasma diffuse into the wafer to inactivate recombination centres. The front surface is yet another facilitator of recombination processes. At this location, the recombination velocity can be reduced by applying a surface-passivation layer like SiO₂ or SiNx. Usage of a layer of silicon nitride has yet another advantage, since it can also act as an antireflective coating. Antireflective coatings can also be formed by TiO₂, Ta₂O₅ and several other substances. Silicon nitride coating has the advantage that besides surface passivation and

antireflective coating the process also allows for hydrogen passivation. In the PECVD (plasma enhanced chemical vapour deposition) process the wafers are placed in a reaction chamber in which an electromagnetic discharge is maintained in an atmosphere consisting of silane (SiH₄) and ammonia (NH₃) diluted with nitrogen. At a temperature of 400-450 °C the silane and ammonia react together to form a complex which is deposited on the wafers. Subsequently the hydrogen from this complex diffuses into the wafer, leaving a layer of SiNx on the surface. At ECN the silicon nitride deposition onto the wafer is performed at 375 °C.

A layer of silicon nitride, SiN_x :H, with up to 40 at.% of hydrogen [39] is deposited onto the front side of the solar cell as an antireflection coating. After screen printing, the Ag contacts are fired through the silicon nitride layer. To minimize optical losses, the SiN_x film has a thickness of around 75 nm and a refractive index of around 2.05. In addition, SiNx:H serves as a good surface passivation to reduce recombination losses of the emitter [40-41]. Furthermore, hydrogen is released from the hydrogen-rich SiN_x :H film during a post deposition anneal, reducing bulk recombination in multicrystalline silicon.

2.3.4 Screen Printing

Screen printing constitutes a fast and reliable metallization technology. For solar cell metallization three printing steps are performed, which take place at high temperatures. In the first step, two bus bars are printed onto the rear side using Ag/Al paste, followed by printing the remaining area with Al paste. Besides metals (Al and Ag, 70-80%) screen-printing pastes contain solvents, resins, fillers and glass frit. Glass frit is used as a binder for the fired paste to silicon wafer. Resins support the solids and solvents are used to dissolve the resins.

The Ag and Al paste consists of:

- (i) Ag or Al powder (70 to 80 wt.%),
- (ii) lead borosilicate glass PbO-B₂O₃-SiO₂ (1 to 10 wt.%), and
- (iii) organic components (15 to 30 wt.%).

The front-side structure is either printed before or after the rear-side printing process. In-between the printing steps, the drying of the paste takes place in a conveyor belt furnace [42-43].

The printing step itself, in which the paste is forced through the openings of the emulsion layer (used to define the pattern) onto the surface of the wafer, can be subdivided into three consecutive phases (see Figure 2.12). In the filling phase, the open areas of the screen are flooded by moving a squeegee (floodbar) over the surface of the screen. In the contact phase a vertical force is applied to the printing-squeegee, pressing the screen onto the wafer and forcing paste through the screen openings. The paste sticks to the substrate due to adhesion forces. In the final phase, the paste is released

from the screen [44-48]. The quality of the print image depends mainly on the screen, the paste and on the printing parameters.

The size of the frame needs to be large enough that the mesh releases from the substrate and paste during the snap-off (see below). In order not to damage the mesh, the screen tension must be smaller than the elasticity limit of the wire material used [47].

The danger of screen breakage increases strongly with reduced finger cross section area and increased finger separation distance. That is the reason why mainly steel wires are used possessing a high tensile strength. In addition, electrostatic charging of steel wires does not occur.



Figure 2.12 Screen-printing process: (1) The openings in the screen are filled with paste; (2) the squeegee brings the screen into intimate contact with the substrate and presses paste through the openings. (3) While the screen is lifted up, paste is released from the screen and sticks to the substrate [49].

As illustrated in Figure 2.13, the screen consists of an aluminium frame, a mesh of wires being clamped to the frame and an emulsion layer.



Figure 2.13 Structure of a screen, consisting of the mesh, the emulsion layer and the frame [48].

2.3.5 Firing of Electrical Contacts

Front Silver Contact

After the paste has been deposited, the wafers are fired in a belt oven. Subsequently the cells pass a zone with a temperature up to 120-150 °C, in which the solvents are evaporated, a 300-400 °C zone, in which the resins are burnt, and a zone with temperatures over 600 °C, in which the glass fritt is sintered. The fritt has been prepared for use by melting (usually together with at least one other material, often a pure silica, to form a fused compound) and grinding. Emissions that occur during the firing process are evaporated solvents and burnt organic compounds [46-47].

The Ag powder sinters during firing and causes good lateral conductivity of the fingers. The $PbOB_2O_3$ -SiO₂ frits are essential for the contact formation. $PbO-B_2O_3$ -SiO₂ etches through the silicon nitride antireflection coating, promotes the adhesion of the Ag contact to the silicon, reduces the melting point of Ag, and prevents Ag to diffuse into the p-n junction causing junction shunting and regions of high recombination. However, the PbO-B₂O₃-SiO₂ layer formed between the conducting finger and the emitter is also a reason for a poor contact resistance of the screen-printed Ag contact [48-49].

The organic components determine the rheology of the paste. The viscosity of the paste reduces with the impact of the squeegee movement. To be extracted easily from the screen, it has to stay at a low viscosity level to form a continuous finger (no string of pearls appearance), but then the viscosity has to increase again to keep a high aspect ratio and avoid that the finger flows apart.

At the end of the printing process, the front and the rear contacts are fired simultaneously in a firing furnace (co-firing).

Rear Aluminium Contact

Aluminium paste is used for the formation of a good ohmic rear contact and a back-surface field (BSF) to the p-type silicon (Al doping of the rear surface region during firing). The doping profile and thickness of the back-surface field (BSF) layer, the rear surface reflectivity, the back-surface field (BSF) homogeneity, and the wafer bow depend critically on the amount of Al paste printed onto the rear side of the wafer, the peak firing temperature, the type of paste and the oxygen supply during firing [50]. A schematic temperature profile for firing wafers is shown in Figure 2.14, featuring a burn-out zone to burn organic binders and a sintering zone with a set peak temperature. In this zone, the front contact and rear contact are formed and the hydrogen of the SiN_x:H layer is released into the bulk of the wafer to passivate electrical defects.


Figure 2.14 Temperature profile for firing through a silicon-nitride layer in a belt furnace. After the burn out of the organic components (binders) the front contact and at the same time the BSF and rear contact are formed in the peak firing step [50].

2.3.6 Bowing of Screen-Printed Silicon Solar Cells

All of the efficiency improvements such as, surface texturing, silicon-nitride optimization, and the selective emitter formation will work equally well with thin cells as with today's standard thickness. However for thin cells, attention should be paid to the Back Surface Field (BSF)/rear contact combination, because of their effect on the mechanical behaviour of the cell and the fact that, as the silicon becomes thinner, the rear surface properties have a larger impact on cell performance [51]. Bowing develops during the contact-firing process, where elastic stresses result from thermal expansion coefficient mismatch of the Ag and Al metallization and the Si, as well as from shrinkage or densification stresses. An amount of bow (deflection at the centre of the wafer from the mid-point of the substrate to the plane connecting the wafer edges) of 1 mm or less is generally considered acceptable for module assembly. However, with thin cells the bowing becomes excessive. Hence thinner cells require the development of a new rear surface process [51-53].

Recently, there has been a lot of work performed on understanding the bow phenomena and developing techniques for bow reduction. Two different types of alternative thin cell rear processes are under study, *i.e.* low bow Al paste and a passivated rear surface. Progress has been made in the development of Al pastes yielding reduced bow [53-54]. Nevertheless, a sufficiently thick Al-BSF layer also requires relatively large amounts of screen-printing paste, representing a significant share of the cost for a solar cell.

2.4 Conclusions

The strong need in Photovoltaics (PV) to minimize the manufacturing costs drives multicrystalline silicon wafer manufacturers to improve the production efficiency and product quality.

The necessity to improve on wafer quality and manufacturing costs results in an on-going effort to further develop production technology and equipment, as well as silicon solar wafer and solar cell processing procedures. With respect to these procedures, the relationship between silicon-wafer material characteristics and solar cell efficiency, as well as mechanical properties characterization is an area of on-going research. It is clear, that the steady reduction in the wafer thickness causes increasing wafer deformation and easier wafer fracture.

Based on the overview given in this chapter, it can be concluded that the major stress and microcrack-inducing processes are wire sawing and screen printing of metallic contacts. Although the knowledge on silicon wafers developed by the electronics industry is inherited, the complex interaction between impurities, crystal structure and their resulted behaviour during solar cell processing, as well as the large variation between solar cell processes, make it very difficult to predict the mechanical stability of solar cells. This has resulted in the situation that there is no generally accepted set of wafer parameters available that assures the quality of a silicon solar cell [4]. Another problem is the lack of appropriate mechanical stability characterization techniques that are well adjusted to solar cell industries. Furthermore, there is insufficient fundamental understanding of material behaviour in silicon solar cells and of the effect of different processing parameters influencing the microstructure and mechanical properties of the entire solar cell.

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CHAPTER 3

An Improved Understanding of Aluminium and Silver Electrical Contact Formation and Its Properties

"Anyone who has never made a mistake has never tried anything new". Albert Einstein

3.1 Introduction

Due to pressure from the photovoltaic industry to decrease costs of solar cell production, there is a tendency to reduce the thickness of silicon wafers. Unfortunately, wafers contain defects, created by the various processing steps involved in solar cell production, which reduce the strength of the silicon wafer significantly. A higher breakage rate is to be expected if thinner wafers are produced with identical fracture strength in combination with the same loading during processing. The most critical processing step during the manufacture of screen-printed solar cells is the firing process, during which the screen printed aluminium and silver layers are simultaneously fired in order to create electrical contacts. Residual stresses are generated within the cell due to mismatch of thermal expansion coefficients and different mechanical behaviour of the materials used in the metallic contacts. The wafer bows and forms a convex or concave body upon cooling, which mechanically loads the cell and may cause fracture [1].

This chapter is based on:

- 1. V.A. Popovich, M. Janssen, I.M. Richardson, T. van Amstel and I.J. Bennett, Microstructure and mechanical properties of aluminium back contact layers, Solar Energy Materials and Solar Cells, 95 (1), January 2011.
- 2. V.A. Popovich, M.P.F.H.L. van Maris, M. Janssen, I.J. Bennett, I.M. Richardson "Understanding the properties of silicon solar cell aluminum contact layers and its effect on mechanical stability", Materials Sciences and Applications, 4(2), February 2013.
- 3. V.A. Popovich, T. van Amstel, I.J. Bennett, M. Janssen, I.M. Richardson; Microstructural and mechanical characterisation of Al back contact layers and its application to thermomechanical multiscale modelling of solar cells. 34th IEEE, Philadelphia, USA, June 9-12, 2009.
- 4. V.A. Popovich, W. Verwaal, M. Janssen, I.J. Bennett and I.M. Richardson; Application of x-ray computed tomography in silicon solar cells. In: Proceedings 35th IEEE Photovoltaic Specialists Conference (PVSC), Honolulu, Hawaii, June 20-25, 2010.

As the thickness of silicon wafers is reduced, cell bowing becomes more pronounced and poses more problems during different processing steps. It is possible to decrease bowing by reducing the amount of aluminium paste or by changing the paste chemistry and firing conditions. However, there is a limit below which screen-printed aluminium paste will lead to a non-uniform back surface field layer, influencing the electrical properties of the cell [2-4]. It is important to find a compromise between electrical properties, strength and costs of the solar cell. To achieve this, it is necessary to have a better understanding of microstructure, stress development and mechanical properties of the cell.

The main focus of this chapter is the analysis of aluminium and silver metallic contacts on a macroscopic as well as on a microscopic level. In this chapter the results are reported from an investigation of the microstructure and mechanical properties of the aluminium at the rear side and silver at the front side of the solar cell. The effect of the processing parameters on the formation and homogeneity of the Al and Ag contact layers is described. The results are summarized in the conclusions and will serve as reference input parameters for the following chapters.

3.2 State of the Art of Electrical Contact Formation

Silver and aluminium contacts are fabricated with screen-printing and rapid thermal processing (RTP), which is the most widely used contact-formation technique for commercial solar cells. The cell passes through a high temperature (peak close to 850 °C) belt furnace to consolidate the thick films to produce the ultimate device.

3.2.1 Aluminium Rear Side Contact Formation: State of the Art

The equilibrium state at the Al-Si interface is described by the Al-Si phase diagram shown in Figure 3.1 [11]. During the firing process, the organic solvents of the paste are first burnt out before the temperature reaches the eutectic temperature of Al and Si (577 °C) [12]. When the temperature increases above the eutectic temperature, Al and Si start to form a "liquid pool" of Al-Si [12, 13] at their interface. The concentration of Si in Al increases with increasing firing temperature according to the phase diagram and at the peak temperature, the maximum amount of Si dissolved into Al is reached. During the cooling process, Si starts to be rejected out of the Al-Si mixture to satisfy the equilibrium concentration indicated by the phase diagram. When the temperature drops below the eutectic temperature, the mixture solidifies to a eutectic layer containing 12.6% Si. The Si rejected from the liquid during the cooling process contains about 1% Al and epitaxially forms the Al p+ layer.



Figure 3.1 Al-Si Phase Diagram [11].

The alloy formation between the Al metal and Si semiconductor is achieved by interdiffusion between Si and Al atoms at the interface (contact area) [13]. During firing a higher amount of silicon will travel into aluminium than vice versa, since the solubility of silicon in aluminium is much higher than that of aluminium in silicon [11, 12].

A detailed model for the formation of the screen-printed rear contact was given by Huster [14] and divided into 5 stages:

1) The aluminium paste consists of aluminium particles of 1 to 10 μ m diameter, a glass frit to enhance sintering, organic binders and solvents. After drying (removal of solvents) a porous paste matrix with a filling of 50 to 70 % is attached to the surface by the binders. A typical amount of aluminium deposition is 6 to 7 mg/cm² (40 μ m thickness) [15].

2) Melting of Al starts at 660 °C. Soon after melting, all Al paste particles reach thermal equilibrium and Si dissolves in Al.

3) At the peak temperature almost 30% of the liquid phase consists of silicon. On the wafer surface there is a "lake" of liquid Al-Si. Huster in [14] suggested that from this lake the BSF is subsequently grown epitaxially and in order to achieve a closed BSF it is necessary to have a full coverage of the rear surface by this lake.

4) During the cooling, process step (3) occurs in the reverse direction; that is, Si is rejected from the melt to recrystallize epitaxially on the wafer surface building up the Al-doped layer (Al BSF).

5) After reaching the eutectic temperature of 577 °C, the remaining liquid phase solidifies instantly.

However this model was not confirmed with any experimental results, neither were the composition and mechanical properties of the reaction layers obtained. The detailed formation and microstructure of Al and BSF layers were not discussed. In the following paragraphs, the aluminium rear contact formation for solar cells, as well as properties of the layers are described and a detailed model of the Al back contact will be proposed. Furthermore, the effect of processing parameters on the uniformity and formation of the Al contact will be described.

3.2.2 Silver Front Side Contact Formation: State of the Art

A majority of the silicon solar panels manufactured today use multicrystalline (*mc*) cells with a planar p-n junction. To reduce optical reflection loss, the sun-facing top surface of these cells (the emitter) is textured and covered with a ~80 nm SiN_x:H anti-reflection coating (ARC). Current collection from the Si emitter is achieved with low cost thick-film Ag conductor to form the front-side Ag contact [22]. Front-side (FS) metallization is an important step in standard crystalline Si (c-Si) industrial cell production. Ag thick-films have been widely used for the front side metallization of Si solar cells. These pastes primarily consist of Ag powder, glass frits, and vehicles for the desired rheological properties of the pastes. Although only a tiny quantity of glass frits is added to the Ag paste, these frits enable the connection of the metal film to the Si wafer during firing. Thus, it is important to understand the effect of firing parameters on the contact formation [22-24].

In order to establish contact to the emitter, the printed Ag paste must remove the SiN_x :H coating. As Ag does not react with SiN_x :H, the paste contains various low melting glasses (*e.g.* PbO or ZnO) which when melted, can chemically etch through the SiN_x :H coating. The resulting front-side Ag contact in *mc*-Si cells is characterized by a complex interfacial region containing a glassy layer, Ag colloids or crystallites, and a textured surface topography [24, 25]. The silver contact formation has a very significant impact on the solar cell costs, because it influences cell performance, throughput and mechanical stability. Therefore, the goal in this section is to improve the fundamental understanding of the formation of screen-printed Ag contacts and influencing factors.

The existing understanding of contact formation and current transport of screenprinted contacts are given by Ballif *et al.* [22, 24] and Schubert *et al.* [25, 26]. According to the above references, below 600 °C the organic components burn out and above 600 °C the contact formation takes place, see Figure 3.2:

- 1) Lead borosilicate glass melts, wets, and etches the SiN surface while the Ag particles sinter to a conductive film.
- 2) A redox reaction between PbO and Si takes place forming liquid Pb. Ag and Si dissolve in liquid Pb etching inverted pyramids into the wafer surface.

- 3) During cooling, Ag and Pb separate according to the phase diagram. The Ag recrystallizes epitaxially in the inverted pyramids forming Ag crystallites at the wafer/glass interface. The Ag crystallites form isolated ohmic contacts to the emitter.
- 4) The current transport between these Ag crystallites into the sintered Ag thick film is assumed to take place at interconnections between crystallites and the sintered film, tunnelling through ultra-thin glass regions or multistep tunnelling via metal precipitates that are formed in the glass layer during cooling.

Many mechanisms have been proposed to explain how contact formation occurs [23-31]. The general understanding of the mechanisms agrees that the glass frit play a critical role in front-contact formation. Silver and silicon are dissolved in the glass frit upon firing and when cooled Ag particles recrystallize [25]. It has been suggested that Ag crystallites serve as current pickup points and that conduction from the Ag crystallites to the bulk of the Ag grid takes place via tunnelling [22, 24].

It was further suggested that lead oxide is reduced by the silicon. The generated lead then alloys with the silver and silver contact crystallites are formed from the liquid Ag-Pb phase [25]. Due to the non-uniform features of the contact interface, more evidence and further study of the microstructure is still needed. The objective of the second part of this chapter is to improve the understanding of front side contact formation based on an analysis of the Ag-bulk/Si contact structures resulting from different firing conditions.

In this section the experiments and results are presented and summarised in an improved model of Ag contact, including microstructural and elastic properties of the phases formed.



Figure 3.2 Current transport from the Si emitter to the Ag grid via a) direct connection between Ag crystallites and the Ag bulk, tunnelling through ultra-thin glass regions, and b) conduction within the glass layer via tunnelling between metal precipitates [29].

3.3 Experimental Procedure to Study Electrical Contacts: Materials and Methods

Processing conditions

Silicon wafers of $156 \times 156 \text{ mm}^2$ and a thickness of 200 µm were sliced off a single multicrystalline silicon block. In this study, only wafers from the middle of the block contributed to the results. A standard industrial cell process, presented in Figure 3.3, was used and the screen printing on the rear or front sides was performed in the conventional H-pattern manner with a 165 mesh screen. The alloying is performed (after drying the paste) by firing the wafers in a lamp-heated conveyor-belt furnace. The firing parameters are set well above the melting temperature of Al, 660 °C. To examine the influence of the type of aluminium and silver pastes on bowing and microstructure, three different commercially available aluminium and silver pastes were used (designated as A, B and C). Two drying temperatures (250 °C and 350 °C) were chosen in order to investigate the influence of metal paste drying conditions on the homogeneity of Al back contact layers. The effect of firing conditions was examined by applying three different peak firing temperatures (750 °C, 850 °C and 950 °C) to both Al and Ag contacts.



Figure 3.3 Industrial solar cell process used for screen printing/firing of Ag and Al metallic contacts.

To analyse the effect of the silicon wafer surface roughness on the Si-Ag front contact formation, three types of specimens were prepared from neighbouring wafers. All the samples were taken from the as-cut state and divided into three groups depending on the pre-processed surface condition:

• the as-cut state, thus including the saw-damage layer.

• the as-cut wafers, which are subsequently textured by an industrial acid texturing/etching process, that includes a two-step texturing in a $HF/HNO_3/CH_3COOH$ acid bath. This serves two main purposes: to remove the damaged layer and to create a highly textured silicon surface in order to trap the light.

• the as-cut wafers, which are subsequently chemically polished (15 μ m removal from both wafer sides in a HF+HNO₃ bath for 60 s).

In order to investigate the Ag/Si interface layer and glass phase distribution within this layer, the following etching steps were applied:

a) no etching and initial configuration – as fired condition.

b) etching with *Aqua Regia* (AR): the Ag finger is removed and the glass and the silver beneath remains.

c) subsequent etching with AR and HF: the glass is also removed and the silver underneath the glass still remains.

d) subsequent etching with AR, HF, and AR: all silver, glass, and silver beneath the glass layer is removed and only the bare emitter remains.

Microstructural Analysis

A JEOL JSM 6500F scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) was used for microstructural analysis of intentionally broken samples of a conventional H-pattern solar cell. In order to characterize the Al-Si reaction layer, samples were polished and etched in a stain etchant of HF-HNO₃-CH₃COOH (1:3:6) for 20 s. Metallic polishing holders were used to prevent any influence of embedding resin on the analysis.

The composition was determined by electron probe micro analyses (EPMA). EPMA measurements were performed with a JEOL JXA 8900R microprobe using an electron beam with an energy of 15 keV and a beam current of 20 nA employing wavelength dispersive spectrometry (WDS). The composition at each analysis location of the sample was determined using the X-ray intensities of the constituent elements after background correction relative to the corresponding intensities of reference materials. The intensity ratios obtained were processed with a matrix correction program CITZAF [5]. The points of analysis were located along a line with increments of 0.5 μ m and involved the elements Al, Si and O. The data were normalized to 100 wt.%.

Phase identification of the as-dried and sintered Al and Ag pastes was conducted by X-ray diffraction using a D8-discover diffractometer (Cu K_{α} radiation) equipped with an Euler cradle. A multiphase structure refinement was carried out by means of a full profile Rietveld method, including refinement of the lattice parameters, atomic positions, scale factor, zero shift, background and Bragg-peak profile parameters. Starting models for the calculation procedure were taken from the inorganic crystal structure database (ICSD) [6]. Results of the structure refinement are analysed with so-called R-factors, which indicate the quality of the fit of the structural model with respect to the measured XRD spectrum: the smaller the R-factors, the better the fit (Rwp and Rp - profile and weighted profile r factor).

The Al particle size distribution via laser diffraction has been measured with a Malvern Mastersizer 2000 in a configuration from 0.02 up to 2000 μ m with a Lorentz-Mie optical model. A Hydro SM 100 millilitre sample dispersion unit has been used for dispersion of the aluminium paste samples. An aluminium paste sample dispersed in ethanol was measured three times and an average was calculated.

A simultaneous application of Thermo-gravimetry (TG) and Differential Scanning Calorimetry (DSC) to a single sample in a Simultaneous Thermal Analysis (STA) was performed in order to evaluate the interaction between the aluminium back contact paste and silicon wafer material. Three different types of aluminium pastes were chosen and tested under measurement conditions close to the conventional industrial firing conditions. In these STA experiments, the aluminium pastes were analysed both with and without contact with silicon wafer material.

High-resolution X-ray computed tomography was used to characterise the microstructure of the Al rear contact and Ag front contact layer, the concentration profile of glass phases and porosity, as well as process-induced defects. The computed tomography was performed with a Nanotom system manufactured by Phoenix X-ray. The system is equipped with a high-power nanofocused tube (180 kV/15 W) suitable for microstructural characterization of solar cells. The Nanotom uses an X-ray cone beam creating two-dimensional X-ray images, while progressively rotating the sample step by step through a full 360° rotation. These projections contain information on the position and density of absorbing object features within the sample. This accumulation of data is used for reconstruction of the volumetric data [7-9]. The reconstructed 3D volume shows object features in grey values based on the differences in material density. It provides three-dimensional images at microscopic resolution. Visualization of porosity and the distribution of different solid phases generally require pronounced variations in atomic composition. The underlying physical principle of CT states that the attenuation of photons depends on their own energy and the atomic number of the material they are passing through. Material with a high atomic number (eg. Bi) causes a greater change in attenuation than does material with low-atomic number components (eg, Si). The grey levels in a CT image correspond to X-ray attenuation, which reflects the proportion of X-rays scattered or absorbed as they pass through each voxel. All elements present in the Al and Ag layers have different atomic numbers: Si – 14, Al – 13, Bi - 83, Ag - 47, Pb - 82, Zn - 30, thus it is possible to observe porosity and glass phase distributions.

In this work, computed tomography 3D images were generated by rotation of the sample over 360° with a step size of 0.33°. The 3D volumetric representation was reconstructed with an algorithm, which includes tools for geometry calibration, detector calibration, noise and beam hardening reduction [9]. Voxel data segmentation and analysis was made by the "VG studio max" software package. The main parameters of the Nanotom system are shown in Table 3.1.

The following parameters were used for solar cell scanning: voltage 110 kV, current 100 μ A. The position of the sample relative to the detector resulted in a voxel size (3D pixel) of 1.25 μ m. The total scanning time for 1080 projections was 90 minutes.

1	
Max. object size (height/diameter)	152 x 127 mm
Max. resolution	<0.5 µm (3D)
Nano focus tube	180 kV / 15 W
Detector	2200×2200 pixels

Table 3.1. Main parameters of Nanotom system.

Mercury intrusion porosimetry (MIP) was performed on small $(30 \times 10 \text{ mm}^2)$ samples to determine the porosity and the pore size distribution in the Al rear face layer. This technique is based on the principle that mercury is a non-wetting liquid and requires a force to penetrate voids. It is only suitable for the measurement of open and connected pores. The experiments were performed on a CE instrument Pascal 140 (low pressure) and Pascal 440 (high pressure) in a pressure range from 0.01 kPa to 2 MPa.

Elastic Properties measurements

Measurements of the amount of cell bowing resulting from screen printing were made by an optical method, using a Quick Vision Mitutoyo system. Five cells from neighbouring wafers were prepared for each type of aluminium paste. Measurements were performed over the full length of the solar cell (156 mm), see Appendix A for Bow measurement details.

Elastic properties of the different solar cell layers were characterized on a polished wafer cross-section by a nanoindentation technique using an MTS Nanoindenter G200 instrument, capable of continuous stiffness measurements. The tester was equipped with a three-sided pyramid (Berkovich) diamond indenter with a 50 nm tip radius. The indenter shape was calibrated before testing using a standard indentation procedure [10]. The shape of the indenter was also checked between each series of measurements to track possible tip damage that could lead to inconsistent results. For these experiments, samples were embedded in a cold setting epoxy resin (Epofix) for a better support during indentation. Indentations have been performed at a constant maximum load of 1.5 mN. For each specimen, at least 30 different indentations

were performed and the mean hardness and Young's modulus values were calculated. If a measurement did significantly differed, an optical image of the indents was examined and defected measurements (performed in porous areas) were excluded from the average and a new test was performed. The results presented here were obtained after a numerical treatment of the load/depth curves using the Oliver and Pharr method [10]. Indentation experiments on the single Al-Si particles were performed using a nanoindenter XP (MTS Nano-Instruments, Oak Ridge, Tennessee) under force control, also equipped with a three sided pyramid (Berkovich) indenter. The maximum force was held constant for 30 seconds at a load of 1.5 mN.

3.4 Microstructure and Mechanical Properties of a Screen-Printed Aluminium Rear Side Contact Layers

3.4.1 Microstructural Investigation of Al-Si Contact Layers

Figure 3.4 (a) shows an SEM micrograph of a polished and etched cross section of a typical screen-printed silicon solar cell consisting of 5 distinct layers: silver, silicon, back surface field (BSF), solid eutectic (Si-Al eutectic) consisting of Si-rich lamellas and Al-rich phases, and porous aluminium.



Figure 3.4 a) SEM micrograph of a cross section of a conventional silicon solar cell $(155 \times 155 \text{ mm}^2, 200 \ \mu\text{m})$, comprising 5 distinct layers; b) Microstructure of porous Al layer with Al-Si spherical particles, surrounded by a thin film of alumina (Al_2O_3) .

The porous aluminium layer was found to have a complex porous microstructure. A closer look into the porous Al layer (Figure 3.4 (b)) reveals the presence of spherical

particles, surrounded by a distinct oxide layer. The thickness of this oxide layer is about 150-200 nm, which is in good agreement with thermo-gravimetrical analysis (TGA).

Thermal analysis results of three different Al pastes show similar patterns for the TGA/DSC curves (Figure 3.5). First, an initial decrease in the TG curve is found around 180 °C, followed by a larger step around 250 °C, accompanied by an endothermic peak in the DSC curve. This indicates evaporation of solvent and binders from the Al paste. After this large drop, an exothermal event appears at around 600 °C, together with a small mass increase. This indicates (partial) oxidation of the aluminium in the paste. This event is immediately followed by an endothermic event with constant mass, around 650 °C, showing the melting of the remaining aluminium.

As can be seen from the EPMA point measurements (Figure 3.6), the concentration of oxygen increases going from the middle to the edges of the Al particles. This is consistent with the presence of a thin oxide film, which creates a shell around the particle, holding the particles in place and thus creating a stable paste structure.

It is expected that particle-to-particle contact is made through the oxide layer. This might lead to only a weak bond between the particles, adversely affecting the mechanical properties of the layer.



Figure 3.5 Typical TGA/DSC result for Al paste during heating.

EDS point analysis is in a good agreement with EPMA results and shows that Al spherical particles have a nearly eutectic Al-Si composition, surrounded by a complex

matrix of Al, Si and O (Figure 3.7). EDS mapping also shows the presence of Bi and Ca - a residue from the initial Al paste. The minor presence of Bi and Ca in silicon wafer can be neglected as it corresponds to the noise of the equipment.

The particle size distribution analysis showed that Al particle diameters increase up to 40% after firing at 850 °C (Figure 3.8). This might indicate diffusion of Si into the Al particles, explaining the presence Si lamellas in the as-fired Al paste.



Figure 3.6 Locations of the individual EPMA measurements and measured compositions (wt. %).



Figure 3.7 EDS mapping of a cross section of the Al-Si layer, indicating the distribution of selected elements.



Figure 3.8 Particle size distribution data of the aluminium paste samples before and after firing treatment and a representative curve of aluminium paste A before and after firing showing the difference in particles size diameter (where D is the surface-weighted mean diameter).

An XRD analysis was performed on the back surface of the cell in order to identify phases present in the Al layer. Measurements were performed on both a mechanically removed Al layer and an as-processed layer on top of a Si wafer. Figure 3.9 shows the X-ray diffraction pattern of the Al paste, mechanically removed after firing. Besides the expected Al and Si, three extra phases were detected, namely γ -Al₂O₃, CaMgSiO₄, and bismuth silicon oxide. The latter two are a residue of the initial glass frit present in the Al paste, added to obtain better sintering properties of the contact layer. The presence of γ -Al₂O₃ is in good agreement with literature results, showing a formation of amorphous alumina between 300 to 550 °C and its further transformation into γ -Al₂O₃ at about 550 °C [16]. The oxide layer keeps the Al particles integrity (due to the Al₂O₃ melting temperature being much higher than the peak firing temperature), hence oxidation of Al particles decreases sintering.

The overall open porosity of the Al layer, estimated by mercury intrusion porosimetry, was found to be around 15%, which is in good agreement with computed tomography results. Mercury intrusion showed that at a relatively low pressure (0.06 MPa) filling of large pores (around 50 microns) occurs. An increase in pressure (0.5-2 MPa) revealed the filling of the remaining small pores, which are about 2 μ m in size.



Figure 3.9 XRD diffraction pattern of as-received dried Al-paste B and mechanically removed Al paste after firing at 850 °C.

In order to evaluate the ratio between Al and Si in the Al back surface layer, a full profile Rietveld refinement was performed, employing FullProf software. As a starting model for the refinement, bulk Al and Si structures were used; glass phases were not included in the refinement. The refinement provided good agreement between observed and calculated profiles. The estimated weight ratios between Al and Si, *e.g.* 83:17 as shown in Figure 3.10, is in good agreement with EDS/EPMA results (three scans were performed).

The concentration of Si is higher in the Al matrix than in the eutectic layer (17% compared to 12.6% of the eutectic), probably because the remaining Si in the Al matrix is not driven back completely during the fast cooling.

A computed tomography analysis was carried out to obtain the amount and distribution of bismuth silicate glass and porosity. Figure 3.11 (a) shows a representative 2D X-ray image of the Al layer (paste B). The yellow parts correspond to a higher atomic number material (bismuth, Z = 83), which absorbs more X-rays, and the grey parts to lower atomic number materials, such as aluminium (Z = 13) and silicon (Z = 14). Based on the digital 3D images of Figure 3.11 (b), the fraction of bismuth glass and porosity in paste B were estimated to be 3.9 and 14 vol. %, respectively. An overview of the results is presented in Table 3.2.



Figure 3.10 Representative Rietveld full profile refinement leading to an estimate of the silicon concentration in the bulk Al layer of around 17%. (where χ – goodness of fit, Rwp and Rp - profile and weighted profile r factor).



Figure 3.11 X-ray computed tomography of the Al layer (paste B): a) 2D image showing the differences in photographic density between different parts (yellow: bismuth, grey: Al and Si, blue: porosity). b) 3D volumetric representation of bismuth glass phase (upper) and porosity (lower) distributions.

3.4.2 Elastic Properties of the Aluminium Layer

The elastic properties of Al particles inside the porous aluminium layer were experimentally obtained by performing nanoindentation in load control. It was empirically verified that a straightforward way of determining whether an obtained force-displacement curve was acceptable, was to compare curves corresponding to a set of identical experimental conditions. During the experiment, it was noticed that the force-displacement curves are significantly affected by the mechanical stability of the sample. A lack of stability leads to an apparent increase of penetration depth and an underestimate of the Young's modulus. A simple metallic clamping of the specimen in the holder was unsatisfactory in most cases. Thus in order to avoid micro-displacements of the sample during indentation, the sample was placed it in an epoxy resin (Epofix) holder. This also made it possible to obtain a smoother surface during polishing, which improved measurement accuracy. With such a procedure, it was observed that the tendency of sample micro-motions was greatly reduced and more reproducible curves could be obtained.

Nevertheless, the first results showed a large spread and a tendency for cracking of Al particles and of interfaces between the particles was noted. Optical observations of the surfaces revealed significant roughness and the presence of a large number of defects taking the form of Al particle pull-outs and micro-scratches originating from polishing.

When indenting those samples, the indenter first makes contact with microasperities which are then deformed in an elasto-plastic manner. As the load rises, microcracks tend to develop in the sub-surface of the material, which can lead to material crushing in severe cases [17]. These forms of damage are responsible for an apparent enhancement of the material compliance or a decrease of the Young's modulus.

It must be pointed out that even after optimizing the polishing and clamping procedure of solar cell cross-sections, a significant amount of surface defects was still noticeable. In such circumstances, it is important to use the combination of experimentally obtained data, such as force-displacement curves, and a direct observation afterwards of each indented particle in order to interpret the results. This reduces possible side effects of surface micro-asperities, pre-existing micro-cracking and sample motion in nanoindentation.

Figure 3.12 shows an illustration of indentation force-displacement data as well as SEM micrographs of the indented Al layer cross section.

The Young's modulus of the Al-Si particles in the porous bulk Al layer was found to be approximately 44.5 GPa at 1.5 mN. This value is representative for the elastic modulus of the porous composite that forms the Al layer as a whole. In order to confirm experimental results, a theoretical calculation was performed, based on the experimentally measured bowing of the as-fired Al layer attached to a silicon solar wafer.



Figure 3.12 a) A representative force-displacement [F,h] curve of an indented Al-Si particle (shown in a SEM micrograph) in the porous Al-layer surface cross section; b) illustration of indentation force-displacement data, were the elastic unloading stiffness, $S = \Delta F/\Delta h$, is defined as the slope of the upper portion of the unloading curve during the initial stages of unloading [10] and an SEM micrograph of the complete indented surface of the Al layer.

Bowing of material layers in contact with each other having different thermal expansion coefficients (Si and Al in this case) can be represented by a bilayer strip model. Assuming only elastic deformation, the resulting deflection, δ , over a length L can be calculated using [18]:

$$\delta = \frac{3(\alpha_{AI} - \alpha_{Si})(T_{f} - T_{m})(t_{AI} + t_{Si})L^{2}}{4t_{AI}^{2} \left(4 + 6\frac{t_{Si}}{t_{AI}} + 4\left(\frac{t_{Si}}{t_{AI}}\right)^{2} + \left(\frac{E_{Si}}{E_{AI}}\right)\left(\frac{t_{Si}}{t_{AI}}\right)^{3} + \left(\frac{E_{AI}}{E_{Si}}\right)\left(\frac{t_{AI}}{t_{Si}}\right)\right)}, \quad (3.1)$$

where *t* is the layer thickness, α is the coefficient of thermal expansion, $T_{\rm f}$ is the firing temperature (contact formation temperature), $T_{\rm m}$ is the measuring temperature (room temperature) and $E_{\rm Si}=E^{\circ}_{\rm Si}/(1-\upsilon_{\rm Si})$ is the Biaxial Young's modulus (where $E^{\circ}_{\rm Si}$ and $\upsilon_{\rm Si}$ are the elastic modulus and Possion's ratio, 160 GPa and ~0.28, respectively), $E_{\rm AI}=E^{\circ}_{\rm AI}/(1-\upsilon_{\rm AI})$ is the biaxial Young's modulus of Al back contact layers (where $\upsilon_{\rm AI} \sim 0.33$).

Validity of the equation (1) implies that the substrate has transversal isotropic elastic properties with respect to the film. Using single crystal silicon substrates featuring moderately anisotropic properties (Si < 100 > oriented wafers) satisfies this transverse isotropy argument. Both the film and substrate are homogeneous, isotropic and linearly elastic. Using experimentally obtained bowing results and equation (3.1), the biaxial Young's modulus of the Al contact layer can be calculated. It should be noted that, since this bimetallic strip model accounts only for two layers, the value obtained for the Young's modulus should be considered as an average for the combination of the porous part of the Al layer and the solid eutectic layer.

Table 3.2, shows the compositions of the three pastes, the amount of bowing and the calculated average Young's moduli for the respective aluminium layers. As can be seen, the theoretical biaxial Young's modulus is in good agreement with the experimental Young's modulus obtained by nanoindentation.

Paste type	As-fired Al particles size, μm	Porosity, %	Bismuth glass, %	Bowing, mm	Porous Al layer/ eutectic layer thickness, µm	Biaxial Young's modulus, GPa
А	5	10	2	1.4	34 / 5.3	41
В	7	14	4	1.8	36 / 6	44
С	11	16	5	2.6	46 / 7.3	46

Table 3.2. Correlation between aluminium paste composition, bowing and Theoretical Young's modulus of the fired aluminium rear side contact.

Furthermore, there seems to be a correlation between the aluminium paste composition (porosity and bismuth glass concentration), bowing and Young's modulus. It should be noted that since $E_{Al}=E_{Al}^{o}/(1-v_{Al})$ is the biaxial Young's modulus of Al back contact layers, the elastic modulus $E_{Al}^{o}=44$ GPa x 0.67 = 29.5 GPa.

Aluminium Back Contact Layers Model

Based on the results presented above, a model was made describing the cross section of the rear face of the silicon solar cell with corresponding microstructural features (Fig. 3.13). The Al layer is represented as a complex composite-like material, consisting of three main components: 1) spherical (3 - 5 μ m) hypereutectic Al-Si particles, surrounded by a thin aluminium oxide layer (200 nm); 2) a bismuth-silicate glass matrix (3.3 vol.%, as an average of three different Al pastes); 3) pores (14 vol.%).

The results of microstructure, nanoindentation analyses and bowing measurements are used for fracture strength evaluation and modelling of fracture stress, see Chapter 4, 5 and 6. These results were used as input parameters for the model that integrates the thermo-mechanical behaviour of the layers at the rear of the cell, allowing bowing of the whole cell to be predicted [19].



Figure 3.13 Model of the rear face of a silicon solar cell with corresponding microstructural features.

In particular, the alloying process can be summarized in five main steps, following the Al-Si phase diagram (Figure 3.14 and 3.15):

- 1. During heating, the solubility of Si in solid Al starts at approx. 300 °C and increases, reaching its maximum at the eutectic temperature ($T_{eut} = 577$ °C) [11].
- An increase in temperature leads the solid aluminium particles to melt (660 °C, 0% Si) [12] and to start alloying with silicon (Si is dissolved by Al during the alloying process and an interdiffusion is present at the interface).

The Al-Si melt will appear locally on the Si surface. It is important to point out that due to the aluminium oxide layer forming around Al particles $[Al_2O_3, see Figure 3.3]$ the paste particles keep their form during sintering, thus the volume of the Al particles is constant and a quantity of Al equal to the volume of silicon incorporated in each particle will flow towards the wafer surface. The Al-spherical particles present in the fired paste can locally fuse together, however the

oxide shells (Al₂O₃) only allow for a weak bond between the particles, which will affect the mechanical properties of the porous Al bulk layer.



Figure 3.14 Al-Si phase diagram showing formation of (a) Al-rich solidus in lamellar structure (b) eutectic (Al - 12.6 % Si) (c) BSF: Si-rich solidus.

- 3. At the peak firing temperature ($T_{\text{peak}} = 850 \text{ °C}$) and assuming equilibrium, the concentration of Si in the Al-Si melt is about 30%.
- 4. During the cooling step, Si is rejected from the Al-Si melt to grow epitaxially at the interface. The concentration of Si in the Al-Si melt decreases with decreasing temperature, following the liquidus line in the phase diagram. The Al-doped region (back surface field BSF) is then formed by both epitaxial recrystallization of Si (highly doped by Al) from the Al-Si melt, and by incorporation of Al atoms in the Si lattice. Another important point is that Si is able to diffuse back into the Al bulk from the Al-Si melt at the interface and remains as "Si lamellas" in the Al layer.
- 5. Below the eutectic temperature (577 °C) the whole liquid solidifies as an Al-Si alloy of nearly eutectic composition.
- A schematic illustrating the formation of the aluminium contact from screen printed Al paste as a result of the firing process is shown in Figure 3.15.



Figure 3.15 Schematic of aluminium rear side contact formation from a screen printed Al paste at a result of a firing process at $T_{peak}=850^{\circ}C$.

3.4.3 Effect of Processing Parameters on the Uniformity of Al-Si Reaction Layers

X-ray computed tomography scanning was performed on industrial multicrystalline solar cells with screen-printed and fired aluminium paste B. As can be seen in Figure 3.16 a, CT scans revealed the presence of spherical voids inside the bulk Al layer. These voids have a regular distribution across the entire Al layer, indicating a process-induced nature of these defects.

Figure 3.16 b, represents an optical cross sectional image of a void, showing the absence of the eutectic and BSF layers underneath the void. Thus, it can be suggested that these defects affect electrical properties as there is no BSF layer locally and mechanical properties of the solar cell (resulting from local stress concentrations). Further investigations showed that the diameter of the voids and dimensions of the steel wires, used in the screen printing process are identical.

The defect distribution pattern is also similar to the screen printing mesh, shown in Fig. 3. 15 c. Hence, it can be concluded that these voids are screen-printing-process-induced defects.

Two different drying temperatures (250 °C and 350 °C) and two screen printing mesh sizes (165 and 325) were used in order to investigate the nature and cause of the defects. CT scans of the samples with two screen mesh sizes did not show any differences in the amount of defects. However, CT detected a significant change in the defect concentrations when using different drying temperatures, Figure 3.17. As can be

seen, drying at 350 $^{\circ}$ C creates larger holes, thus producing a more porous layer, while drying at 250 $^{\circ}$ C gives smaller holes and thus a denser Al layer structure.



Figure 3.16 a) Cross section CT representation of the solar cell (upper image) and a 2D X-ray image of the Al layer (lower image), showing the screen-printing-processinduced defects (black part: voids, white: bismuth, grey: Al and Si). The dashed red line represents a reconstructed screen printing mesh. b) Optical image of a solar cell cross section showing a process-induced cavity. c) Industrial screen printing mesh, used for the application of metallic pastes [20].

The aluminium paste layer needs special care during the drying process (a slow heat-up ramp), otherwise volatilizing solvent can build cavities in the paste. These cavities produce unalloyed regions and porosity, which are correlated with the locations of the screen mesh openings of the screen printing process. Drying at 250 °C can be recommended as the most optimal temperature, creating fewer defects.

Figure 3.18 presents optical micrographs of different Al pastes showing a very important feature of the eutectic layer thickness variation; the thickness of the layer is the largest at the valley of the surface texture and the smallest at the peak of the texture. This indicates that during the formation of the eutectic layer, the melt initially fills up the texture valley. However, this effect is less pronounced for paste A with small Al particles (1-3 μ m); the waviness seems to increase with increasing Al particle size. Furthermore, it is known that the surface roughness has an effect on melting, because

the surface texture of Si wafers is formed by [111] faceted planes, which are closepacked and make it more difficult for atoms to interdiffuse [21]. Hence, Al alloys more slowly and less uniformly with Si with a textured surface than with flat parts of the textured surface. This leads to nonuniformity in the resulting eutectic layer.



Figure 3.17 Effect of Al paste drying temperature on the formation of voids: left – drying at 250 °C, right – drying at 350 °C.

Larger paste particles (paste C) tend to get trapped in the gaps between the peaks of the Si surface texture. As the temperature increases, the melting starts from where silicon contacts the Al particles stacked in the gaps, causing the top of textures to melt first. During cooling the melt tries to regrow epitaxially over Si. This doped BSF layer of Si follows the topology of the Si surface.

In the case of the finer paste (paste A), smaller Al particles will preferentially fill the bottom of the textured surface, where the interdiffusion and alloving would be facilitated by a lower melting temperature of the fine particles, resulting in a thicker and more uniform eutectic alloy. Generally, finer particle sizes will show faster neck growth and less sintering time or lower sintering temperature to achieve a similar degree of sintering. Larger particles will sinter more slowly and will require higher sintering temperatures or longer times. For the same reason, during firing, the finer Al particles at the top would undergo more rapid sintering and densification, which may give rise to a denser and less voluminous porous Al bulk layer. This increase in density and reduction in volume of the porous Al layer can lead to higher stresses at the interface with the eutectic Al-Si alloy resulting from the thermal expansion mismatch. Thereby, it can be suggested that a finer Al particle size (finer than 3 µm) could result in a fired porous Al layer that can be easily peeled off from the Al-Si alloy layer (this will be discussed in detail in chapters 4 and 5). Furthermore, the smaller the particle is at the Al/Si texture interface, the easier the interdiffusion of atoms is and the quicker the alloy forms during firing.



Figure 3.18 Effect of paste type on uniformity of eutectic layer: a) Al paste A, mesh 165; b) Al paste B, mesh 165; c) Al paste C mesh 165; d) Al paste B, mesh 325 (half the amount of Al paste is screen printed). Figures b) and d) show the result of using different amounts of Al paste. As can be seen, if the amount of Al paste is too low (Fig. d), only a thin non-uniform Al-Si reaction layer is formed and there are areas where no eutectic layer is formed.

Thus, it can be concluded that the eutectic layer waviness depends on Al particle size, amount of Al paste and textured surface roughness of the silicon wafers.

3.5 Microstructure and Mechanical Properties of a Screen-Printed Silver Front Side Contact

A layer of conventional Ag paste type A grid 165 was screen printed on top of the SiNx antireflection coating and fired at 850 °C through the SiN_x layer onto the emitter surface. Figure 3.19 shows cross-sectional SEM microstructure pictures of silver paste A, both after drying and after the firing process. As can be seen, the initial as-dried Ag particles have a mixture of flake like and spherical shapes with 0.3 - 0.5 μ m size. As a

result of the firing process the Ag spheres and flakes have sintered together, and formed a dense but porous structure.



Figure 3.19 Ag paste A a) after drying at 250 °C, showing the distribution of silver particles before firing and b) after firing at 850 °C, showing a porous Ag layer structure.

To investigate the cross section of the silver contact, samples were laser cut from the complete cells, subsequently embedded in resin and polished to a 1 μ m finish. Figure 3.20 shows EDS mapping of a polished cross section of the fired Ag layer, revealing 3 distinct areas: silver; silicon; ZnO, and PbO rich phases, which are residues of the initial glass phases. Between the silicon and the porous bulk Ag structure a continuous layer containing oxide phases was detected.



Figure 3.20 EDS mapping of a cross section of an as-fired Ag front contact.

An Improved Understanding of Aluminium and Silver Electrical Contact Formation and Its Properties

A closer look into this Ag/Si interface reveals a non-uniform glass layer separating bulk Ag and Si and large conjugated Ag particles (~150 nm in width) on the silicon wafer, Figure 3.21 a. A further EDX analysis of point 1 (Figure 3.21 c) shows that the Ag/Si interface has Si and Ag as major constituents, together with Pb and Zn. Therefore, it has the composition of an alloy Ag-Si-M (where M is Zn, Pb). The glass particles in the Ag paste are expected to etch through the passivation layer into the silicon surface, facilitating wetting of the Ag on the Si and hence alloying.



Figure 3.21 SEM micrograph of Ag paste A fired at 850 °C a) Ag crystallites and ZnO/PbO-based glass layer at the Ag/Si interface (left image) and an enlarged view of glass layer and sintered Ag particles (right image); b) enlarged Ag crystallites 'trapped' inside the textured silicon pyramid; c) EDX analysis of interface of Ag-Si alloy.

However, in this work, no clear Ag crystallites etched into the Si emitter surface were found. It is believed that, at elevated temperatures (> 550 °C), the glass frit is molten and etches the SiN_x antireflective coating (ARC) [25]. In this way the glass frit brings the Ag particles in the direct contact with the Si. The glass, depending on the grain orientation, etches the silicon isotropically or anisotropically.

Metals oxides (*e.g.* PbO, ZnO) present in the glass react with the outer layer of the Ag particles and create Ag-solvent metal alloy. This alloy fills the pits etched by the glass on the silicon surface. Hence, on isotropically etched silicon, it appears as a round shape and on anisotropically etched silicon it appears as an inverted pyramid, which can explain pyramidal Ag imprints observed by other authors [25, 29].

An XRD analysis was performed on the front surface of the cell in order to identify phases present in the fired Ag contact layer. Measurements were performed for both as-dried and as-fired Ag paste, Figure 3.22. Besides the sharp Ag peaks, two extra phases were detected in the fired Ag layer spectrum, namely ZnO and PbZnSiO₄. The latter two are residues of the initial glass frit present in the Ag paste to obtain better sintering properties of the contact layer. However, it is known that initially only two oxide phases were present in the Ag paste, namely ZnO and PbO. It is suggested, that ZnO and PbO formed a complex ceramic crystallite phase due to etching through the SiN_x antireflective coating (ARC) and reaction with the Si wafer during the firing process, resulting in crystallization of larsenite (PbZnSiO₄).

It was proposed by Schubert [25], that upon heating, the glass frit fluidizes and wets the SiN_x surface, dissolving the silver and etching the silicon nitride. The etching of SiN_x takes place by a redox reaction, where lead oxide and zinc oxide are reduced by the silicon [32]:

$$xSi + 2MO_{x,glass} \rightarrow xSiO_2 + 2M$$
. (3.2)

The resulting lead and zinc are then alloyed with the silver and silver contact crystallites are formed from the liquid Ag-Pb phase. This mechanism results in "solvent metal" (M) being present wherever glass and Si are in contact. It would also suggest the existence of a thin layer of SiO₂ at the interface, which in our case is a complex oxide layer of PbZnSiO₄. However, in contrast to the above mentioned theory, no detectable precipitates of Pb or Zn were found in the investigated cells.

It is suggested that in the investigated cells Ag crystallites are formed at the paste/Si interface without the aid of liquid Pb formation. When the Ag particle/agglomerates are in direct contact with the molten glass, the redox reaction between the PbO in the glass and the Si is suppressed.

The following alternative Ag contact formation mechanism is proposed and is also shown schematically in Figure 3.23.



Figure 3.22 XRD of the front surface of Ag paste A dried at 250 °C and fired at 850 °C (x-axis is displaced for clarity).

After Ag-paste deposition the solvents are evaporated in a drying step, leaving behind the metal and glass particles embedded in the organic matrix of the binder. In the subsequent firing step the organics are combusted. As the firing temperature increases above the softening temperature of the glass frit (613°C for lead silicate glass), the glass frit becomes fluidized, wets the Si surface and a thin layer of liquid glass (L) surrounds the Ag particles. Because Ag and L react to form an alloy of much lower melting point (than Ag), this mechanism leads to the formation of a melt around the Ag particle. With further heating up to the peak firing temperature, some of the Ag powder dissolves in the glass and sintering of the Ag powder occurs (an example of sintered Ag particles can be seen in Fig. 3.21 b). Ag can dissolve in glass as Ag atoms, however it is a slow process, which can be suppressed by simultaneously occurring oxidation of Ag to Ag+ ions through an interaction with oxygen from the ambient atmosphere [33]:

$$4 \operatorname{Ag}_{(\operatorname{in glass})} + \operatorname{O}_{2(g)} \to 4 \operatorname{Ag}_{(\operatorname{in glass})}^{+} + 2O^{-2}_{(\operatorname{in glass})}.$$
(3.3)

Subsequently, silver and oxygen ions dissolved in the liquid glass (L) from reaction 3.3 react with SiN_x layer and etches it away:

$$\operatorname{SiN}_{x\,(s)} + 4\operatorname{Ag}^{+}_{(\operatorname{in} glass)} + 2\operatorname{O}^{2^{-}}_{(\operatorname{in} glass)} \to \operatorname{SiO}_{2\,(\operatorname{in} glass)} + 4\operatorname{Ag}^{o}_{(\operatorname{in} glass)} + x/2\operatorname{N}_{2\,(g)}.$$
 (3.4)
As a result of the reaction (3.4), silicon wafer comes into direct contact with the liquid glass and the silver and oxygen ions diffuse further toward the glass/Si interface and create inverted pyramidal pits on the Si wafer surface via the redox reaction:

$$4 \operatorname{Ag}^{+}_{(\text{in glass})} + 2O^{-2}_{(\text{in glass})} + \operatorname{Si}_{(s)} \to 4 \operatorname{Ag}^{o}_{(\text{in glass})} + \operatorname{SiO}_{2}_{(\text{in glass})}.$$
 (3.5)

In this model, metal oxides (PbO and ZnO) in glass located close to the silicon wafer could also be reduced to liquid Pb or Zn (M) though the reaction 3.2, leading to the formation of Ag-M-Si alloy around the particles. However, some of the liquid Pb or Zn phase (M) may be dissolved back into the glass via:

$$4Ag^{+}_{(\text{in glass})} + 2O^{2-}_{(\text{in glass})} + Zn_{(\text{l})} \rightarrow 2Ag^{o}_{(\text{in glass})} + ZnO_{(\text{in glass})}.$$
 (3.6)



Figure 3.23 Proposed schematic model for the ionic reduction mechanism during Ag front contact formation under normal industrial firing conditions (850 °C).

When during cooling the molten Si-Ag-M alloy solidifies, it is likely to produce a grading in the composition of the interface between Si and Ag.

As a result of reactions 3.5, the glass in the etch pits is enriched by Ag atoms and SiO_2 . It is known, that Ag^+ ions diffuse faster in fluidized glass than do Ag atoms [34].

Therefore, there is a steady flux of Ag^+ ions toward the Si surface that allows reaction (3.5) to occur continuously, whereas the Ag atoms reduced via reaction (3.4 and 3.6) accumulate in the glass located at the etch pits on the Si surface.

It should be noted, that reaction (3.5) competes with reaction (3.2) in etching the Si wafer during firing, however it could locally and simultaneously take place.

With increasing Ag powder content mixed with the glass frit, the amount of Ag^+ and O^{2-} ions dissolved in the molten glass is expected to increase, due to the increased area available for reaction (3.3) and, therefore, the rate of reaction (3.5) would increase as well. Hence, during the subsequent cooling process, normally by air cooling, the Ag atoms reduced by the reaction with the Si substrate can precipitate as Ag particles in the molten glass during firing or precipitate at the apexes of the inverted pyramidal pits during the subsequent cooling process. Subsequently, the Ag precipitates grow into inverted pyramidal Ag crystallites as the Ag solubility of the glass decreases with decreasing temperature, resulting in the microstructure shown in Figure 3.21 a and b. These results agree well with a recently proposed theory by Hong [35], who proposed that inverted pyramidal Ag crystallites were formed by the precipitation of Ag atoms dissolved in fluidized glass during the subsequent cooling process after firing and that PbO in the glass frit does not participate directly in the reaction with the Si wafer. The proposed model leads to the formation of a chain of clusters of Ag-particles within the bulk of the contact. It should be noted, that if the glass has a low solubility for Ag atoms, the Ag atoms exceeding the solubility limit can precipitate as Ag particles in the fluidized glass (Figure 3.21 b).

A computed tomography analysis was carried out in order to obtain the amount and distribution of the glass phase and the porosity in the as-fired Ag contact (Figure 3.24).



Figure 3.24 a) 2D X-ray computed tomography image of the Ag layer, showing the differences in photographic density between different parts (yellow: porosity, red: zinc/lead glass, grey: silver). b) Cross section volumetric representation of zinc/lead glass phase (red) and porosity (yellow) distributions.

A 2D X-ray image of the Ag layer (Figure 3.24 a), reveals the differences in photographic density between different parts. A 2D cross section representation of the silver layer shows the zinc glass phase (red) and porosity (yellow) distributions (Figure 3.24 b). Based on these CT results, the volume fractions of the glass and the porosity in fired Ag paste A was estimated to be 6.5% and 7.5%, respectively.

Elastic properties of the bulk Ag layer were experimentally obtained by performing nanoindentation, using an MTS NanoIndenter-XP equipped with a threesided pyramid (Berkovich) diamond indenter, operating in load control. The experiments were performed as described in section 3.2. Figure 3.25 shows a typical example of indentation force-displacement data.



Figure 3.25 A representative force-displacement curve during nanoindentation of the Ag bulk layer. The cross section of the indented Ag layer is shown in the optical image.

The Young's modulus of the sintered Ag bulk layer was found to be approximately 54 GPa at a load of 1 mN. However, it should be pointed out that this value is only representative for the elastic modulus of the sintered Ag agglomerates in the porous composite-like Ag layer.

3.5.1 Effect of Processing Parameters on the Formation of the Ag Contact Layer

Effect of Peak Firing Temperature

It is well known that molten glass etches the underlying silicon and that the etch rate depends on temperature, crystal orientation, defects and glass composition [25]. Glass provides anchorage (*i.e.* adhesion) points for the metal grid to stick to the silicon

surface. Thus, it is important to investigate the effect of peak firing temperature on adhesion and contact formation.

Cross-sectional analyses of solar cells fired using 750 °C, 850 °C and 950 °C peak temperatures were carried out. It should be noted that actual peak cell temperature is ~100 °C lower than the peak firing temperature indicated by the belt furnace [36]. Figure 3.26 shows SEM images of the cross-sectioned samples fired of different peak temperatures.

As can be seen, the cell conventionally fired at 850 °C shows several features:

1. large agglomerates of Ag particles fused together into a region of continuous Ag;

- 2. some Ag particles separated by regions of glass, and
- 3. some isolated particles of Ag that have the appearance of precipitates.

At a low firing temperature of 750 °C the Ag layer is porous and there are some discontinuities in the Ag layer coverage of the silicon wafer. Furthermore, the glass layer is thin and only a small amount of silver is expected to be dissolved at this temperature. Figure 3.27 shows that there is no or very weak Ag crystallite formation at 750 °C, which can be explained by the lack of a reaction between the glass frit and the SiN_x, which in previous studies was found to start at temperatures of ~680 °C [37]. Hence, the low firing temperature of 750 °C (the actual cell temperature will be ~650 °C) is most likely not sufficient to fire though (i.e. penetrates) SiN_x and allow the formation of Ag crystallites. This would also explain the relatively low amount of bowing found after firing (see Table 3.3), which is probably the result of delamination of the weak Ag/Si contact interface.



Figure 3.26 SEM micrographs of Ag paste fired on a silicon wafer of different firing temperatures (cross section view).

A higher firing temperature promotes Ag particles agglomeration as well as the aggressiveness of the etching reaction between the glass frit and the SiN layer. Thus, for

the 850 °C and 950 °C firing condition the SiN is completely etched, allowing the glass frit with dissolved Ag to reach and partly dissolve the underlying Si. With increasing firing temperature the amount of generated glass increases too, since more SiN_x is removed and hence more Si from the SiN_x reacts with the glass frit to SiO_x . Thus, the thickness of the glass coating is expected to increase with increasing temperature. As can be seen in Figure 3.27, this statement is only true for 850 °C.

To make the pictures shown in Figure 3.27a, Aqua Regia (AR) etching was used to remove the bulk Ag layer in order to expose the surface of the Si emitter covered with a glass layer. From the etching results, it is clear that regions of the metallization that do not directly react with Si are held together by the glass (Fig 3.21 a and b), which ensures good mechanical contact. As can be seen, firing at 850 °C creates more glass layer coverage than 750 °C and 950 °C.

Firing the cell at 950 °C results in only local coverage of the silicon surface with glass globules, and hence this non-uniform glass layer could explain low bowing at 950 °C. A substantial delamination was observed at the edges of the fired cell, indicating on a high shear stress at the edges. Edge delamination and poor glass coverage explain a reduction of bowing as compared to firing at 850°C, where a more uniform contact with no delamination is created.

Firing temperature, °C	Bowing, mm
750	1.8
850	2.5
950	1.8

Table 3.3. Effect of peak firing temperature on the maximum bowing.

In order to verify the phase state of silver layer components after the firing process, XRD was performed on the samples fired at 750 °C, 850 °C and 950 °C, Figure 3.28. Crystallite peaks of Ag, ZnO and PbZnSiO₄ were identified. The cell fired at 850 °C seems to have the largest amount of ZnO phase, according to the peak intensities. Conversely, firing at 950 °C creates more PbZnSiO₄, which is consistent with the increase in aggressiveness of the etching reaction between the glass frit and the SiN layer. The eutectic reaction of Ag-Si is expected to start at 835 °C [38]. When ZnO-PbO is at 850 °C, which is at a firing temperature of 950 °C, Ag precipitation from the molten glass, as shown schematically in Figure 3.23, could be suppressed and result in a weak mechanical contact (in accordance with bowing results).

The crystallization of the PbZnSiO₄ in the glass probably occurred only due to the temperature rising above 850 °C, as nearly no PbZnSiO₄ phase was identified in the 750 °C and 850 °C firing spectra. Thus the formation of the PbZnSiO₄ crystalline phase during firing above 850 °C is expected to occur according to:

$$PbO_{(in glass)} + ZnO_{(in glass)} + SiO_{2(in glass)} \rightarrow PbZnSiO_{4(cryst.)}.$$
 (3.7)

An Improved Understanding of Aluminium and Silver Electrical Contact Formation and Its Properties

As can be seen from Figure 3.27 b, with increasing temperature, the size of the crystallites increases. However it should be pointed that firing at 950 °C creates less Ag crystallites, even though their size is larger than those from the 850 °C firing. It is suggested, that the crystallization of PbZnSiO₄ in the glass at the high temperature of 950 °C hinders the dissolution of Ag in the glass due to an increase in viscosity. The reduction of the ZnO peak intensity at 950 °C as compared to 750 °C can also be explained by the formation of the PbZnSiO₄ phase (equation 3.7). Therefore, the crystallization in the glass during firing can affect the formation and penetration of Ag on and into the Si emitter.



Figure 3.27 SEM micrographs of the surfaces of Ag contact layers fired at different temperatures a) after Aqua Regia etching, showing the distribution of the glass phase under the bulk Ag contact layer; b) after etching with Aqua Regia + HF, that removes the glass layer to reveal the formation of silver crystallites.



Figure 3.28 XRD spectrum of Ag paste A fired on a silicon wafer under different firing temperatures.

A possible further high temperature mechanism occurs during firing at 950 °C, which heats the paste to above the Ag-Si eutectic temperature of 845 °C, where Ag paste etches away the SiN_x layer and subsequently forms Ag-Si liquid. During cooling Si and Ag phases segregate and crystallize from the Ag-Si liquid into the inverted pyramids created in the silicon by preferential etching. The widely distributed Ag crystallite sizes (Figure 3.27 b) may result from variations of local Ag concentration in the Ag-Si liquid and/or local fluctuation of Si melting depth when the cell is at temperatures above the Ag-Si eutectic point. It is concluded that firing at 950 °C creates a mechanically weak contact, due to the high crystallization of glass (at temperatures above 800 °C), which prevents the viscous flow of frits and due to the penetration of Ag into the Si emitter in combination with nearly no glass layer formed at the Ag/Si interface. Hence, only local Ag crystallites form in the places where Ag particles make direct contact with the Si wafer. This provides a low degree of bonding between the layers, resulting in a low bowing of the fired cell.

Another feature that should be taken into the account is that an increase in firing temperature up to 950 °C increases the ratio of liquid phase to the Ag-rich solid phase. The existing liquidized phase can lower the sintering temperature of silver because it increases the mobility of silver particles, and also fills the large voids between silver particles, increasing the relative density (Figure 3.26). Thus, higher temperatures can also increase the sintering driving force, accelerate the silver atom diffusion and

bonding, increase the sintered bulk density, and thus significantly improve the properties of sintered Ag. However, a more porous microstructure (as in case of 750 °C and 850 °C firing) can provide the compliance necessary to relieve the thermomechanical stresses generated by mismatch of the Ag/Si coefficients of thermal expansion, thus leading to better reliability. Therefore, a combination of a denser Aglayer microstructure with poor glass layer coverage between the Ag/Si interface can weaken the interface bonding and affect the bowing and the strength of the entire wafer.

Effect of Silicon Wafer Surface Treatment

At temperatures typically above 600 $^{\circ}$ C, glass frit particles melt and exhibit a sufficiently low viscosity to allow an essential rearrangement of the particles and their compaction by capillary action. As a result, wetting occurs and the underlying SiN_x layer is penetrated, allowing interaction with Si to take place. This leads to the formation of Ag crystallites and a good mechanical bonding at the Ag/Si interface. Thus, it can be expected that the silicon surface condition may affect the wettability, the spatial distribution of the glass layer and ultimately the bonding of the layer.

Three neighbouring *mc*-Si wafers were prepared with different surface conditions: as-cut, textured and polished in order to study the effect of surface finish on Ag layer formation. These wafers were screen printed with identical amounts of Ag paste and fired at 850 $^{\circ}$ C. Figure 3.29 shows SEM micrographs of polished cross sections of the Ag contact layer created with different Si wafer surface conditions.



Figure 3.29 SEM micrographs of cross section of Ag paste fired on different silicon surfaces: polished, textured and as-cut.

As can be seen, a textured surface creates large voids and inhomogeneities at the Ag/Si interface. However, a polished silicon surface results in a rather uniform distribution of Ag agglomerates. Finally, there are cracks visible from the surface of the as-cut silicon wafer.

In order to investigate the effect of surface roughness on the quality (bonding) of the Ag/Si interface, the bulk of the Ag layer was etched off using Aqua Regia, leaving behind the glass layer and the Ag crystallites (Figure 3.30 a).

As can be seen, for the polished surface the glass layer coverage is higher and much more uniform as compared with the textured surface. Furthermore, for the textured surface the glass layer is only continuous within the texture valleys. This indicates that melted glass initially fills up the texture valleys. Any excess glass would be expected to spill over the valleys and then build up. However in this case, the edges between the valleys are too high to cause any spill over.



Figure 3.30 SEM micrographs of surfaces of Ag contact layers fired on silicon with different surface conditions: a) after Aqua Regia etching, revealing glass phase distribution underneath Ag bulk contact layer; b) after etching with Aqua Regia + HF, that removes the glass layer to reveal the Ag crystallite distribution underneath.

Etching away the glass layer reveals the distribution of the Ag crystallites underneath the glass, Figure 3.30 b. For the polished surface, imprints of numerous Ag crystallites can be seen underneath the glass. This type of Ag/Si interface is expected to create a good mechanical bonding between the layers. Conversely, the textured surface shows that Ag crystallites have formed underneath the glass in the texture valleys. The area where Ag particles can be in direct contact with the Si surface also shows formation of Ag crystallites, but now without the aid of a glass phase. This is not found on the polished surface, as on this surface the silicon is almost entirely covered with a glass layer.

Thus, the glass-wetting behaviour on the Si surface has a crucial role in determining the glass layer distribution.

Based on the results, a simplified model for the glass layer and Ag crystallite distribution on textured and polished silicon surfaces is proposed in Figure 3.31.

In this model polishing of the silicon surface gives a better wetting by the glass layer, resulting in a lesser incidence of large voids, compared to highly textured surfaces. The non-uniformity of the glass layer and large voids at Ag/Si interface are expected to have a negative effect on the mechanical strength of the solar cell. These aspects will be addressed in more detail in chapters 4 and 5, where mechanical strength of solar cells is discussed.



Figure 3.31 A schematic of the glass layer and Ag crystallite distribution on textured and polished silicon surfaces.

As can be seen from Figure 3.30, it is rather difficult to determine the exact pattern of glass phase distribution of as-cut samples, probably due to the absence of a

regular pattern. Computed tomography was applied to look inside the Ag layer on the as-cut Si surface. Figure 3.32 a-b, shows the glass-phase distribution in the silver front-contact layer of an as-cut sample.

As can be seen, the glass phase (corresponding to the red areas in Fig. 3.32 a, b) concentrates at the Si/Ag interface (Fig. 3.32 a). A top view shows the glass is distributed in well-defined parallel lines at the interface between Ag and Si. It is suggested that these lines correspond to the local glass phase etching/penetrating into the silicon wafer surface. The nature of the parallel lines can be explained by the wire-saw-cutting process, which creates a damage layer on the silicon wafer surface, Figure 3.32 c. This explanation is confirmed by removing the damaged layer via a texturing process. As can be seen in Figure 3.32 d, the glass distribution pattern has changed to random, probably showing the location of etch pit valleys, where the glass phase prefers to localize, as was shown before.



Figure 3.32 a) CT cross-section image, showing glass distribution (red) in the silver layer fired on an as-cut Si surface; b) CT top-view image of the interface between silver layer fired on an as-cut silicon wafer, showing a preferential distribution of glass (red) in well-defined parallel lines; c) Confocal microscopy image of as-cut silicon wafer surface, showing wire-saw-damage; d) CT image of the textured silicon surface with Ag front contact (top view, white areas represent glass phase, grey areas – silver).

3.6 Conclusions

In this work the microstructure and mechanical properties of fired aluminium and silver contacts of a solar cell were investigated in detail.

It was shown that the outer porous part of the Al layer has a complex compositelike microstructure, consisting of three main components: 1) spherical $(3 - 5 \mu m)$ hypereutectic Al-Si particles, surrounded by a thin aluminium oxide layer (150-200 nm); 2) a bismuth-silicate glass matrix (3.3 vol.%) 3) pores (14 vol.%). It is concluded that the variation of the eutectic layer thickness depends on Al particle size, amount of Al paste and surface roughness of the textured silicon.

Furthermore, it was found that the aluminium layer needs special care during the drying process (a slow heat-up ramp), otherwise volatilizing solvent can build cavities in the paste, which might affect mechanical stability of the entire solar cell. Drying Al paste at 250 °C gives smaller cavities and thus a denser Al layer structure.

The Young's modulus of the Al back contact layer, obtained by nanoindentation, was found to be 44.5 GPa and showed a good agreement with the Young's modulus, calculated on the basis of bowing data and a bilayer strip model. These results will be used in chapter 4 and 5 as input parameters for fracture strength calculations.

In this chapter, an attempt was made to investigate and understand the formation of screen-printed Ag front contact layers. An alternative Ag contact formation mechanism was proposed, as described in Figure 3.23. It was suggested, that under an oxidizing ambient (atmosphere) Ag dissolves as Ag^+ ions into the molten glass and there is a redox reaction between diffused Ag and silicon substrate, which creates inverted pyramidal pits on the Si surface. During the cooling stage the Si-Ag-M alloy solidifies and is likely to produce a grading in the composition of the interface between Si and Ag. The Ag atoms reduced by the reaction with the Si substrate can precipitate as Ag particles in the molten glass during firing or as Ag crystals in the inverted pyramidal pits during the subsequent cooling process, resulting in the microstructure shown in Figure 3.21 a and c.

Furthermore, it was found that there are two main processing parameters affecting the uniformity of the Ag/Si interface, namely peak firing temperature and silicon surface roughness. Silicon surface polishing gives a better wetting of the silicon surface by the glass layer, resulting in a good contact and lower incidence of large voids, compared to the case of highly textured surfaces. The non-uniformity in the glass layer and large voids at the Ag/Si interface (in the case of a textured surface) are expected to have a negative effect on mechanical strength of the solar cell.

Results of this chapter will serve to explain effects described in chapters 4, 5, 6, in which four-point bending and ring-on ring tests will be discussed and the effect of different processing parameter on the mechanical stability and residual stress of the solar cell will be examined.

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CHAPTER 4

Fracture Strength of Multicrystalline Silicon Solar Wafers and Solar Cells Tested by Four-point Bending

"The use of solar energy has not been opened up because the oil industry does not own the sun"

Ralph Nader (1980)

4.1 Introduction and Background

Material reliability issues are of prime importance in the photovoltaic industry. Silicon is currently the base material in 95% of the commercially available photovoltaic cells. However, silicon is a brittle material, and as such, it can fail by brittle fracture (with little or no plastic deformation) if the applied stresses during manufacturing or handling surpass a certain limit. Silicon wafer breakage during wafer/cell processing and handling is becoming a significant issue in the photovoltaic (PV) industry limiting the production yield and further cost reduction [1]. Micro-scale flaws and residual and applied stresses pre-existing in the PV silicon wafers, mainly generated during the wafer sawing process, are the most critical factors affecting wafer breakage. Currently, more than 80% of the PV silicon wafers are sliced by a slurry-wire or diamond-wire sawing technology [2, 3].

This chapter is based on:

^{1.} V.A. Popovich, A. Yunus, A.C. Riemslag, M. Janssen, I.J. Bennett, I.M. Richardson, Characterization of multicrystalline silicon solar wafers fracture strength and influencing factors, International Journal of Material Science, 3(1), March 2013.

^{2.} V.A. Popovich, M. Janssen, I. J. Bennett, I.M. Richardson, Breakage issues in silicon solar wafers and cells, Photovoltaics international, 12, 2011.

^{3.} V.A. Popovich, A. Yunus, M. Janssen, I.M. Richardson, I.J. Bennett, Effect of silicon solar cell processing parameters and crystallinity on mechanical strength, Solar Energy Materials and Solar Cells, 95 (1), January 2011.

V.A. Popovich, A, Yunus, M. Janssen, I.J. Bennett and I.M. Richardson, Mechanical strength of multicrystalline silicon solar cells and influencing factors. In: Proceedings 25th European Photovoltaic Solar Energy Conference and Exhibition / 5th World Conference on Photovoltaic Energy Conversion, Valencia, Spain, September 2010.

These wafer sawing processes, which can be regarded as a series of overlapping micro-indentations by sharp, abrasive particles, yield distinct damage patterns reaching tens of micrometers deep into the silicon surface and which are not completely removed by damage etching steps [4-6]. Micro-scale flaws in the damaged layer, such as cracks and chips, are inherent stress concentrators and can significantly degrade the average fracture strength of the PV silicon [7-9]. Furthermore, state-of-art silicon solar cells are textured with pyramid structures to improve light-trapping in these devices. These pyramids can behave as crack initiation points under the thermal stresses induced during the firing of front silver and rear aluminium paste layers and lead to the breakage of complete solar cells.

In the future, as the thickness of PV silicon wafers is reduced to $120 \ \mu m$ or less, wafer breakage issues due to the presence of micro-scale flaws will become even more detrimental. Understanding the fracture behaviour of silicon wafers and solar cells with pre-existing micro-scale flaws and their residual and process induced stresses is critical to predict the mechanical performance and reduce silicon solar cell breakage. This emphasises the importance of establishing a standard mechanical testing method for evaluating the mechanical strength of silicon solar cells. The data resulting from such testing could be used by manufacturers to enhance production yields, improve cell reliability and durability, and ultimately to establish mechanical design criteria that would reduce cell costs.

For strength characterization of brittle materials such as silicon, a transverse bending test is most frequently employed, in which a rod specimen having either a circular or rectangular cross section is bent until fracture using a three-point or fourpoint loading technique.

The fracture strength of PV silicon and wafer breakage has been studied by several groups. Funke et al. studied the impact of surface microcracks on wafer breakage using a biaxial fracture test [8]. The maximum stress was located at the centre of the wafer, while the effect of microcracks at the wafer edge was eliminated. They found that the fracture stress of as-sawn PV silicon wafer is related to the crack-length distribution and the crack density. Silicon wafers broke at higher stresses when more of the damaged layer was removed by etching. Brun and Melkote performed full-field deformation measurements on PV silicon wafer using a Bernoulli gripper and obtained the in-plane tensile stress indirectly from a finite element analysis (FEA) [9]. They found that wafer breakage followed the linear elastic fracture mechanics theory and the breakage stress is proportional to the inverse square root of the edge crack length. Rupnowski and Sopori [10] proposed a model to predict the mechanical strength distribution of cast PV silicon wafers with surface, edge and bulk flaws and found surface microcracks to be the dominant factor in wafer breakage. The strength distribution of mc-Si with randomly distributed surface cracks with varying length and depth was obtained from a Monte Carlo simulation under a uniaxial tension mode.

Unfortunately, all of these studies were performed on as-sawn silicon wafers with randomly distributed micro-flaws both at the surface and the edge, and the applied test methods were not suitable for thin silicon samples ($\leq 300 \ \mu$ m). Consequently none of the above studies were based on accepted standards (*e.g.* ASTM), which makes it difficult to reproduce the data and to apply the results to real solar cell processing conditions. Furthermore, there is a lack of knowledge on quantitative analyses to predict deformation, stress, and fracture properties of metallized solar cells and until today there are no standardized tests. Thus, it is desirable to develop a test method for quantifying fracture strength of thin silicon wafers and solar cells and for determining the impact of different solar cell processing conditions on fracture strength.

4.2 Experimental Procedure for Mechanical Testing of Silicon Wafers and Solar Cells

4.2.1 Specimen Preparation

Specimen preparation was based on ASTM C 1161-02c - the standard test method for flexural strength of advanced ceramic at ambient temperature [11]. This test method describes the use of specimens with prescribed rectangular cross-sections in combination with a fixture for applying a bending load. With some adjustments the standard is appropriate for this research, because at ambient temperature mc-silicon solar cells specimens have a behaviour similar to that of advanced ceramics.

All specimens were prepared at ECN using the industrial processing standard ECN-CX-04-119 (process specification ECN mc-silicon cell processing) [12]. The samples were laser-cut from neighbouring wafers, taken from the middle of a single cast block, assuring a relatively low defect density. The preparation started from multicrystalline silicon wafers with dimensions of 155 mm × 155 mm and a thickness of 0.190 mm. These wafers were then laser cut to the desired dimensions as illustrated in figure 4.1. For a number of specimens used in this study, the thickness also comprises that of metal layer(s) which were applied prior to laser cutting. The thickness of the silicon wafers is 0.190 ±0.004 mm and the thickness of metal layer(s) varies from 0.04 – 0.06 mm, depending on the metal paste type and the mesh size of the screen-printing process.



Figure 4.1 Dimensions of silicon wafer specimens (mm).

Fracture Strength of Multicrystalline Silicon Solar Wafers and Solar Cells Tested by Four-Point Bending

The ASTM standard indicates that test specimens must have a span-to-thickness ratio (L/d) that produces tensile or compressive failure in the outer fibre under a bending moment. If the L/d ratio is too low, the specimen may fail due to shear stresses, producing an invalid test. Thin multicrystalline silicon solar cells require higher L/d ratios to prevent failure due to shear stress. The standard allows modification of the test geometry based on the geometry of available material, so the dimensions that were used in the testing have an L/d ratio > 60:1, in accordance with ASTM recommendation to use a higher L/d [13].

The edges of all specimens were polished to a 1 μ m finish and carefully examined under an optical microscope. Because of the probabilistic nature of the strength of the brittle material, a sufficient number of test specimens for each test condition is required to be able to perform a statistical analysis. In this research, 15 specimens were used for every test condition, to enable a statistical description of the results.

Samples with specific types of crystallinity were prepared in order to investigate the effect of such crystallinity features on the mechanical strength of silicon wafers. For each crystallinity type 15 neighbouring specimens (thus featuring the same crystallinity features) were prepared. The specimens were divided into 6 groups according to the crystallinity type in the centre of the specimen, see Figure 4.2, namely: one big grain, a twin boundary, a grain boundary perpendicular to the loading direction, several grains, a triple junction and many small grains.



Figure 4.2 Groups of specimens showing typical crystallinity features.

To analyse the effect of surface roughness, three types of specimens were prepared from neighbouring wafers, thus having the same crystallinity. The surface condition of these specimens included:

- the as-cut state, thus including the saw-damage layer.
- a surface textured by etching for 30 s in a $HF(10\%) + HNO_3(30\%) + CH_3COOH(60\%)$ solution. This etching serves two main purposes: to remove the

damaged layer and to create a highly textured silicon surface in order to trap the light.

• a chemically polished surface (15 μ m removal from both wafer sides in a HF+HNO₃ bath for 1 min.).

Confocal microscopy was used to evaluate the obtained surface roughness profiles. Measurements of the amount of bowing that results from metallization were made by an optical method over the full length of the solar cell (156 mm), using a Quick Vision Mitutoyo system, for more details see Appendix A.

A standard industrial solar cell process was used to apply metal layers [12], where screen printing of Al on the rear and Ag on the front was performed with a 165 mesh screen and 250 °C drying temperature. In all cases neighbouring multicrystalline wafers were studied. To examine the influence of the aluminium paste composition on the strength of the cells, three different commercially available pastes were examined (pastes designated A, B and C).

To investigate the effect of the maximum firing temperature of the Al back contact, three neighbouring wafers were processed with identical conditions, but with different peak temperatures, *i.e.* 700, 750, 800, 850, and 950 °C.

In order to examine the influence of the aluminium layer thickness on the fracture strength of the solar cells, screen print mesh sizes of 165 and 325 were selected.

Two drying temperatures (250 °C and 350 °C) were chosen to examine the influence on the microstructure and fracture strength of solar cells.

4.2.2 Four-Point Bending Strength Measurements and Calculations

A four-point bending test was chosen in this research because this type of loading results in a uniform bending moment along the central part of the specimen. Silicon is a crack-sensitive material and its failure is driven by tension rather than compression. Fracture mechanics predicts that fracture will initiate on the tensile side at the location where the largest surface or edge defect is present. Loading a significant part of the specimen length to uniform tension reduces the spread obtained in the strength results.

To a large extent, the test configuration complies with ASTM standard C 1161-02c [11], which is on the measurement of the flexural strength of ceramic material at ambient temperature. The bending tests were performed using a 100 kN Instron 5500R tensile machine equipped with a 10 N load cell. During the test the load and crosshead displacement were recorded until fracture. The crosshead speed was set such that the outer-fibre strain rate in the specimen was of the order of 10^{-4} s⁻¹.

For this research, a new test fixture was designed especially for the thin silicon specimens taken from silicon wafers. The configuration of the fixture is shown in Figure 4.3. The test fixture had a loading span equal to half the support span (*i.e.* a four-point - $\frac{1}{4}$ point configuration) and was semi-articulating.

It should be noted, that both loading and supporting rollers are fixed \emptyset 1.0 mm cylinders. This deviates from ASTM standard C 1161, which prescribes that:

- the roller diameter should be approximately 1.5 times the specimen thickness. However, such a small diameter would not be very practical in this case.
- during the bending test the loading and supporting rollers should be free to rotate inwards and outwards respectively. The fixed configuration used in this work will inevitably introduce some friction between rollers and specimen.

In order to investigate possible effects of friction, three different types of rollers were considered: as received, polished to 1 μ m and covered with 300 μ m thick PFTE foil. However, based on observations of load-displacement curves, polished rollers were chosen in order to minimize frictional constraints between rollers and the specimen surface as much as possible.

The friction occurring at the loading rollers will induce a tensile stress in the central part of the specimen. It can be reasoned, that for the four-point bending configuration the ratio of this friction stress σ_f and the outer-fibre bending stress σ_b is equal to

$$\frac{\sigma_f}{\sigma_b} = \frac{4df}{3L} \quad , \tag{4.1}$$

where d is the specimen thickness, f is the friction coefficient between roller and specimen and L is the support span. Considering the very low value for d/L in our setup (0.0063), the resulting stress ratio will always be very small. Therefore the use of fixed rollers is not expected to significantly influence the results.

The test results were plotted in terms of a load-displacement curve, *i.e.* flexural force as a function of flexural deflection, see figure 4.4 for a typical example. As can be seen, this graph contains two distinct regions: a nonlinear part at small applied loads, followed by a linear part up to final fracture. The nonlinear part can be explained by the specimen geometry, *i.e.* straightening of a slightly warped specimen, and clearance in the loading fixture and the testing machine. Thus, it does not represent a property of the material. In all results the deflection should be corrected to compensate for the nonlinear part by determining a corrected zero point for the deflection. In this case it is assumed that the above mentioned effects no longer occur above a force of 1.5 N. The linear part of the curve above 1.5 N is thus extrapolated to zero force giving the corrected deflection, see Figure. 4.4.



Figure 4.3 Illustration of the four-point bending test setup and a corresponding bending moment diagram.



Figure 4.4 Typical example of 4-point bending test result (silicon wafer featuring many small grains in the middle) showing the deflection correction.

Typical 4-point-bending load-displacement curves of silicon samples with different crystallinity features are shown in Figure 4.5. In order to prevent errors due to improper loading, load-displacement curves were closely monitored during the tests.



Figure 4.5 Representative load-displacement curves for samples with different crystallinity.

As can be seen, the curves are almost identical with the exception of the failure loads. They exhibit linear behaviour up to the failure point, so a stress distribution is assumed over the specimen thickness on the basis of linear-elastic deformation. The outer-fibre stress σ in a rectangular beam specimen loaded in the 4-point bending configuration used [11] is:

$$\sigma = \frac{3PL}{4bd^2} \quad , \tag{4.2}$$

where P is the applied force and b the width of the specimen.

However, for metallized silicon solar cell specimens, this standard formula is not appropriate, because the specimens should be represented as a composite beam consisting of two or three materials with different stiffnesses, namely silicon, the Al back contact metal layer and / or the Ag front contact metal layer, which are securely bonded to form a single solid composite beam.

A linear strain distribution is assumed across the composite beam thickness. If the specimen is loaded, this strain distribution will be as shown in figure 4.6, where ε_c is the compressive strain at the upper side of the beam, ε_t is the tensile strain at the lower side and ε_i is the strain at the interface of the silicon and the aluminium metal layer. The neutral axis, *i.e.* where the strain is zero, is the *z* axis. The stress acting on the cross section can be obtained from the strains by using the stress-strain relationships for the two materials assuming that both materials behave in linear-elastic manner, thus Hooke's law is valid.



Figure 4.6 Distribution of strains (ε) through the cross section of a composite beam loaded in bending.

The stresses in the different layers are obtained by multiplying the strains by the modulus of elasticity for silicon (E_{Si}) and for the aluminium metal layer (E_{Al}) respectively, leading to the stress distribution given in Figure 4.7. The stress distribution is largely affected by the differences in elastic moduli ($E_{Si} = 160$ GPa and $E_{Al metal layer+eutectic} = 43$ GPa, which is the average for three different pastes (Chapter 3). The elastic modulus of the Al layer is affected by particle size, glass frit and porosity, so this value is lower than the elastic modulus for bulk Al.

The compressive stress at the upper side of the beam is $\sigma_{\text{Si c}} = E_{\text{si}} \varepsilon_{\text{c}}$ and the tensile stress at the lower side is $\sigma_{\text{Al t}} = E_{\text{al}} \varepsilon_{\text{t}}$. At the interface the stresses in the two materials are different because their moduli are different. In the silicon the stress is $\sigma_{\text{Si t}} = E_{\text{si}} \varepsilon_{\text{i}}$ and in the aluminium metal layer it is $\sigma_{\text{al t}} = E_{\text{al}} \varepsilon_{\text{i}}$ [14].



Figure 4.7 Distribution of stress (\sigma) in a silicon beam with an aluminium layer.

The maximum tensile stress in the silicon and in the metal layer can be calculated by using composite beam formulas [14]:

$$\sigma_{x1} = \frac{MyE_1}{E_1I_1 + E_2I_2}$$
(4.3)

$$\sigma_{x2} = \frac{MyE_2}{E_1I_1 + E_2I_2}.$$
(4.4)

The location of the neutral axis, which is defined by h_1 and h_2 in figure 4.6, can be calculated from:

$$E_1 \int_1 y dA + E_2 \int_2 y dA = 0 \quad , \tag{4.5}$$

where σ_{x1} and σ_{x2} are bending stresses in material 1 and 2; *M* is the bending moment, *y* is the distance from neutral axis, h_1 and h_2 are the distances from the neutral axis to the top and bottom of the specimen, E_1 and E_2 are the moduli of elasticity of materials 1 and 2, I_1 and I_2 are the moment of inertia of cross sections of materials 1 and 2 about the neutral axis, and *A* is the cross sectional area.

This equation is based on the assumption that for pure bending (where no force is applied in the x direction), the stress in the x direction over the area of the entire cross section vanishes.

4.2.3 Statistical Data Analysis

There is considerable scatter in the fracture strength data of brittle materials, such as silicon. Specimens produced from identical material and using identical test methods fail at different applied loads. The reason is that the fracture strength of a brittle material, such as silicon, is determined by the presence of defects that lead to crack initiation. These defects, however, show a random distribution with respect to their location, size and orientation.

In a brittle material only a single critical flaw or crack can lead to final fracture, a phenomenon often referred to as the weakest link principle. Therefore the volume of material that is mechanically loaded also influences fracture strength. The larger this volume is, the higher the probability of having a flaw that becomes critical and consequently the higher the probability to have a low fracture strength.

The two-parameter Weibull distribution provides a statistical method to quantify the probability of failure and the strength distribution of a specimen [15-17]. The probability of failure of a specimen is given by the equation:

$$P_f = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_\theta}\right)^m\right] , \qquad (4.6)$$

where P_f is the probability of failure at an applied tensile stress σ , and σ_{θ} and *m* are the characteristic strength and the Weibull modulus of the specimen respectively.

The characteristic strength, σ_{θ} , is the tensile stress at which 63.2% of all samples are expected to fail. The Weibull modulus is the slope of the cumulative probability curve that gives information about the scatter of the specimen's strength. A large value of *m* stands for little scatter with respect to strengths measured from specimen to specimen, which can be associated with a narrow defect distribution in terms of size and orientation. The average strength of the material then adequately represents the strength of the material. A low Weibull modulus reflects a high variation in measured strength, *i.e.* the flaw distribution is relatively broad. Material with a low Weibull modulus shows a larger inconsistency in strength, thus the average strength can not adequately represent the performance of the material.

Estimates for the parameters σ_{θ} and *m* of the two-parameter Weibull representation of strength data are found by making a plot of $\ln\{\ln[1/(1-P_f)]\}$ as a function of $\ln(\sigma_{max})$, where σ_{max} is the strength of the specimen represented by the maximum stress occurring during testing of that specimen. Data for this plot are obtained on the basis of experimental results on a sufficiently large number of similar specimens using the procedure described in [15]. This graphical procedure involves ranking the strength data obtained from a laboratory test series in ascending order. Next, a probability of failure P_f is assigned to each test result, according to the estimator:

$$P_{\rm f} = (i - 0.5)/N$$
, (4.7)

where : $P_{\rm f}$ is the probability of failure, *i* is $i_{\rm th}$ datum and *N* is the number of specimens.

Figure 4.8 shows an example of a Weibull distribution for samples covered with Al paste type B. The Weibull characteristic strength for the specimens under consideration is the value at which the probability of failure is 63 %. The Weibull modulus for the specimens is 6.4, determined from the linear regression slope.



Figure 4.8 Example of a Weibull distribution with Weibull modulus m = 6.4 and characteristic strength $\sigma_{\theta} = 266$ MPa.

4.2.4 Microstructure and Fracture Surface Analysis

Specimens were mounted in Epofix resin for microscopy investigation of cross sections. The mounted specimens were first ground and then polished to a 1 μ m surface finish. After the polishing process, the specimens were observed using an Olympus BX60M optical microscope equipped with AnalySIS version 5.0 software. If appropriate, the thickness of the metal layer(s) was measured and microstructure pictures were made.

Fracture surface analysis was performed by a Scanning Electron Microscope (SEM). The specimens were placed in a suitable holder for SEM observations. The fracture surfaces of some specimens were observed and some pictures were made.

The effects of saw-damage removal were analyzed using Raman spectroscopy by comparing results from as-cut wafers with those from etched specimens. In all cases only neighbouring wafers were used. Raman measurement was carried out at room temperature in the backscattering configuration. A Renishaw Raman spectrometer was used, equipped with a He-Ne laser with an excitation wavelength of 633 nm and a 100× objective, resulting in a focused spot with a diameter of ~1 μ m and a penetration depth of a few μ m in silicon. The measurement was performed in 3 accumulations with 5% of the total 50 W power. The c-Si peak was fitted to a Lorentzian distribution (for more details see chapter 6.4.1).

4.3 Mechanical Behaviour of mc-Silicon Wafers

4.3.1. Effect of Saw Damage on Mechanical Strength

The effect of cutting silicon specimens using a conventional multi-wire-sawing process on microstructure and mechanical strength was investigated.

Figure 4.9 represents a schematic illustration of the wire-saw cutting process in which a steel wire under high tension moves at high speed along the surface of the substrate. The wire is submerged in an abrasive slurry, consisting of abrasive grit suspended in a carbon based fluid (a mixture of powdered SiC suspended in oil) [18]. Especially when the abrasive particles are large, considerable damage is caused to the Si surface and there are several deep grooves across the surface. The region near these grooves contains significant damage and residual stresses.

Figure 4.10 shows a typical surface of an as-cut multicrystalline silicon wafer, containing a large number of smooth grooves. As-cut silicon samples were analyzed with a Raman spectrometer to investigate the nature of smooth grooves and to check for phase transformations in the damaged surface layer.

The Raman spectrum, shown in Figure 4.11, clearly indicates the presence of amorphous Si (a-Si) next to polycrystalline Si on the as-cut surface. Several points (\sim 10) at different positions on the smooth parts on the wafer surface have been measured and in most of them, a similar a-Si peak was found.

As shown in figure 4.9, the microscopic silicon-removal process can be seen as the interaction of loose, rolling SiC particles that are randomly indented into the silicon surface until small crystal pieces are chipped away. Since SiC particles are facetted and contain sharp edges and tips, they can introduce very high local pressures on the surface [19].



Figure 4.9 Schematic illustration of rolling–indenting in the wire-sawing cutting process in which the wire introduces force on the rolling abrasive SiC particles, thus chipping the contact interface and removing materials from the surface.

It is known that when silicon is indented/scratched, the locally induced high pressures cause a phase transition from cubic diamond (Si-I) into a metallic (ductile) β -tin structure (Si-II) [20]. During fast unloading, this ductile phase in not stable and transforms into a layer of amorphous silicon. Conversely if the unloading is slow enough a mixture of amorphous and metastable phases (Si-XII - rhombohedral structure and Si-III- body-centred cubic structure) is formed [20, 21].



Figure 4.10 Scanning electron micrograph of a typical surface of an as-cut multicrystalline silicon wafer.

In this study, the Si phase transition into amorphous silicon was found only in the smooth grooves (Figure 4.11). The rough parts of the as-cut silicon wafer surfaces, where material is chipped off, mainly consist of stable crystalline silicon.

In order to see the influence of saw damage on the mechanical strength of silicon wafers, 2 types of specimens were mechanically tested: as-cut specimens and specimens etched by an acidic solution to remove the damaged layer. The results, presented in Table 4.1, show that the as-cut specimens have a lower Weibull characteristic strength, σ_{θ} , which is presumably due to the presence of microcracks at the surface loaded in tension.

It is known that wafer strength is directly related to the orientation, location and the size of microcracks [22, 23]. If the size of microcracks is larger, the probability that a macrocrack initiates and leads to failure for a given stress is also higher. Microcracks are induced during the sawing process while slicing the wafers from the ingot, which explains the lower strength in specimens in the as-cut state. Additionally, the presence of the transformed a-Si phase could possibly also affect mechanical stability of the ascut wafers, due to the local stresses induced by the phase transformation.



Figure 4.11 Representative Raman spectrum for the as-cut wafer surface (smooth part), showing local indentation-induced transformation of Si into amorphous Si.

As a result of the etching process, the depth of surface microcracks is reduced, some cracks disappear completely and some crack tips might become more blunted. Furthermore, the layer of transformed a-Si is removed. All these effects reduce the probability of macrocrack initiation, increasing the specimen strength.

Table 4.1. Effect of damaged layer on Weibull characteristic strength (σ_{θ}) and modulus (*m*).

Surface	$\sigma_{ heta}$	m ()
condition	(MPa)	<i>m</i> (-)
as-cut	155	9.4
after etching	234	8.3

4.3.2. Effect of Surface Roughness on Mechanical Strength

In order to investigate the effect of surface roughness on strength, three sets of specimens taken from neighbouring wafers (thus featuring the same crystallinity) were tested with as cut, textured and polished surface conditions.

In this study, the as-processed silicon wafer thickness remains the same, and the wafer edges are mechanically polished to a 1 μ m finish. Therefore these factors will not influence the strength and the surface roughness primarily determines the fracture strength of the multicrystalline silicon wafer specimens.

Figure 4.12 shows representative confocal microscopy surface roughness profiles, taken after the respective surface treatments in the same areas of the neighbouring samples. Table 4.2 contains the determined roughness parameters *Sz* and *Sdr* (where Sz

is an average difference between the 5 highest peaks and 5 lowest valleys and Sdr is the developed Interfacial Area Ratio, which is expressed as the percentage of additional surface area contributed by the texture compared to an ideal plane the size of the measurement region [24]).



Figure 4.12 Representative surface roughness profiles for as-cut, textured and polished neighbouring wafers: a) areas including the grain boundary (marked as red), b) in the grain (marked as blue).

As can be seen, samples with a textured surface show a significantly higher surface roughness compared to the as-cut state, presumably due to the formation of etch pits. It should also be noted, that etching/texturing creates a much rougher surface at the grain boundaries, probably due to local preferential etching (etched sample in Figure 4.12b).

The low value of the Weibull modulus for the textured samples (m = 8.3; see Table 4.2) shows that apparently there is considerable variation in the size of the largest defects present at the tensile surface. However, despite the increase of the surface roughness, there is an increase of 50% in the characteristic strength as a result of the etching/texturing, probably due to the removal of the damaged layer. Thus, it is suggested, that the size of microcracks in the damaged layer is a more dominant factor affecting mechanical strength of silicon wafers than the surface roughness.

Polishing the silicon wafers showed the expected reduction in surface roughness, as well as a significant increase in fracture strength (Table 4.2). A larger Weibull modulus, as compared to the as-cut and the textured state, indicates that the polishing process gives a much smoother silicon surface and a narrower defect distribution.

It can be concluded that, as long as saw-damage is removed, the surface roughness profile is the second most detrimental factor affecting mechanical strength of silicon wafers.

It can also be concluded, that the fracture strength of polished and textured silicon wafers is inversely dependent upon the surface roughness.

4.3.3 Effect of Crystallinity on Mechanical Strength

Specific types of neighbouring silicon wafers crystallinity were chosen for this research to investigate the effect on mechanical strength. All specimens were etched by an acidic solution for 30 s to remove the damaged layer induced by the sawing process. Four-point bending tests were performed and strength was calculated using Eq. (4.2). The results are given in Table 4.3 in terms of the Weibull characteristic strength (σ_{θ}) and the Weibull modulus (*m*) based on 15 tests.

As can be seen from Table 4.3, it is possible to define three main characteristic groups, based on the strength results. The specimens with one big grain in the middle have a much higher strength than those with many small grains in the middle. The four other crystallinity types, all having several grains in the middle, have intermediate strengths.

Silicon Surface	In the Grain		Grain Boundary		σ_{θ}	m
Treatment	Sz	Sdr, (%)	Sz	Sdr, (%)	(MPa)	(-)
As Cut	5.70	14.6	6.11	12.2	160	9.4
Textured	12.7	28.2	13.7	45.8	240	8.3
Polished	9.73	10.8	10.6	10.0	285	10.1

Table 4.2. Effect of surface roughness parameters on bending strength and Weibull parameters of multicrystalline silicon wafers.

As for most brittle materials, the fracture strength of a multicrystalline (mc) silicon wafer depends on both material-intrinsic properties, such as grain size, grain boundaries and crystal orientation, and on extrinsic variables such as flaws and microcracks [24, 25]. Both intrinsic and extrinsic properties can reduce the strength of a multicrystalline silicon wafer. The strength reduction due to the presence of many small grains might be related to the number of grain boundaries, which is proportional to the

number of grains. Alternatively the surface roughness might be different for different crystallinity types. Grain boundaries can be treated as weak regions where cracks can easily initiate and propagate along, since they are less strongly bound than bulk atomic planes. Thus material containing many grain boundaries has a larger probability of containing weak regions that negatively affect the strength. It should also be pointed out that grain boundaries can continue up to the specimen edge, thus creating potential vulnerabilities at the edges.

Apart from the effect of grain boundaries, the surface roughness might be different for different crystallinity types, due to preferential etching of the grain boundaries. Surface roughness parameters of the three main crystallinity groups are given in Figure 4.13. As can be seen, there again seems to be a correlation between surface roughness and the fracture strength: the higher the surface roughness, the lower the fracture strength, see Figure 4.13c.

Crystallinity type	σ_{θ} (MPa)	<i>m</i> (-)
One big grain	287	7.9
Twin boundary	256	8.6
Triple junction	255	5.9
GB perpendicular to the loading direction	241	8.4
Several grains	228	5.5
Many grains	208	5.7

Table 4.3. Effect of crystallinity type on mechanical strength for etched wafers.

In order to minimize the effect of surface roughness, samples with crystallinity features similar to those shown in Figure 4.2 were chemically polished to further reduce the surface roughness. As can be seen from Table 4.4, polishing the samples, leads to higher Weibull characteristic strengths and moduli, probably due to a reduction of the roughness at the grain boundaries (smoothening of the etch pits).

It should be pointed out, that a significant increase of strength is only observed in samples with many grains, which can be related to the levelling off (by the polishing) of etch pits that were formed at the grain boundaries during the texturing/etching process.

Nonetheless, samples with polished surfaces show the same correlation between crystallinity and fracture strength; namely, the higher the number of grain boundaries, the weaker the sample. Furthermore, fracture patterns of the polished silicon samples subjected to 4-point bending revealed a preferential propagation of the cracks along the grain boundaries (Figure 4.14).

From these results it can be concluded, that for polished silicon wafers crystallinity is the most significant factor affecting the strength, probably due to a lower

strength of the grain boundaries leading to intergranular fracture. Conversely, there is a mixed type fracture (transgranular and intergranular) for textured and as-cut silicon wafers, where surface roughness and a damaged surface layer are the most detrimental factors.



Figure 4.13 Representative surface roughness profiles of etched samples: a) one big grain, b) triple junction and c) surface roughness parameters and characteristic strengths.

Table 4.4. Effect of crystallinity type on mechanical strength for polished wafers.

Crystallinity type	σ_{θ} (MPa)	<i>m</i> (-)
One big grain	293	8.5
Twin boundary	274	8.9
Triple junction	268	6.7
GB perpendicular	266	9.1
to the loading direction		
Several grains	260	7.4
Many grains	251	6.9



Figure 4.14 Example of the fracture pattern of a polished mc-silicon sample showing deflection of the crack along the grain boundary.

4.4 Mechanical Behaviour of mc-Silicon Solar Cells

4.4.1 Effect of Al Metallization Paste Type on Mechanical Strength of mc-Silicon Solar Cells

Three types of aluminium metal pastes were investigated in order to find the influence of the microstructure resulting from firing at 850 °C on the mechanical strength of silicon solar cells. It should be noted, that these specimens were treated as composite beams, consisting of two layers, *i.e.* a bulk mc-silicon wafer and an aluminium layer. The bending strength of the specimens was corrected using the appropriate flexural formulas (equations 4.3 and 4.4). Using these formulas, it was possible to obtain the 4-point bending tensile strength for each of the mc-silicon solar cells. Unfortunately, the strength of the silicon wafer and the Al layer (*i.e.* the composite beam) cannot be determined individually in this research due to uncertainty in which layer the fracture originates.

Tables 4.5 and 4.6 give the results for the maximum bending tensile stress at fracture in the silicon and aluminium layers. Results presented in table 4.5 are for the sample position with the aluminium layer under tension, while table 4.6 presents the results with the silicon surface under tension. In order to have concise tables, the aluminium paste types were defined as follows:

- (A). Si + Al layer (Al paste A, mesh 165, drying temperature 250 °C)
- (B). Si + Al layer (Al paste B, mesh 165, drying temperature 250 °C)
- (C). Si + Al layer (Al paste C, mesh 165, drying temperature 250 °C)

It should be noted that there is only one Weibull modulus (m) coupled to the characteristic strengths of the silicon wafer and the aluminium layer.

Type of	Max. bending tensile stress in silicon wafer		т	Max. bendin stress in alum	ng tensile inium layer
paste	(Al under	tension)		(Al under	tension)
	$\sigma_{mean}\left(MPa\right)$	σ_{o} (MPa)		σ_{mean} (MPa)	σ _o (MPa)
Α	249 ± 47	266	6.3	103 ± 19	110
В	227 ± 41	237	6.5	90 ± 16	94
C	210 ± 53	217	4.8	80 ± 20	82

Table 4.5. Effect of aluminium paste type on stresses at fracture, tested with the Al layer surface under tension.
	Max. bending tensile stress			Max. bending compressive	
Type of	in silicon			stress in alumit	nium layer
paste	(Si under tension)		т	(Si under te	ension)
	σ_{mean} (MPa)	σ_{o} (MPa)		σ_{mean} (MPa)	σ _o (MPa)
А	211 ± 28	206	7.8	72 ± 9.6	71
В	191 ± 27	195	8.5	66 ± 9.5	68
С	191 ± 23	193	9.6	66 ± 8.2	67

Table 4.6. Effect of aluminium paste type on stresses at fracture, tested with the silicon wafer surface under tension.

As can be seen from the tables, the specimens with Al paste A lead to the highest bending tensile stresses at fracture, while specimens with Al paste C have the lowest bending tensile stresses. Thus the type of aluminium paste has a significant effect on the strength when the specimens are loaded with the Al layer in tension. In this loading condition, both specimen layers, *i.e.* the silicon wafer and the Al layer, are loaded in tension. Furthermore, due to its higher stiffness, the silicon wafer experiences the highest tensile stresses. For the reverse loading condition the effect of Al paste type on the mechanical strength is not significant.

It should be noted that specimens with an Al layer show an increase in bending strength (as compared to the reference etched silicon wafer specimens, possibly due to the formation of a eutectic layer (~12% Si) and a BSF layer ($1-2 \times 10^{18}$ Al atoms/cm³ Si) (*cf.* Figure 3.13).

The maximum tensile stress in the silicon wafer will be located at the interface between the silicon wafer and the aluminium bulk layer, *i.e.* in the BSF layer.

From chapter 3, it was found that the Al porous layer has a composite-like microstructure, consisting of three main components: 1) spherical hypereutectic Al-Si particles, 2) bismuth silicate glass and 3) porosity. It was found, that the Al layer is not uniform and does not fully cover the eutectic layer. The eutectic layer, however, represent a uniform Al-Si bulk alloy, being in full contact with the BSF layer, and as a result with the silicon wafer. The presence of the eutectic layer is expected to have a significant effect on the mechanical behaviour of the silicon wafer. Since silicon is a very brittle material that only exhibits elastic behaviour, the presence of a continuous eutectic layer will alter the stress distribution, affecting possible crack initiation. Furthermore, the eutectic layer can show some plasticity, and thus can serve as a bridge for possible critical microcracks, thus improving the strength of mc-silicon solar cells.

The different effects of Al pastes on the mechanical strength of mc-silicon solar cells can be explained by the differences in microstructures, as well as by differences in eutectic layer thickness and uniformity. The microstructures resulting from the

aluminium pastes were studied in details in chapter 3 and shown in Figure 3.18. Al paste A produces the finest microstructure, with small Al particles homogeneously distributed throughout the layer, thus creating a compact structure, which also affects the as-fired Al layer thickness and creates a more uniform eutectic layer (see section 3.4.3).

Computer tomography (CT) scans were made in order to investigate the microstructural differences between the Al pastes. Results of these CT scans are presented in table 4.7, together with the measured characteristic stresses at fracture. In general, three main parameters affect the mechanical strength of mc-silicon solar cells with an aluminium contact layer, namely the thickness and uniformity the eutectic layer, the Al layer thickness (which results from the Al particle size and its distribution), and the amount of porosity and the bismuth glass fraction. It was observed that the larger the Al particle size, the more nonuniform and 'wavy' the resultant eutectic layer is, which could result in a reduction of fracture strength, due to local stress concentrations.

The SEM image of the fracture surface presented in Figure 4.15 shows delamination along the interface between the silicon wafer and the Al layer (*i.e.* eutectic layer). In general, this figure shows the different crack patterns that develop in bulk silicon and in the eutectic layer. The fracture surface of the silicon wafer shows a V pattern (chevron), as is typical for brittle materials. However, the eutectic layer demonstrates delamination following a distinctive pattern, suggesting the presence of plasticity in the eutectic layer.

Figure 4.16 shows that the crack most probably initiated at the edges of the specimen and propagated perpendicular to the loading direction from the right to the left. Figure 4.15 and 4.16 do not give any indication that the cracks initiated at the surface of the silicon wafer or at the eutectic layer; instead the cracks seem to have initiated at the edge of the specimens, potentially from microcracks. It should be noted, that an accurate determination of the layer in which the crack originated is difficult.



Figure 4.15 SEM images of the fracture surface of an mc-silicon solar cell specimen (Si + *paste B aluminium layer), tested with the Al layer under tension.*



Figure 4.16 SEM image of the fracture surface of an mc-silicon solar cell specimen (Si + Paste B aluminium layer, tested with the Al layer under tension), showing crack initiation from the edge.

Type of	Characteristic stresses at fracture (MPa)		Al layer	Porosity	Bismuth-
paste	σ _{Si} (Al under tension)	σ _{Al} (Al under tension)	thickness (μm)	(vol. %)	fraction (vol. %)
А	266	110	40	10	2
В	237	94	50	14	4
С	217	82	60	16	5

Table 4.7. Effect of aluminium paste type on the characteristic stress at fracture.

4.4.2 Effect of Screen-Printing Mesh Size on Mechanical Strength of mc-Silicon Solar Cells

In order to investigate the effect of Al layer thickness on mechanical strength, two different types of screen-printing mesh sizes were used in this research, namely mesh 165 and mesh 325. The mesh size is defined as the number of threads in the mesh that cross per square inch. For instance, a 165 mesh screen has 165 threads crossing per square inch. The higher the mesh count, the finer the treads and holes are in the screen. Both mesh sizes were applied in the metallization process with 3 types of aluminium paste: A, B and C. A summary of the results is presented in table 4.8.

As can be seen from Figure 4.17, the screen printing mesh size affects the thickness of the aluminium layer. The thickness with mesh size 165 is approximately twice that of mesh size 325.

Based on the results it can be concluded that the mesh size (*i.e.* 165 and 325) and hence Al layer thickness does not affect on the strength of the silicon wafer. One would

expect, however, that the thickness would have an effect on the strength of the Al layer itself. It could be reasoned that, since a thicker Al layer does not strengthen the silicon wafer, the strength mainly depends on the type of Al paste. The behaviour of interfaces, such as between the eutectic and the BSF layer and the eutectic and the Al bulk layer, might also be very important for the strength of silicon wafers.

Type of paste		Al layer thickness	Max. bending tensile stress in silicon wafe (Al layer under tensio		т	Max. bending tensile stress in Al layer (Al layer under tension)	
1 y	pe of puste	(µm)	σ _{mean} (MPa)	σ _o (MPa)		σ _{mean} (MPa)	σ _o (MPa)
	Mesh 165	40 ± 2	250 ± 47	266	6.3	103 ± 19	110
A	Mesh 325	20 ± 2	232 ± 50	264	5.5	76 ± 16	86
D	Mesh 165	50 ± 2	228 ± 41	237	6.5	90 ± 16	94
D	Mesh 325	25 ± 2	221 ± 37	237	7.0	73 ± 12	78
C	Mesh 165	60 ± 2	211 ± 54	217	4.8	78 ± 20	82
	Mesh 325	30 ± 2	207 ± 37	219	6.4	64 ± 11	68

Table 4.8. Effect of screen-printing mesh size on the bending stress at fracture.



Figure 4.17 a) Microstructure of Al paste C, mesh size 325, dried at 350 °C; b) Microstructure of Al paste C, mesh size 165, dried at 350 °C.

4.4.3 Effect of Drying Temperature on Mechanical Strength of mc-Silicon Solar Cells

Two different Al-paste drying temperatures (250 °C and 350 °C, with 165 screen print) were chosen in order to investigate the influence on mechanical strength. A summary of the results is presented in table 4.9. The paste-drying temperature has an effect on the bending tensile stresses at fracture in mc-silicon solar cells. Specimens dried at low temperature (250 °C) show higher characteristic stresses at fracture than specimens dried at high temperature (350 °C).

Formation of the aluminium back-contact layer has been described in chapter 3. The drying of aluminium paste is the 2^{nd} step, necessary to drive-off organic solvent from the paste. After drying, a porous Al layer covers the silicon wafer surface. This may lead to insufficient Al deposition, because the porous Al layer reduces the amount of Al directly in contact with the silicon surface. As a result, a non-uniform and thin Al-Si layer is formed, as the alloying process only occurs locally on the silicon surface (Figure 4.18 a).

	Max. bending tensile				Max. bending tensile	
		stress in silicon wafer			stress in Al	layer
]	Гуре of	(Al layer under	tension)	т	(Al layer under	tension)
	paste	σ _{mean} (MPa)	σ _o (MPa)		σ _{mean} (MPa)	σ _o (MPa)
	250 °C	249 ± 47	266	6.3	103 ± 19	110
Α	350 °C	213 ± 36	229	6.8	89 ± 15	95
	250 °C	232 ± 50	264	5.5	76 ± 16	86
В	350 °C	206 ± 28	216	8.8	67 ± 9	70

Table 4.9. Effect of drying temperature of aluminium paste on bending tensile stress at fracture of mc-silicon wafers.

In chapter 3, a computed-tomography (CT) study of the Al back-contact layer revealed the presence of spherical voids inside the porous bulk Al layer. It was shown that these voids have a regular distribution across the entire Al layer, and was caused by screen printing-induced defects. It was found that there is a significant difference in the defect volume fraction between samples processed at different drying temperatures. Drying at 350 °C creates relatively large holes with a diameter of 10 - 20 μ m resulting in a more porous layer, while drying at 250 °C gives smaller holes and a denser Al layer structure. The presence of voids in the aluminium layer (Figure 4.18 b) produced by the screen printing process, creates stress concentrations at the interfaces, affecting the

strength. Hence, drying aluminium paste at lower temperature (250 °C) can be advised as the most optimal condition from a mechanical stability point of view.



Figure 4.18 a) Schematic representation of the melting of aluminium at 660 °C and the start of the alloying process; b) Large voids in the Al layer (paste A, mesh size 165) after drying at 350 °C.

4.4.4 Effect of Maximum Peak Firing Temperature on Mechanical Strength of Silicon Solar Cells

Another process-related effect that was investigated in the course of this study is the relationship between the maximum firing temperature of the aluminium back contact layer and the fracture strength of the silicon solar cell. For this purpose, six neighbouring wafers were processed with the same conditions (Al paste B), but with different peak temperatures: 750 °C, 800 °C, 850 °C, 900 °C and 950 °C.

Table 4.10 shows the effect of the maximum firing temperature on the characteristic stresses at fracture in silicon solar cells. As can be seen, there is a strong correlation between the maximum firing temperature and the stresses at fracture, *i.e.* the higher the firing temperature, the higher the characteristic stresses at fracture in the Al and Si layers. Furthermore, it should be noted, that increasing the firing temperature increases the amount of bowing of the complete cell.

As can be expected from the Al-Si phase diagram [26], increasing the firing temperature leads to an increased amount of Si dissolution and thus increased amount of liquid phase, which will result in a thicker eutectic layer. Thus these effects can be explained by the increase in eutectic-layer thickness with peak firing temperature, Figure 4.19.

Thus, both the thickness of the eutectic layer as well as the uniformity of the aluminium back contact layer (fewer defects) can be considered as the most important parameters controlling mechanical stability of silicon solar cells.

Firing temperature	Characteristic stresses at fracture (Al under tension)		Bowing of complete	Eutectic/Al layer thicknesses,	
(°C)	σ _{Si} (MPa)	σ _{Al} (MPa)	(mm)	(µm)	
750	149 ± 11.5	59 ± 4.6	0.5	4 (non uniform, "pyramid like") / 50	
800	171 ± 16.1	68 ± 6.3	1.2	5 - 6 / 50	
850	187 ± 20.3	73 ± 7.6	1.4	7 - 8 /50	
900	193 ± 22.5	77 ± 8.9	1.45	10 - 11/ 52	
950	203 ± 18.0	80 ± 7.2	1.8	12 - 13 / 52	

Table 4.10. Effect of maximum firing temperature on the characteristic stresses at fracture, the bowing of the silicon solar cells and the eutectic/Al layer thicknesses.



Figure 4.19 Effect of maximum firing temperature on eutectic layer thickness.

4.4.5 Effect of Silver Metallization on Mechanical Strength of mc-Silicon Solar Cells

Three different cell-metallization configurations treated with similar testing conditions [12] were compared in order to find effects on the mechanical strength. The mc-silicon wafer, *i.e.* without any metal layers, was used as a reference. A summary of the result is presented in table 4.11. The three metallization configurations in this table are defined as follows:

- (A) silicon wafer after etching 30 s (reference)
- (B) silicon wafer + Al paste A mesh 165, dried at 250 °C (silicon wafer covered by Al layer on one side) used as a reference

- (C) silicon wafer + Ag paste A, mesh 165, dried at 250 °C (silicon wafer covered by Ag layer on one side)
- (D) Al paste A + silicon wafer + Ag paste A, mesh 165, dried at 250 °C (silicon wafer covered by Al layer on one side and Ag layer on the other side)

Table 4.11. Effect of the metallization configuration on stresses at fracture of mc-silicon solar cells.

Configuration	ion bowing, (mm) Max. Cell		x. bending tensile ss in silicon wafer etallic layer under tension)		Max. b tensile s metal (Metall under t	ending stress in layer ic layer ension)
		σ _{mean} (MPa)	σ _o (MPa)		σ _{mean} (MPa)	σ _o (MPa)
А	-	227 ± 33	234.0	8.3	-	-
В	1.4	250 ± 47	265.8	6.3	104 ± 19	110.2
С	4	235 ± 27	238.5	10.4	84 ± 10	85.8
D	2.8	213 ± 42	210.4	6.9	72 ± 14	70.8

In general, different metallization configurations have different effects on the strength of the silicon wafer and metallization layers (Al layer and Ag layer). As can be seen, the presence of an Al layer increases the strength of the silicon wafer, compared to the reference (configuration B). As was already discussed in section 4.4.1, the eutectic Al layer adjacent to the outer fibre of the silicon can show some plasticity, thus providing a higher bending tensile stress at fracture.

Covering the specimens fully by silver on one side (configuration C) does not give any significant effect on the strength of the silicon wafer (when loading the silver layer in tension). It might be expected, that the dense microstructure of the bulk Ag layer, as presented in Figure 4.20, can increase the strength of the silicon wafer compared to the reference. However, the internal stresses induced by the thermal expansion coefficient mismatch between the silicon wafer and the silver layer (see bowing values in Table 4.12) during the metallization process might make the influence of the silver layer not so pronounced.



Figure 4.20 Microstructure of Ag paste A, mesh 165, dried at 250 °C.

The situation is different for specimens that are metallized on both sides (configuration D - with Al layer under tension). A cross section is presented in Figure 4.21. The stress at fracture in the silicon wafer is below that of the reference specimen. This means that this metallization configuration decreases the bending tensile stress at fracture of the silicon wafer. A possible explanation of this phenomenon is the presence of higher residual stresses, so if the bending stress is applied, these stresses sum up and the specimen fails at a lower applied force.

Due to metallization on both sides, the silicon wafer will be in compression. However, in which layer fracture actually initiates can not be determined (see Figure 4.22). It could be that the Al layer, which is tested in tensile, contains a higher residual tensile stress level due to the presence of Ag layer on the other wafer surface. This suggests that the internal stresses induced from metal layers on both sides have a significant effect on the mechanical stability of mc-silicon solar cells. The influence of internal stress (residual stress) due to thermal coefficient (CTE) mismatch between metal layer and silicon wafer will be described in chapter 6.

Regarding the fracture surface, Figure 4.22 shows that delamination is present at the interface between the Al layer and the silicon wafer, while no delamination can be found at the interface between the Ag layer and the silicon wafer. The possible reason for this is the different contact formation of these layers during firing. The eutectic layer, that is present at the interface between the Al layer and the silicon wafer, can serve as a ductile phase that shows some plasticity and alters the mechanical behaviour of the silicon' outer fibre. At the same time no plasticity is observed at the interface between the Ag layer and the silicon wafer.



Figure 4.21 Cross section of Ag paste A + Si + Al paste B, dried at 250 °C.



Figure 4.22 SEM images of fracture surface of a multicrystalline silicon solar cell, a) Ag paste A + silicon wafer + Al paste A, tested with the Al layer under tension; b) Ag paste A + silicon wafer + Al paste A, tested with the Ag layer under tension.

4.4.6 Effect of Ag-Si interface roughness

To study the effect of the Ag/Si interface surface roughness on the mechanical strength of the as-fired solar cells, four neighbouring mc-Si wafers were prepared with different surface conditions: as-cut, textured and polished (see table 4.12). As discussed in section 3.6.1.2, there are specific microstructural aspects that result from each silicon surface condition, namely:

- a textured surface leads to large voids and inhomogeneities at the Ag/Si interface;
- a polished silicon surface results in a rather uniform distribution of Ag agglomerates;
- an as-cut silicon surface will contain cracks.

Figure 3.31 shows a model of the Ag/Si contact interface for textured and polished silicon surfaces. In this model polishing of the silicon surface gives a better wetting by the glass layer, resulting in a lesser incidence of large voids compared to highly textured surfaces, which explains the larger bow and higher strength for polished silicon surface samples.

	Thickness, (µm)	Bow, (mm)	Bending tensile stress in Ag, (MPa)	Bending tensile stress in Si, (MPa)
As cut	230	3.7	33	94
Textured	220	4.0	37	103
10 µm polish	210	4.1	62	174
15 μm polish	205	4.5	59	163

Table 4.12. Effect of Ag/Si interface roughness on strength and amount of bowing.

For textured surfaces, the non-uniformity of the glass layer and large voids at Ag/Si interface gives a negative effect on the mechanical strength of the solar cell. Furthermore, the presence of cracks at the Ag/Si interface for as-cut samples, significantly reduces the strength of solar cells. Based on the results (bending stresses in Si and general stability of chemical etching process), it could be concluded, that a polished 10 μ m silicon surface gives a better Ag/Si bond and increases the strength of the entire cell.

4.5 Conclusions

The mechanical strength of multicrystalline (mc) silicon solar wafers and solar cells was investigated using four-point bending tests. The maximum principal stresses in the specimens before failure during bending were calculated as a measure for the fracture strength.

The study of silicon wafer fracture strength showed that:

- the surface layer damaged by the sawing process contains a mixture of indentation-transformed amorphous silicon and a stable crystalline silicon phase;
- damage-layer removal by etching increases the strength of the mc-silicon wafer by about 50%;
- samples with a removed damaged layer show an inverse dependency between the surface roughness profile and the fracture strength;

- mc-silicon wafer crystallinity has a significant effect on the mechanical strength. For polished silicon wafers crystallinity is the most significant factor affecting the strength, suggesting a relative weakness of the grain boundaries, leading to an intergranular fracture mode of polished multicrystalline silicon wafers;
- surface and edge defects, such as microcracks, grain boundaries and surface roughness are the most probable sources of mechanical strength degradation; a reduction of these defects leads to an increase of the fracture strength of a mc-silicon wafer;
- results suggest, that there is a mixed type fracture (transgranular and intergranular) for as-cut and for textured silicon wafers;
- polishing of silicon wafers where more than 15 μ m is removed, further increases fracture strength.

Silicon solar cell samples were treated as composite beams, consisting of two layers, namely: bulk mc-silicon wafer and an aluminium or silver layer. It was possible to determine the maximum stress in each layer at the moment of specimen fracture. Unfortunately, the strength of the silicon wafer and that of the metal layer (*i.e.* the composite beam) cannot be determined independently in this research, due to uncertainty concerning in which layer the fracture originates. The results of silicon solar cell fracture tests showed that:

- There is a relationship between aluminium paste composition, mechanical strength of a cell and the degree of cell bowing, which is affected by the Al layer thickness, porosity, bismuth glass concentration and the thickness and uniformity of the eutectic layer. The larger the Al particle size the more nonuniform the eutectic layer is, which results in a reduction of fracture strength.
- When loaded in tension, the aluminium layer improves the strength of a solar cell. The Al-Si eutectic layer adjacent to the outer fibre of the silicon wafer can show some plasticity and can serve to retard possible critical microcracks at the silicon wafer surface, thus improving the strength of the mc-silicon wafer.
- The screen printing mesh size affects the thickness of the resulting metal layer (thickness for mesh 165 is about twice that for mesh 325). However, the mechanical strength of a mc-silicon wafer is not affected by the Al layer thickness, indicating that the porous part of the layer is too loose to contribute significantly to the mechanical strength of the cell as a whole.
- Drying aluminium paste at a lower temperature (250 °C) yields a better mechanical strength than drying at a higher temperature (350 °C); The aluminium paste layer needs special care during the drying process (a slow heat-up ramp), otherwise the volatilizing solvent can build cavities in the paste.

These cavities produce unalloyed regions and porosity at locations that correlate with those of the screen mesh openings of the screen printing process. Thus, drying at 250 °C can be recommended as the most appropriate of the drying temperatures examined, creating fewer defects.

- There is a strong correlation between maximum firing temperature, bowing and fracture strength of solar cell. The higher the firing temperature, the higher the fracture strength and the amount of bowing.
- The metallization process (from both sides) can either decrease or increase the mechanical strength of mc-silicon solar cells depending on the bending direction. It is suggested that the decrease of strength is caused by the development of internal stresses inside the specimen during the metallization process.
- Si wafer surface roughness has a significant effect on the Ag/Si interface bonding, affecting mechanical strength and bowing of the as-fired solar cell. It is concluded, that a prior removal of 10 μm of the silicon surface by polishing results in the best Ag/Si contact from a mechanical point of view.

Based on the results of this chapter, it is concluded that a new fracture strength test method is required to validate the effect of edges. The new test will exclude possible effects of edge defects and thus will allow a more accurate evaluation of the effects of different processing conditions on fracture behaviour of a silicon solar cell. A new biaxial fracture strength test method, especially developed for thin solar cell samples is described in chapter 5.

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CHAPTER 5

Fracture Strength of Silicon Solar Wafers and Solar Cells Tested by Ring-on-ring Method

"In the middle of difficulty lies opportunity"

Albert Einstein

5.1 Introduction and Background

Wafer breakage is a big challenge in the photovoltaic silicon industry limiting production yield and further price reduction. Microflaws generated from wafer sawing, impurity precipitations, structural defects, and residual stresses are the leading cause of the degradation of mechanical strength in silicon wafers. Standard mechanical testing methods are not capable of stressing a large area of the cell specimen uniformly.

The mechanical properties of solar cells have been investigated by several test methods; however the most common testing method for testing the fracture strength of a silicon wafer is by a bending (uniaxial) test or a ring-on-ring (biaxial) test.

Chapter 4 described the 4-point bending tests results of both single crystalline (Cz) Si and multicrystalline Si samples with and without Al and Ag metallization layers. Rectangular specimens of $30 \times 10 \text{ mm}^2$ were tested in order to determine the effect of mc-Si crystallinity, metallization parameters and surface roughness condition on mechanical strength [1]. However, an important restriction of the 4-point bending test is the edge effect, *i.e.* the edge quality (possible cracks, defects) might induce premature fracture of the entire solar cell. The use of a biaxial (ring-on-ring) test is required in order to exclude the influence of edge defects and thus to more accurately investigate the effects of different processing conditions, such as surface texture, impurities, and metallization types, on the bulk fracture strength of silicon solar cells. The ring-on-ring bending test is described in an ASTM standard [2]. The test uses a large support ring and a smaller loading ring to deform the sample.

The most important reasons for choosing the ring-on-ring set-up are that testing occurs in a bi-axial stress state, analytical models are available and the test is reliable. The peak stress level on the tested sample is present within the inner ring and its stress distribution is schematically shown in Figure 5.1. Thus, as can be seen, the fracture is not dependent upon the conditions of the edges of the specimen [3-4].



Figure 5.1 Bending tests for the determination of the strength of wafers, also schematically showing the stress distribution in the specimen during loading a) Ring-on-ring test; b) Four-point-bending test [3].

The ring-on-ring test method is used in this chapter to evaluate effects on strength of biaxial loaded samples and is based on ASTM C 1499-09 [2]. This test method has previously been studied rather extensively on glass [5] and multi-layered ceramics [6-7]. The stresses for multi-layered specimens were investigated for dental ceramics. The specimen thicknesses investigated were in the same order of a typical solar cell 100-500 μ m [6-7]. The strength of silicon wafers has been investigated with artificial damage using a ring-on-ring bending test in [8-12]. However none of these works were based on ASTM standards; no simulations were performed in order to calculate stresses and no as-metalized solar cells were tested using this method. Thus, it is important to develop a new reliable ring-on-ring test suitable for thin solar cells, which allows investigation of surface mechanical properties of thin silicon wafers and solar cells and determination of the impact of different solar cell processing conditions on fracture strength. Details of the stress distribution in the specimen during ring-on-ring testing were described in [3].

In order to determine the strength of silicon solar cells, the test method should be able to stress sample areas as large as possible (due to the statistical weakest link theory and large values spread). Since the thickness of the solar cell is so small, large sample deflections are expected. However, there are no analytical solutions for large deflection. The use of finite element (FE) modelling is necessary to calculate the stresses in the sample. To validate the FE model the deflection profile of the specimen during loading is recorded using a digital image correlation (DIC) system. The experimental procedure will be discussed in more detail in the following section. Despite the disadvantages ring-on-ring test method is simple, and appears to be useful to determine the strength of the materials, which will be completely determined by surface conditions. Above all, data regarding the biaxial strength of silicon is of interest and importance for comparison with 4-point bending results obtained in chapter 4.

5.2 Experimental Procedure

5.2.1 Ring-on-ring Test Configuration

A test configuration has been designed in accordance with the ASTM C 1499-09 standard and it was also made compatible with a digital image correlation (DIC) system [2, 14]. The equipment is shown schematically in Figure 5.2. and consists of a supporting ring and a loading ring.



Figure 5.2 Schematic representation of the ring-on-ring bending setup.

The ASTM standard allows the use of different sample sizes [14]. The dimensions are determined using appropriate formula. There are some limitations to the use of the standard for the thin silicon specimens used in this work, namely:

- 1. Only small deflections are allowed up to 25% of the specimen thickness and the samples used should be flat within 0.0005 times the diameter. It should be noted that samples with Al and/or Ag metallic layers deviate from this, since these are warped to some extent.
- 2. The radius of the center loading ring should be greater than or equal to 1.7 times the thickness of the sample.

Since deflections needed to fracture the specimens are expected to be significantly higher than the limitation of 25% of the thickness, the use of the biaxial strength test for solar cells cannot meet condition 1 and can cause stress concentration at the centre

loading ring, hence the calculations provided in the standard [14] are not suited for the current samples. In order to solve this problem FE modelling has been used to calculate the stresses at fracture (Appendix B and D). The DIC system was combined with the ring-on-ring test to measure the deformed shape as a function of the applied load, in order to validate the FE model.

Digital image correlation is a technique that can be used to monitor the deformation of a sample by comparing a reference image with an image of the deformed state [15]. This can be done in 2D with one camera or in 3D, where a minimum of 2 cameras is used. In this research a 2 camera setup was employed, because a 3D deformation profile is required for comparison with the FE model.

The complete test setup with the ring-on-ring fixture and the two cameras of the DIC system is shown in Figure 5.3.



Figure 5.3 Ring-on-ring test setup with two cameras for the DIC system.

The ring-on-ring setup has been designed in such a way that the two rings automatically align when a load is applied. This is achieved by placing the loading and supporting ring on a rotating axle. The alignment of the two rings is ensured by using a special alignment tool before testing. The supporting ring with a diameter of 20 mm is mounted in the lower part of the setup and the loading ring with a diameter of 10 mm is mounted in the top part. The rings are made from hardened stainless steel of 37 Rockwell C. The loading and supporting rings have a radius of 0.25 mm in accordance with the calculations provided in the standard [14]. The configuration of the rings and the field of view of the cameras are schematically shown in Figure 5.4.

The geometry of the supporting ring ensures a good visibility for the two DIC cameras during sample loading. The area visible by the cameras is limited to a square

section of $12 \times 12 \text{ mm}^2$ due to the positioning of the cameras on the tensile machine. It should be pointed out, that this is the main area of interest, because it represents the largest deflections.



Figure 5.4 Cross section of ring-on-ring test set-up.

The DIC procedure requires the tested samples to be covered with a random speckle pattern. The image correlation algorithm is then applied to a subset (indicated in red in Figure 5.5) of the speckles by comparing the deformed state to the undeformed state, as shown in Figure 5.5. For DIC measurements in 3D it is important that the position of the two cameras relative to each other, the magnifications, and all other imaging parameters are known. Using this information the absolute 3D coordinate of any specific point can be calculated.

Before any measurement in case of 3D-DIC, a system calibration was necessary to determine the imaging parameters of each of the cameras (intrinsic parameters - focal length, principal point and radial and tangential distortions of the lenses) as well as the external positions and orientations of the cameras with respect to a global coordinate system (extrinsic parameters, translation vector and rotation matrix). The system calibration was needed for transforming image positions on the CCDs of the two cameras of a specimen surface point to the corresponding 3D coordinates of that point. Calibration errors are potentially a major source of systematic evaluation errors, limiting the resolution of the DIC system.



Figure 5.5 Speckle pattern on a sample and a detail of a subset of speckles; left: undeformed, right: deformed [16].

The measurement system used in this research (Limess 3D Digital Image Correlation System with two 5MPixel cameras) has, for a successful measurement, a calibration procedure incorporated in the measurement and analysis software. The calibration was performed using a Limess A12 10x10 mm² calibration grid and a 3D residuum of 0.25 or lower was achieved for every calibration (see Appendix C for further details). A test plate with a chess model on it is moved in front of the cameras. The software automatically registers the nodal points of the test plate and calculates the intrinsic and extrinsic parameters. [15-17]. The camera signal and analog signals are collected using a Limess DAQhw data acquisition box. The load and displacement of the tensile machine have been acquired on a 10 V signal, which corresponds to the load of 250 N and the displacement of 5 mm. The data acquisition is synchronized to that of the images. The details of the DIC parameters used in this work are described in Appendix C.

5.2.2 Sample Preparation

The samples used for the ring-on-ring test were laser cut from a $156 \times 156 \text{ mm}^2$ silicon wafer. Laser cutting was selected in order to avoid unnecessary mechanical loading on the wafer and samples.

The standard samples were cut from the wafers into round shapes with a diameter of 21.44 mm (Figure 5.6 a). The outer edges of the solar cell show more defects and possible metal layer delamination, thus samples were not taken from this area.

The samples were cut from the wafers in a specific pattern in order to investigate the effect of silicon crystallinity. The mc-Si wafers were initially scanned and a distinction was made between three different types of grain morphology: one big grain, several large grains and many small grains, which were subsequently cut from neighbouring mc-Si wafers. The sample cut-out pattern for the mc-Si wafers is shown in Figure 5.6 b. The thickness measurements of the samples and all layers were performed using Leica optical microscope at 5 different positions per embedded sample.

The speckle pattern for the samples tested with the DIC system was applied using a spray technique. Initially a thin layer of white paint was applied to the samples and subsequently a speckle pattern of black paint was applied. The samples with a metallization layer were only painted using a black speckle pattern. The samples were dried for several hours before testing in order to prevent sticking of the paint to loading and supporting rings.



Figure 5.6 a) Standard Si wafer/cell cut-out pattern; b) MC-Si wafer cut-out patterns.

5.2.3 Ring-on-Ring Finite-Element Model

For small deflections the ring-on-ring test shows a linear relationship between the applied load and the radial and circumferential stresses. Due to the geometrical non-linearities that arise, the stress state deviates from the stress profile predicted by the ASTM standard at larger deflections. Therefore a FE model was implemented for the stress calculations using ANSYS software [18]. Three different models were made for three different sample types:

- One layer: silicon-only wafer samples
- Two layers: silver-metalized samples
- Three layer: aluminium-metalized samples

The FE models are based on the assumption that the stress profile in single and multi-layered specimens during ring-on-ring testing is axisymmetric [19]. This

assumption changes the nature of the model from 3D to 2D, which reduces the calculation time, allows for a finer simulation mesh, and promotes a more accurate simulation result.

The elastic properties of silicon are anisotropic, however in view of the complexity of implementing such anisotropic behaviour in the simulation, bulk properties of silicon are used. This allows a good comparison between single and multicrystalline samples, because the same material properties are used. The FE models are based on static calculations allowing for non-linear geometrical behaviour [20]. The different models will be described in more detail in the following sections.

The deformation and stress are calculated as a function of the applied load. The relations between the load and the resulting deformations and stresses are compared to DIC measurement results. The procedure for comparing the results from FE modelling and DIC simulation is discussed in more detail in Appendix D.

It should be pointed out that several assumptions were made for this FE model:

- The ring-on-ring model is based on the assumption of axial symmetry. Thus it is assumed that the stress state in any radial cross section is the same.
- Material properties are isotropic. The material properties used are based on the bulk properties.
- Plasticity is bi-linear due to the limited data available.
- Contact between layers is perfect.
- The contact and load are applied on a point. The contact in reality is distributed over a certain area, however the assumption of a point load only creates irregularities close to the contact. This assumption is used to reduce the calculation time and ensure reliable results independent of the various contact assumptions that would otherwise be needed if contact is included.
- It is assumed that friction can be neglected, because the support can freely move in the *x* direction. Contact elements would increase simulation difficulty and influence the accuracy.
- The contact for the metalized specimen is applied onto the silicon layer instead of the metal layer. This prevents large deformations in the plastically deforming metal layer, which are not supported by the software used.
- The solution is calculated stepwise (see appendix D2).
- The calculation model allows for large deformations and non-linear geometric effects; *e.g.* membrane stresses, the component of normal stress which is uniformly distributed and equal to the average value across the thickness of the section under consideration.

One Layer Model: Silicon Wafer

A one layer model was used for the simulation of silicon wafers. A schematic representation of the model is shown in Figure 5.7. The variable for this simulation is the sample thickness depending on the sample type. The mechanical properties used in this model are shown in Table 5.1.

Table 5.1. Elastic properties used for one layer model of silicon wafers.

Young's modulus [21]	163 GPa
Poisson ratio [21]	0.29

The load is applied as a point load and the support is simulated as a rolling support, allowing free movement along the x axis in order to simulate a frictionless support. The use of point loads is justified because the peak stresses generated near this node are far away from the region of interest.



Figure 5.7 Schematic representation of the FE model for a silicon wafer.

Two Layer Model: Silicon Wafer with Ag Front Contact

The model for simulation of samples with a silver metallic layer is shown in Figure 5.8. The model consists of two layers: silicon and silver. It is assumed that the two layers are bonded perfectly. The elastic properties used for the simulation are shown in Table 5.2. Not only the applied load, but also the support load act on the silicon layer. The reason is that locally excessive deformation of elements would occur should the support load be applied on the silver layer. This repositioning of the contact point does not affect the stress state in the centre of the wafer, which is the region of interest.

The ring-on-ring model allows for plastic behaviour of the silver layer. The mechanical properties used for the silver layer are shown in Table 5.3. The material properties have been found by fitting the model to DIC results [22]. The plastic

behaviour is within the range of expected theoretical values for silver when effects of porosity are taken into account. Due to the limited data that is available, it is assumed that the silver layer shows linear work hardening.

Material	Young's modulus (GPa)	Poisson ratio
Silicon [21]	163	0.29
Silver [21]	54 [see Figure 3.24]	0.3

Table 5.2. Elastic properties used for the two layer model.

Table 5.3. Mechanical properties of the silver layer.

Material	Yield strength	Tensile strength	Elongation
	(MFa)	(MFa)	(70)
Silver [23-24]	44	104	12



Figure 5.8 Schematic representation of the FE model for a wafer with silver metallization.

Three Layers Model: Silicon Wafer with Al-Si Eutectic and Porous Al Bulk Layers

As shown in chapter 3, the Al rear-side contact comprises a eutectic Al-Si reaction layer formed during the firing process. Thus the model simulating a silicon sample with an Al contact necessarily consists of three layers, as can be seen in Figure 5.9. The elastic properties used for this simulation are shown in Table 5.4. The load is applied onto the silicon layer to prevent excessive deformation of elements, as discussed for the simulation of samples with a silver metallization layer.

Material	Young's modulus (GPa)	Poisson ratio
Silicon [21]	163	0.29
Eutectic layer [25]	76	0.3
Porous aluminium layer [25, 26]	44	0.3

Table 5.4. Elastic properties used for the three layer model.

The plastic properties used for the eutectic and porous aluminium layer are shown in Table 5.5. The eutectic properties have been taken from the literature [25]. The plastic properties of the porous aluminium layer have been determined from simulation results comparing the ring-on-ring and the bow model [22]. Again, it is assumed that there is linear work hardening in both layers.

Table 5.5. Plastic properties of aluminium contact layers.

Matarial	Yield strength	Tensile strength	Elongation
Material	(MPa)	(MPa)	(%)
Eutectic layer [25]	55	130	12
Porous aluminium layer [23-24]	4	8	12



Figure 5.9 Schematic representation of FE model for a wafer with an aluminium metallization layer.

5.2.3.1 Validation of the Model and Fracture Statistics

Linear and Non-Linear Mechanical Behaviour

ASTM standard C 1499 includes calculations of the biaxial outer fibre stress at fracture for single layered specimens [2]. However, the formulas given by the ASTM standard are only applicable when the sample fractures within a deflection up to 25% of the sample thickness. The formulas presented also have limitations for the dimensions of the specimen used. There are several sources presenting mathematical descriptions of the ring-on-ring test for thin samples, which are valid for the specimen thickness and sample geometry employed in this research [19-20]. Even an analytical formulation of the stresses in multi-layered specimens is available [20, 27]. However, these analytical solutions still have a limit with respect to the maximum deflection for which the formulas can be used. The use of the FE model is needed to calculate the stress when the deflection exceeds the limit of the above-mentioned analytical models [28].

Load - deflection curves for a silicon specimen are shown in Figure 5.10.



Figure 5.10 Deflections of the specimen centre and the loading ring as a function of the load for a 180 μ m thick silicon wafer, a) Deflections for low loads, b) Deflections for higher load.

Both the displacement of the centre of the specimen and that of the loading ring are shown (blue and red lines respectively). The analytical solution presented in this figure is calculated using Roark's formulas [27], and is regarded valid up to a deflection (at the specimen centre) of half the specimen thickness (90 μ m). A detailed description of this analytical solution is given in appendix B. The FE model and analytical model show good correlation for small displacements. There is a small difference due to the simplification of the analytical solution that neglects the effect of the differences between sample and support ring diameters, which increases the stiffness and results in a slightly lower deflection of the FE model. The FE model shows a strong non-linear relationship when the displacement is increased above 0.2 mm and the limitation of the analytical solution.

The stress calculations are also affected by the non-linear behaviour of the sample when the limit of small displacement is exceeded. The stress obtained from analytical solutions is compared to the results of the FE model. The bi-axial stress state consists of a radial stress (σ_r) and a circumferential stress (σ_{θ}) both are shown in Figure 5.11.



Figure 5.11 Stress notation.

The stress calculated using analytical solution represents both the radial and circumferential outer fibre stress in the whole area within the loading ring. The stress considered in the FE model is the radial outer fibre stress at the loading ring. The stresses from the analytical solution and the FE model are both shown in Figure 5.12. A good correlation is found up to the limit of the analytical solution (2.5 N), while for high loads a non-linear stress - load relation is obtained from the FE model (when compared to the extrapolated analytical solution).



Figure 5.12 Outer-fibre stress at the specimen centre and at the loading ring as a function of the load for 180 μ m thick silicon wafer a) stress for low loads, b) stress for high loads (green line represents radial stress).

Stress Profile

The stress profile from the FE model for a silicon wafer of 180 μ m thick is shown in Figure 5.13 for a load of 1 N (linear behaviour). The stress is constant for both the radial and circumferential stress from the centre of the specimen up to the position of the loading ring (5 mm from the centre). The stress drops for from the loading load towards the edge of the specimen. This profile corresponds with the stress profile corresponding to linear analytical ring-on-ring profile equations.

The stress for a high load shows a very different stress profile as can be seen in 5.13 b. There is a clear peak stress at the position of the loading ring (5 mm from the centre). The stress levels for the radial and circumferential stress start to deviate from the centre towards the loading ring. This non-linear behaviour demonstrates the necessity of the FE model for calculation of the stress at fracture for large deflections, for which analytical solutions are not valid.



Figure 5.13 Radial and circumferential stress profiles resulting from the FE model for a silicon wafer of $180 \mu m$ thickness: a) at an applied load of 1 N with a linear stress - load behaviour and b) at an applied load of 50 N for a non-linear stress - load behaviour.

The subsequent test results in this chapter will be presented in terms of the peak values of the radial stresses (peak value of an inhomogeneous unbalanced biaxial stress), since these are the highest stresses occurring in the samples (in silicon) at the fracture load. The stresses are calculated separately for every sample using the results from the FE model (Appendix D). A Weibull distribution is fitted to the resulting fracture stresses and the characteristic peak stresses and moduli are presented.

The results of the DIC measurements are compared with load/deflection data obtained from the FE model. The deflection used is the nodal solution for the deflection of the centre of the sample. FE model description and validation are shown in Appendix D. In this validation the deflection of the loading ring is used as a reference. The DIC fitting procedure in described in Appendix C.

The stresses are represented at the point where the stresses are the highest, thus the peak stresses. It should be noted, that the presented stress results are taken from the elemental solution, since this solution is the most accurate (nodal solutions represent only average stresses), see Appendix D2.

5.2.4 Fourier Transform Infrared Spectroscopy

Carbon and oxygen are the most important light element impurities in PV silicon. The role they play in determining the mechanical properties of silicon has not been investigated in detail. Fourier Transform Infrared Spectroscopy (FTIR) is the method most often employed for the measurement of dissolved light element concentrations in PV silicon due to its fast, non-destructive and inexpensive features [29]. In general, when light interacts with matter, the photons which make up the light may be absorbed or scattered, or may not interact with the material and may pass straight through it. If the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and its excited state, the photon may be absorbed and the molecule promoted to the higher energy excited state. Absorption spectroscopy can measure this change of energy state by the detection of the loss of energy in the radiated light. The absorption occurs at a wavelength that is specific for certain vibrations, which are also sensitive to minute structural changes. Infrared absorption at a wavenumber of 1107 cm^{-1} is due to oxygen in an interstitial position with two neighbouring silicon atoms. It should be noted that oxygen present as clusters or in different lattice sites will not contribute to the 1107 cm⁻¹ absorption peak. It is believed that the 1107 cm⁻¹ FTIR measurement of oxygen concentration will be proportional to the oxygen concentration. For SiO_x, where x ranges from 1 to 2, absorption bands at 1030, 1075, 1124 and 1224 cm^{-1} have been reported [30]. Substitutional carbon has an absorption peak at 605 cm^{-1} , and interstitial nitrogen pairs have strong peaks at 963 and 766 cm^{-1} .

The FTIR measurements have been measured for mc-Si samples with different grain morphologies and from different positions in the cast mc-Si block.

The FTIR measurements in this study were performed in a BRUKER Vertex 70 spectrometer in the transmission mode. The infrared light is focused onto the photodiode of a liquid nitrogen-cooled, wide band DLaTGS W/KBr detector with a normal spectral response of 250 to 12000 cm⁻¹. Measurements were taken from a $10 \times 10 \text{ mm}^2$ area of the sample. Before measuring the samples, an FTIR spectrum for the background is collected in a temperature-stabilized chamber; this spectrum represents absorption from the atmosphere in the chamber. Then, one silicon sample with oxygen and carbon concentration below detection limit is used as a reference sample. The output was recorded by OPUS software. Each spectrum is the average from 64 scans. The spectrum resolution is 0.5 cm⁻¹. During analysis, the background spectrum was subtracted from spectra of all the samples and the reference.

In order to exclude possible effects of the thickness, the samples and the reference were chosen with identical thicknesses of $182 \ \mu m$.

5.3 Results and Discussion of Ring-on-ring Fracture Tests

5.3.1 Mechanical Strength of Single and Multicrystalline Silicon Wafers and Affecting Factors

5.3.1.1 Effect of Wafer Position in the Cast Mc-Si Ingot and of Silicon Crystallinity on the Mechanical Strength

The mechanical properties of mc-Si samples have been tested to examine the influence of crystallinity (grain morphology) and the impurity concentration (determined as a function of the position within the cast mc-Si ingot).

The samples were taken from 10 neighbouring polished mc-Si wafers, thus ensuring an (almost) identical crystallinity. Three different grain morphologies have been tested, with a minimum of three locations selected per grain morphology; examples are shown in Figure 5.14.



Figure 5.14 Examples of tested grain morphologies; left: one large grain, middle: several large grains, right: many small grains. (Red lines show the edge of the laser cut sample and black dotted lines indicate the loading ring position).

The concentration of oxygen and carbon was measured for different positions in the ingot using an FTIR - BRUKER Vertex 70. The FTIR results are shown in Figure 5.15. Only two distinct peaks were found for Si wafers taken from different ingot positions, namely 1107 cm^{-1} and 605 cm^{-1} . The concentration of interstitial oxygen impurities corresponds to the peak at 1107 cm^{-1} . There is an increase in the peak heights for the wafer taken from the top of the mc-Si ingot, which points to a relatively high concentration of oxygen. The concentration of substitutional carbon impurities corresponds to the peak at 605 cm^{-1} , indicating that the concentration of carbon is higher near the bottom of the ingot.



Figure 5.15 FTIR measurement showing the qualitative concentration of substitutional carbon (605 cm⁻¹) and interstitial oxygen (1107 cm⁻¹) as a function of mc-Si ingot position; left: samples with one large grain, right: many small grains.

The ring-on-ring test results are shown in Table 5.6. Both the grain morphology and the impurity concentration show a significant effect on the characteristic peak stress at fracture. The average characteristic peak stress shows an increase from the top towards the bottom of the ingot

Carbon is one of the most important light element impurities in PV silicon. Its role in the mechanical properties of silicon has been investigated by high temperature tensile testing at 800 °C and 900 °C, where it was observed that a higher carbon concentration increases the strength of the silicon wafer [31-34]. However, no results on the effect of carbon concentration on the mechanical strength of mc-Si at room temperature have been published. Since carbon concentration in mc-Si is usually rather high, due to the lower-quality silicon feedstock and the direct contact with crucible walls, it is likely that carbon affects the fracture strength of mc-Si wafers.

The results suggest that in samples with many small grains the characteristic peak stress increases by up to 30% as a result of the increasing carbon concentration from the middle to the bottom ingot position (Table 5.6). It should be pointed out that the thermal history of the silicon at the different ingot positions might also play a role. The reason is that this history most probably influences the fracture strength due to residual stresses that develop as a result of thermal gradients during solidification.

Position in mc-Si ingot	Grain morphology	Characteristic peak stress (MPa)	Modulus (-)	Average specimen thickness (µm)	
Тор	many small grains	295	5.7		
	several large grains	323	3.8		
	one big grain	298	5.7		
Middle	many small grains	282	3.7	182	
	several large grains	320	3.8		
	one big grain	351	4.3		
Bottom	many small grains	399	6.3		
	several large grains	375	7.9		
	one big grain	361	5.1		

Table 5.6. Effect of wafer position in the mc-Si cast ingot and grain morphology on fracture strength.

At room temperature, fracture of silicon involves breaking silicon bonds and creating new surfaces, which is a purely brittle mechanism not involving dislocation generation or movement during the initiation and propagation of cracks [35-36]. Carbon is introduced from crucible graphite parts in the furnace and occupies substitutional lattice sites in silicon. The dissolved carbon atoms and their associated residual stresses and defects can affect the fracture strength in two ways: (1) through the formation of cracks during the wire-saw cutting, which can be considered as an indentation process (as described in Chapter 4), and (2) by changing the propagation of cracks when a tensile stress is applied. In addition, carbon can enhance the nucleation of oxygen clusters at structural defects in mc-Si [35]. The presence of high levels of dissolved carbon atoms and the enhanced oxygen clusters may increase the surface energy of new surfaces, making cracking more difficult and thus improving the fracture strength.

The top of the ingot shows a decrease in the strength of the tested samples (Table 5.6), which may be related to an increase of the interstitial oxygen concentration at the top of the ingot. Point defects are involved in the nucleation process of oxygen precipitates, represented by the SiO_2 phase. The higher oxygen concentration at the top of the ingot is likely to enhance the formation of SiO_2 , which would facilitate the nucleation of dislocations at solidification and result in the lower strength found. A volume mismatch occurs as the precipitates grow in size and a variety of defects, including stacking faults are associated with precipitate formation. Furthermore, these defects attract fast-diffusing metallic species and thus the concentrations of other (non) metallic impurities/inclusions are also expected to be higher in the top of the cast, which is expected to also reduce the strength.

The concentration of impurities is expected to be the lowest in the middle part of the cast ingot. Thus this middle part is the most representative to study the effect of grain morphology on mechanical strength and to compare with the 4-point bending results obtained in Chapter 4. As can be seen from Table 5.6, there is a clear trend in the results, namely the samples with more grain boundaries tend to have lower strength than samples with fewer grain boundaries. Hence, grain boundaries seem to represent weak points where cracks can easily initiate and propagate along. This result is in good agreement with the 4-point bending strength data shown in Tables 4.3 and 4.4.

5.3.1.2 Effect of Damage Layer Removal on the Mechanical Strength of Single Crystalline Silicon Wafers

The effect of the saw-damage-removal depth on mechanical strength was investigated by means of single crystalline silicon samples with an initial thickness of 195 μ m. The ring-on-ring results for three etching depths are shown in Table 5.7. It is clear that the strength of the wafer increases from 404 MPa to 455 MPa when the etch depth is increased from 15 μ m to 35 μ m. When the etch depth is increased further to 55 μ m there is a further strength increase up to 491 MPa.

The large increase in strength can be attributed to removal of more small cracks due to the chemical polishing process. The results are in good agreement with 4-point bending results discussed in section 4.3.1. The modulus shows a decrease with increasing etching depth, which indicates more spread in the peak stress at fracture. The wafer with an etch depth of 55 μ m shows the largest standard deviation for the sample thickness, which is due to non-uniform etching of certain areas and the creation of over-etched islands on the silicon wafer surface. Thus it is concluded that damage etch removal up to 35 μ m is preferable in view of wafer strength improvement.

Etch depth (µm)	Characteristic peak stress (MPa)	Modulus (-)	Average specimen thickness (µm)	Standard deviation thickness (µm)
15	404	7.2	185	1.6
35	455	6.0	159	6.4
55	491	4.7	138	7.3

Table 5.7. Effect of damage-layer removal on fracture strength.
5.3.1.3 Effect of Surface Finish of Single and Multicrystalline Silicon Wafers on the Mechanical Strength

The effect of silicon wafer surface finish (roughness) was investigated for as-cut, textured and chemically polished conditions. The surface treatment parameters were chosen identical to those for the 4-point bending tests discussed in Section 4.3.3. The tests were performed on single crystalline silicon and the results are shown in Table 5.8. From these results it can be seen that the strength increases when the surface quality/roughness is improved (thus for smoother surfaces). The lowest strength was found for specimens with an as-cut surface finish, which is in good agreement with the 4-point bending results shown in Table 4.2.

The fracture strength increases for specimens with textured surfaces, which can be explained by the removal of the damaged surface layer. Textured surfaces yield a lower Weibull modulus compared to as-cut surfaces, which points to a larger spread in the peak stress at fracture. The highest characteristic peak stress was found for specimens with polished surfaces, probably due to the smooth surface and further removal of the damaged layer (see section 4.3.3. for more details). The Weibull modulus for polished samples has again decreased compared to that for samples with a textured surface.

Surface	Characteristic peak	Modulus	Average specimen
quality	stress (MPa)	(-)	thickness (µm)
as-cut	122	8.1	195
textured	347	9.1	176
polished	487	3.5	159

Table 5.8. Effect of surface finish of single crystalline wafers on fracture strength.

The effect of surface quality has also been investigated for mc-Si samples, the results of which are shown in Table 5.9. The same relationship can be seen for the stress at fracture as compared for single crystalline Si samples. The magnitude of the difference between the peak fracture stress for as-cut and textured samples is much smaller. This can be attributed to preferential etching of the grain boundaries, which will decrease the peak fracture stress of specimens. As can be seen from Table 5.9, the stress for polished mc-Si samples is again the highest.

The strength of both the textured and the polished mc-Si samples is somewhat lower than the equivalent single crystalline samples (*cf.* Table 5.8). The largest difference is found for textured samples, which is probably due to the damage etching itself. However the as-cut fracture strength for both types of silicon crystallinity cannot be directly compared due to the differences in cutting processes for cz-Si and mc-Si wafers. Furthermore, there is a different level of impurities and residual stresses resulting from solidification of single and multicrystalline silicon. Nevertheless, it can be concluded that the cutting process itself is the most detrimental (compared to other surface treatment procedures) for fracture strength of both silicon crystallinity types.

Surface quality	Characteristic peak stress (MPa)	Modulus (-)	Average specimen thickness (µm)
as-cut	206	9.8	195
textured	223	9.4	182
polished	349	7.0	173

Table 5.9. Effect of surface finish of multicrystalline wafers on fracture strength.

5.3.1.4 Effect of Antireflection SiN_x layer on Mechanical Strength

The effect of an antireflection SiN:H coating on the mechanical strength of silicon wafers is shown in Table 5.10. As can be seen, there is a significant decrease in the fracture strength after the antireflection coating (ARC) is applied. The Weibull modulus also shows a significant increase, suggesting a more uniform distribution of flaw sizes. This could be attributed to thermal stresses in the SiN_x coating. It should be noted that the SiN_x layer is approximately 100 nm thick. It was found by Tien *et.al.* [37], that for a temperature difference of 110 °C a residual tensile stress of 120 MPa is created in the silicon nitride layer. [37]. However, the high application temperature of the SiN_x layer, which contribute to the decrease in the stress at fracture. High residual stresses could cause fracture in the SiN_x layer, which consequently could result in a failure of the complete wafer. Furthermore, it was shown in [35] that during SiN:H deposition itself, hydrogen diffuses into the silicon wafer.

Surface quality	Characteristic peak stress (MPa)	Modulus (-)	Average specimen thickness (µm)
textured with ARC	264	14.5	173
textured	347	9.1	176

Table 5.10. Effect of antireflection SiN layer on fracture strength.

5.3.2 Mechanical Strength of Single and Multicrystalline Silicon Solar Cells and Affecting Factors

The results of the following sections will be discussed on the basis of the peak tensile stress occurring in the silicon wafer itself rather than the stresses in the metallic contact layer. The underlying assumption is that fracture will initiate in the silicon and not in the metal layer.

5.3.2.1 Effect of Aluminium Rear Side Contact Metallisation Conditions

Effect of Aluminium Paste Type

The effect of the aluminium paste type on polished single crystalline (Cz) Si wafers was investigated for three different Al paste types, namely paste A, B and C. The results of the ring-on-ring test are shown in the Table 5.11. Aluminium paste type has a significant effect on the fracture strength of the sample, as well as on the cell bow (the measurement of this is described in Appendix A). The highest stresses are found for samples with Al paste type A (788 MPa) and paste types B (715 MPa). Paste type C has a significantly lower strength of 507 MPa.

Al paste type	Characteristic peak stress (MPa)	Modulus (-)	Average thickness silicon (µm)	Average thickness eutectic layer (µm)	Average thickness porous aluminium layer (µm)	Average cell bow (mm)
А	788	5.4	177	6.1	36.8	0.74
В	715	11.3	170	7.4	46.5	0.97
C	507	6.6	178	5.4	33.5	1.54

Table 5.11. Effect of aluminium paste type on fracture strength.

The Al paste type properties are discussed in chapter 3. The average aluminium particle sizes and layer compositions are shown in Table 5.12. It was found that several parameters influence the properties of the aluminium layer. The particle size is an important parameter because this affects the number of contact points between the Al paste particles and the silicon substrate. The eutectic layer after firing has a more uniform thickness for Al paste with smaller aluminium particles and shows a more non-uniform layer when the Al particle size increases. Non-uniformity of the eutectic layer increases the spread of the fracture load and thus will result in a lower modulus. Apart from this, the porosity of the aluminium paste increases when its particle size becomes larger. Both these aspects affect the cell bow and the fracture strength of a metalized solar cell.

Al paste type	As-fired particle size (µm)	Porosity (%)	Bismuth glass fraction (%)	Average Young's modulus (GPa)
А	5	10	2	41
В	7	14	4	44
С	11	16	5	46

Table 5.12. Aluminium pastes properties.

The ring-on-ring test results show a good agreement with 4-point bending results, namely Al paste A is better from a mechanical point of view.

The effect of the aluminium-layer thickness was investigated by screen printing Al paste B though two different mesh sizes: 165 and 325; and results are shown in Table 5.13. The fracture strength increases for the thicker paste layer, however the cell bow and thus residual stress also increase. The Weibull modulus for the thinner Al layer (mesh 325) is lower compared to that for the thicker Al layer (mesh 165). This is attributed to larger eutectic layer thickness variations for the thinner Al layer, resulting in a larger spread in the measured fracture load.

Table 5.13. Effect of aluminium layer thickness on fracture strength.

Al layer mesh	Characteristic peak stress (MPa)	Modulus (-)	Average thickness silicon (µm)	Average thickness eutectic layer (µm)	Average thickness porous aluminium layer (µm)	Average cell bow (mm)
325	437	10.3	170	5.5	26.8	0.78
165	715	11.3	170	7.4	46.5	1.54

The ring-on-ring results show a different trend than the 4-point bending data obtained in chapter 4, where mechanical strength of mc-silicon wafer was not affected by the Al layer thickness. This could indicate that the edges in 4-point bending specimens have a dominant effect on strength. Furthermore, there could be a possible effect of plastic deformation in Al layer.

Effect of Silicon Surface Treatment

The effect of the Si surface finish prior to the application of the Al contact layer, *i.e.* as-cut, textured and chemically polished, was investigated for multicrystalline silicon samples with aluminium paste type B, which is the most commonly used Al pastel; the results are shown in Table 5.14.

The strength for metalized specimens is compared to that of pure silicon samples. To do this, neighbouring mc-Si wafers were used for all as-cut, textured and polished non-metallised and metallised samples. Characteristic peak stresses of 122 MPa, 347 MPa and 487 MPa were found for the as-cut, textured and polished samples respectively. The strength of metallised samples has increased due to the presence of the eutectic layer, resulting in a higher critical stress for flaws in the silicon wafer.

The lowest fracture strength of 442 MPa was found for samples with an as-cut surface quality, which can be attributed to the presence of microcracks at the Si surface below the Al-Si reaction layer. The strength is increased for a textured surface to 567 MPa, which indicates the removal of microcracks and there is a further strength increase for a polished surface (623 MPa), which is probably due to a more uniform eutectic layer. Furthermore, the Weibull modulus increases from 5.8 for as-cut samples to 7.4 for polished samples, suggesting that there is a broader flaw-size distribution for polished samples. The modulus will not only be affected by the presence of cracks in the silicon, but also by non-uniformities in the eutectic and porous aluminium layers. The microstructure shows significant variations in the thickness and porosity of these layers for as-cut samples (Figure 5.16), while polished Si wafers lead to a more uniform eutectic layer. Thus, it is suggested that both eutectic layer uniformity and microcrack removal contribute to the improvement of mechanical strength for samples with a polished surface finish prior to metallization.

Silicon surface quality	Characteristic peak stress (MPa)	Modulus (-)	Average thickness silicon (µm)	Average thickness eutectic layer (µm)	Average thickness porous aluminium layer (µm)	Average cell bow (mm)
as-cut	442	5.8	185	7.8	48.8	1.43
textured	567	6.6	178	8.0	45.4	1.22
polished	623	7.4	170	8.3	45.4	1.54

Table 5.14. Effect of Si surface treatment on fracture strength of samples with Al rear contact layer.

In order to establish the minimum depth the Si wafer should be polished to in order to create a mechanically optimal Al-Si interface, samples were tested which were chemically polished to three different depths: 10, 20 and 40 μ m. The results of the effect of polishing depth on fracture strength of silicon solar cells are shown in Table 5.15.



Figure 5.16 Optical microscopy images of cross sections of Al-Si interfaces for as-cut and polished silicon wafers.

The strength increases for samples with a thinner silicon wafer thickness (*i.e.* a larger etch depth) from 715 MPa for 170 μ m thickness to 819 MPa for 140 μ m. This suggests that the surface quality is more important than the internal stresses from the firing process.

The larger spread of the fracture stress (lower Weibull modulus) for thinner samples is due to relative thickness variations as a result of the chemical etching process. Thus the strength of the silicon solar cell can be further increased by a polishing process, but when too much material is removed the variations (nonuniformity) in the sample thicknesses cause more spread in the stress at fracture.

Silicon layer thickness (µm)	Characteristic peak stress (MPa)	Modulus (-)	Average thickness eutectic layer (µm)	Average thickness porous aluminium layer (µm)	Average cell bow (mm)
170	715	11.3	7.4	46.5	1.54
160	731	11.1	7.3	43.5	2.01
140	819	3.4	6.8	43.3	2.61

Table 5.15. Effect of silicon wafer thickness on fracture strength.

5.3.2.2 Effect of Silver Front Contact Metallisation Conditions on Fracture Strength

Effect of Silver Paste Type and Thickness

The effect of the silver paste type on fracture strength is shown in Table 5.16. Three types of Ag paste, screen printed with a 165 mesh and subsequently fired on textured cz-Si wafers (in order to exclude the effect of Si crystallinity), were investigated.

The results of Table 5.16 indicate that the paste type has no significant influence on fracture strength of solar cells. It is also found that the stress at fracture in the silicon

of Ag-metallised samples is close to the strength measured for silicon wafers (347 MPa). Thus, contrary to our expectations, the addition of the silver layer does not increase the strength. This could indicate that Ag metallization creates high local residual stresses during the firing process, which does not change the fracture strength of metalized samples as compared with reference silicon samples.

The Weibull modulus is higher than to that of the non-metallised silicon samples (m=9.12), which suggests that there is a narrower flaw size distribution in the sample. During the silver metallization process the silicon wafer is etched via the reaction with the glass phase present in the Ag paste, which could create local stress concentrations and thus the etching process results in a narrow flaw-size distribution.

Ag paste type	Characteristic peak stress (MPa)	Modulus (-)	Average thickness silicon (µm)	Average thickness silver (μm)
А	338	16.1	178	21.2
В	309	13.2	179	21.6
С	333	19.2	178	30.6

Table 5.16. Effect of silver paste type on fracture strength.

The effect of the thickness of the silver layer applied onto textured cz-Si wafers using silver paste type A is shown in Table 5.17. The strength slightly decreases from 357 MPa to 338 MPa for the larger silver layer thickness. Furthermore, the cell bow is more than doubled for the thicker Ag layer.

Table 5.17. Effect of silver	layer thickness	of fracture strength.
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Mesh size	Characteristic peak stress (MPa)	Modulus (-)	Average thickness silicon (µm)	Average thickness silver (µm)	Average cell bow (mm)
325	357	12.4	176	11.5	1.11
165	338	16.1	178	21.2	2.88

The decrease in strength could be the result of an increased amount of etching of the silicon by the glass phase. The occurrence of this increased etching is supported by the higher Weibull modulus, indicating a narrower flaw-size distribution. Additionally, the strength decrease could be related to the increased residual stress level suggested by the higher observed cell bow.

Thus the thinner Ag metallization can be considered better for solar cell front contact formation from a mechanical point of view.

Effect of Silicon Surface Treatment

The effect of the Si surface treatment prior to metallization for single crystalline (Cz) silicon samples is shown in Table 5.18. The specimens with polished surfaces have the highest fracture strength. The as-cut samples have a low strength due to the presence of cracks introduced during the wire-sawing process (a more detailed discussion was given in section 4.3.1) and there is a narrower distribution of flaw sizes in view of the higher Weibull modulus.

Table 5.18. Effect of Si surface treatment of single crystalline silicon solar cells on fracture strength.

Surface quality	Characteristic peak stress (MPa)	Modulus (-)	Average thickness silicon (µm)	Average thickness silver (µm)	Average cell bow (mm)
as-cut	271	18.4	196	20.0	1.52
textured	334	10.5	177	20.6	1.95
polished	566	7.5	180	20.7	2.19

The textured samples have a slight increase in fracture strength compared to the as-cut condition, which can be explained by the removal of the damaged layer containing cracks. Furthermore, the relatively low strength compared to the polished samples can be explained by the non-uniform glass layer and silver crystallites present in samples with a high surface roughness. As discussed in section 3.6.1.2 (Figure 3.19 and 3.20), polishing of the silicon surface gives a better wetting by the glass layer, resulting in a lesser incidence of large voids, compared to highly textured surfaces. The non-uniformity of the glass layer and large voids at the Ag-Si interface have a negative effect on the mechanical strength of the solar cell and results in a lower Weibull modulus for the textured samples. Samples with a polished Ag-Si interface show the highest strength as a result of the stronger Ag-Si contact resulting from a good glass wetting of the silicon surface.

5.3.2.3 Effect of Al and Ag Metallic Contact Firing Temperature

Effect of Silver-Paste Firing Temperature

The effect of the firing temperature has been examined for textured cz-Si wafers with a silver paste type A metallization layer. The effect of the silver contact firing temperature on fracture strength is shown in Table 5.19. As can be seen, changing the firing temperature results in stress differences at fracture. For a low firing temperature of 750 °C, the silver layer is more porous than for higher temperatures, as discussed in chapter 3 (see Figure 3.26). At this temperature only a small amount of silver dissolves

in the molten glass layer, resulting in a limited formation of silver crystallites and thus giving a weaker Ag-Si bond and a lower cell bow compared to firing at 850 °C. The formation of silver crystallites was investigated and discussed in detail in section 3.6.1.1 (see Figure 3.27). Firing the silver paste at 850 °C and 950 °C creates a denser silver layer and increases the glass etching rate, which results in stronger Ag-Si bonding. The aggressiveness of the etching is clearly demonstrated by the increase of the Weibull modulus from 10.5 to 14.5 resulting in a more narrow distribution of flaw sizes (Table 5.19). The reduction of fracture strength for samples fired at 850 °C is explained by the higher residual tensile stresses that develop in the Ag layer, which is supported by the high cell bow found for this firing temperature.

Firing	Characteristic	Modulus	odulus Average		Modulus Average Average thickness		Average thickness		Average cell
temperature	peak stress	(-)	thickness	silver	bow				
(°C)	(MPa)		silicon (µm)	(µm)	(mm)				
750	387	9.7	177	24.5	1.95				
850	334	10.5	177	20.6	2.88				
950	381	14.5	175	24.5	1.82				

Table 5.19. Effect of silver paste firing temperature on fracture strength.

From the results of chapter 3, it was concluded that firing Ag paste at 950 °C creates a mechanically weaker Ag-Si contact, due to the high crystallization of glass, preventing viscous flow of frits, and due to the penetration of Ag into the Si emitter in combination with almost no glass layer formation at the Ag/Si interface. Hence, local Ag crystallites only form at locations where Ag particles make direct contact with the Si wafer. This provides a low degree of bonding between the layers, resulting in some degree of delamination. The amount of bowing of the fired cell remains low and less residual stress develops compared to firing at 850 °C.

Effect of Aluminium-Paste Firing Temperature

The effect of the aluminium paste (type B) firing temperature was studied on textured single crystalline Si wafers for three temperatures and the results are presented in Table 5.20. An increase in firing temperature mainly affects the eutectic layer thickness and the density of the aluminium layer. The samples fired at 750 °C appear to have almost no eutectic layer (Figure 4.19). This temperature is too low for intensive alloying of Al and Si. The eutectic layer thickness increases with increasing the firing temperature. The strength of the silicon wafer is significantly increased by increasing the firing temperature from 750 °C to 850 °C. This is because the eutectic layer allows for higher stresses at the interface. The increase in the firing temperature from 850 °C to 950 °C does not lead to any significant change in the stress at fracture, which is

possibly the result of higher residual stresses formed during the firing process (suggested by the bow results in Table 5.20). Thus, it is concluded that firing temperatures between 800 $^{\circ}$ C to 850 $^{\circ}$ C are the most optimal for Al contact metallization.

Firing temperature (°C)	Characteristic peak stress (MPa)	Modulus (-)	Average thickness silicon (µm)	Average thickness eutectic layer (µm)	Average thickness porous aluminium layer (µm)	Average cell bow (mm)
750	401	10.2	175	0.0	45.6	0.06
850	689	13.7	169	8.6	45.4	1.81
950	686	11.5	169	10.5	45.2	2.37

Table 5.20. Effect of aluminium paste firing temperature on fracture strength.

5.4 Conclusions

The mechanical strength of multicrystalline (mc) and single crystalline (cz) silicon solar wafers and solar cells was investigated using a ring-on-ring bending test in combination with digital image correlation.

The study of the fracture strength of silicon solar wafers showed that:

- Multicrystalline silicon wafer crystallinity has a significant effect on the mechanical strength of polished multicrystalline silicon wafers for the samples with low concentration of impurities, taken from the middle of an mc-Si cast ingot; the more grain boundaries the weaker the silicon wafers. Furthermore, the obtained results are in good agreement with 4-point bending data, indicating that weak grain boundaries are more detrimental than edge defects that (possibly) affect results from the 4-point bending test.
- It was found that there is an effect of mc-Si cast block position on mechanical strength, namely samples taken from the bottom of the ingot up to 30% stronger than those taken from the top. This effect was most significant for samples with many grain boundaries.
- There is a high concentration of carbon in the bottom part of the ingot, most probably due to the contact with the hot crucible during the casting process. The dissolved carbon atoms and their associated residual stress and defects can affect the fracture strength in two ways: (1) through the formation of cracks during wire-saw cutting, which can be considered as an indentation process and (2) by changing the propagation of cracks when a tensile stress is applied. In addition, carbon can

enhance the nucleation of oxygen clusters at structural defects in mc-Si. The presence of a high level of dissolved substitutional carbon atoms and the resulting enhanced nucleation of oxygen clusters (due to the easiness of carbon and oxygen pairing) may increase the surface energy of the new sub-surface and make the cracking more difficult to initiate and propagate and thus improving the fracture strength.

- Samples taken from the top of the cast ingot showed a decrease in the strength, which is related to a higher interstitial oxygen concentration. This higher concentration possibly helps the formation of SiO₂ (lower concentration of carbon at the top of the ingot makes silicon and oxygen pairing more favourable) which then facilitates the nucleation of dislocations and lowers the strength. The concentration of other (non) metallic impurities/inclusions is also expected to be higher in the top of the cast ingot, which will also decrease the strength of wafers.
- There is a significant decrease in fracture strength when the ant-reflective coating is applied. The high application temperature of the SiN_x coating, 375 °C, will create large thermal stresses in the SiN_x layer, which potentially causes a decrease in fracture strength. The high residual stresses may cause crack formation in the SiN_x layer, resulting in failure of the complete wafer at lower applied loads.
- Damage layer removal by etching increases the strength of the single crystalline silicon wafers by about 300% and by 15% for multicrystalline silicon wafers. Furthermore, damage etch removal up to 35 µm was found to be preferable for wafer strength improvement.

Silicon solar cell samples were treated as composite materials, consisting of two or three layers, namely the bulk mc-silicon wafer and a silver layer or the bulk mc-silicon wafer and an aluminium bulk layer plus an Al-Si eutectic layer.

The results of silicon solar cell ring-on-ring fracture tests showed that:

- There is a relationship between aluminium paste composition and mechanical strength of a cell. Important microstructural aspects are the Al layer thickness, porosity, bismuth glass concentration and the thickness of the eutectic layer. Furthermore, a larger Al particle size in the paste leads to a less uniform eutectic layer, resulting in a reduction in fracture strength. The ring-on-ring test results show good agreement with 4-point bending results, namely Al paste A can be considered the most optimal from a mechanical point of view.
- The eutectic layer can serve to retard possible critical microcracks at the silicon wafer surface, thus improving the strength of mc-silicon wafer;
- It is found that different screen-printing mesh sizes produce different thicknesses of the Al layer (thickness for mesh 165 is roughly twice the thickness for mesh 325), affecting the mechanical strength of mc-silicon solar cell. There is an increase in strength for thicker layers, specifically related to the thickness of the eutectic layer.

- Both eutectic layer uniformity and microcrack removal contribute to the improvement of mechanical strength for samples with a polished Al-Si interface.
- The Ag paste type has no significant influence on fracture strength of solar cells.
- Samples with a polished Ag-Si interface show the highest strength as a result of a stronger Ag-Si contact interface that forms due to a good glass wetting of the silicon surface. The non-uniformity of the glass layer and large voids at the Ag/Si interface observed for textured and as-cut conditions have a negative effect on the mechanical strength of the solar cell and result in a lower Weibull modulus for the textured samples.
- There is a strong correlation between maximum firing temperature of the Al rear contact, the amount of bowing and the fracture strength of solar cells. The higher the firing temperature, the higher the cell bowing. However the strength increase is observed only for a firing temperature of 850 °C. There is no further strength increase with increasing the firing temperature above 850 °C. Furthermore, Al contact firing temperatures between 800 °C to 850 °C are the most optimal.
- It was found, that there is a reduction of fracture strength for samples with Ag contacts fired at 850 °C, which is explained by higher residual tensile stresses in the Ag layer as a result of the firing process.

A new biaxial fracture strength test method, combined with finite-element modelling, was especially developed for this work on thin solar cell samples. The model has been validated by means of digital image correlation. The use of the ring-onring test can be recommended for those applications where bulk properties of solar cells have to be investigated, such as the effect of crystallinity and impurity concentrations on fracture strength.

Based on the results presented in this chapter, it is concluded that a combination of 4-point bend and ring-on-ring test methods is advised to obtain a deeper understanding of the effects of different processing conditions on the fracture behaviour of silicon solar cell.

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CHAPTER 6

Residual and Applied Stress Characterization in Silicon Solar Cells

"Sooner or later we shall have to go directly to the Sun for our major supply of power. This problem of the direct conversion from sunlight into power will occupy more and more of our attention as time goes on and eventually it must be solved..." Edison Pettit, Wilson Observatory, (1932)

6.1 Introduction

One of the major current technological problems for the PV industry is to identify and eliminate potential causes of ultimate breakage of silicon wafers and solar cells. The problem is of increasing concern as a result of trend to reduce silicon wafer thickness. Residual stresses refer to stresses that remain after processing of a material, such as crystal growth, thermal processes, and mechanical processes. For thin silicon wafers used for PV cells, residual stresses are important because of their contribution to early failure or wafers during handling. Sensitivity to residual stresses increases with decreasing wafer thickness. Microcracks present in the wafer easily propagate into regions of high residual stress, causing breakage.

Nowadays solar cells and solar panels represent a complex interconnected system with different interfaces in a multi-layer/multi-stacked package. Residual stresses develop within the cell due to mismatch of thermal expansion coefficients of the materials used in the metallic contacts and soldered interconnections.

This chapter is based on:

^{1.} V.A. Popovich, N. van der Pers, M. Janssen, I.J. Bennett, K.M.B. Jansen, J. Wright, I.M. Richardson, Residual and Bending Stress Measurements by X-Ray Diffraction and Synchrotron Diffraction Analysis in Silicon Solar Cells, IEEE, Austin, 2012.

^{2.} V.A. Popovich, J.M. Westra, R.A.C.M.M van Swaaij, M. Janssen, I.J. Bennett, I.M. Richardson, Raman Spectroscopy characterization of residual stress in multicrystalline silicon solar wafers and solar cells: relation to microstructure, defects and processing conditions, IEEE, Seattle, 2011.

^{3.} V.A. Popovich, N.M. van der Pers, M. Janssen, I.J. Bennett, I.M. Richardson, Stress Measurement by X-Ray Diffraction in Multicrystalline Silicon Solar Cells, IEEE, Seattle, 2011.

Cracking of solar cells has become one of the major sources of solar module failure. Therefore, it is not only important to investigate the electrical properties of silicon solar cells, but also the stress state development during the manufacturing of solar cells. In order to take into account the effect of residual stresses during the design and processing of solar cell, the actual stress level in the material has to be determined.

Residual stress can be measured by several methods, depending on the size and type of material under consideration, and the availability, testing speed, and cost of the equipment. Each method can be categorized as either destructive or non-destructive. Destructive methods involve the creation of a new state of stress in a material by either machining or layer removal. Detection of the local change in stress is based on measuring the strain or displacement [1-2]. Destructive methods include strain-gage hole drilling, layer removal and sectioning. Non-destructive methods involve the establishment of a relationship between the physical or crystallographic parameters and the residual stress. The following techniques are considered to be non-destructive: X-ray diffraction, neutron diffraction, ultrasonic and magnetic measurements.

There are a number of techniques that can be used to measure stress in silicon and metallic contacts (Table 6.1.).

Method	Non-	Surface/	Penetration	Spatial	Accuracy	
	Destructive	Bulk	depth	resolution	1 100 01 000 j	
Hole drilling	N	В	$\sim 1.2 \times hole$	50 µm	~ 50	
The drining	IN	Б	diameter	depth	MPa	
Crack compliance	Ν	В	-	-	-	
> Curveture	N/V	S/D	$1/10^{-1/2}$	1/20 of		
	1N/ 1	5/D	thickness	thickness	-	
			< 50 µm			
→ Laboratory	Y	S	(Al)	1 mm	20 MPa	
A-ray unnaction			<2 µm (Ag)			
Eddy current	Y	S	-	-	-	
Ultrasonic	Y	В	> 10 cm	5 mm	10%	
Acoustic resonance	Y	В	-	-	-	
Thermoelastic methods	Y	В	1 mm	500 µm	-	
\rightarrow Synchrotron	V	S or P	High	Down to		
diffraction	1	5015	Ingn	10 µm	_	
\rightarrow Raman spectroscopy	Y	S or B	<1 µm	1 µm	50 MPa	

Table 6.1. Summary of various stress measurement techniques [1-5].

 \rightarrow indicates stress measurement methods that were chosen in this work

However, they all have limitations when applied to materials encountered in silicon solar cells. Either the resolution is limited, they are destructive, or not suitable for Al and Ag metallic contacts (Raman spectroscopy) or the indirect measurement technique requires complex modelling of measured data (bowing-curvature method). Thus, it is necessary to combine different stress measurement methods in order to obtain a realistic picture of the macroscopic stress state in silicon solar cells. The results of stress characterization using diffraction methods and Raman spectroscopy are described.

Several aspects related to solar cell processing conditions and metallization are described in relation to residual and applied stresses. The purpose of chapters 6 is to characterise stresses and their relationship to the microstructure, defects and processing conditions of multicrystalline silicon solar cells.

6.2 X-Ray Diffraction Stress Determination

6.2.1 Background

The X-ray diffraction (XRD) method enables a non-destructive determination of residual stresses. It can readily be applied to multicrystalline materials with a relatively small (*i.e.* "fine") grain size. Unfortunately this method is difficult to apply to multicrystalline silicon material, due to its coarse grain microstructure. XRD relies on the elastic deformations within a polycrystalline material to measure internal strains.

In its most basic form, X-ray diffraction consists of an X-ray beam incident on a specimen that is diffracted by the specimen's crystalline lattice (Figure 6.1). The resulting diffraction pattern, known as a Laue pattern, is captured with a detector. Within this basic framework the specifics of specimen, beam characteristics, and detector size can vary widely. The diffraction process is governed by the well-known Bragg's Law [6],

$$n\lambda = 2d_{\rm hkl} \sin\theta , \qquad (6.1)$$

where, *n* is an integer, λ is the beam wavelength, d_{hkl} is the distance between {hkl} lattice planes, and θ the angle between the beam and the plane of interest. A crystal lattice consists of different sets of atomic planes, each identified by its Miller indices, {hkl}[7].

X-ray diffraction can be used to determine the residual stress using the distance between crystallographic planes, *i.e.* the *d*-spacing, as a strain gage. When a tensile stress is applied perpendicular to the {hkl} lattice planes, the *d*-spacing increases and, when for compressive stresses the *d*-spacing decreases.



Figure 6.1 X-ray diffraction schematic.

A typical metallic sample will consist of a large number of small grains or crystals, randomly oriented, as shown schematically in Figure 6.2. The state of stress can therefore be determined by measuring the lattice spacing at different orientations. A set of planes in a crystalline sample that is free of elastic strains will have an average lattice spacing d_0 , which is defined as the stress-free lattice spacing. Consider a metal that is uniaxially loaded by a stress σ_{ϕ} in a direction along the surface ϕ , as schematically shown in Figure 6.2 (a), where N_s is the normal to the surface, and N_d the normal to the diffraction planes [8-9]. It should pointed out that only the grains with their lattice planes oriented perpendicular to N_d will contribute to the diffraction. The elastic strain in the direction normal to the surface (ε_{\perp}) can be expressed as:

$$\varepsilon_{\perp} = \frac{d_{\rm n} - d_{\rm 0}}{d_{\rm 0}} \quad , \tag{6.2}$$

where, d_n is the spacing of lattice planes oriented parallel to the surface. Assuming that the material is isotropic, Hooke's law can be used to find the stress σ_{ϕ} :

$$\sigma_{\phi} = -\frac{E}{\upsilon} \left(\frac{d_{\rm n} - d_{\rm 0}}{d_{\rm 0}} \right) \quad , \tag{6.3}$$

where, E is the Young's modulus, and v is Poisson's ratio.



Figure 6.2 Principle of X-ray stress measurement, with (a) diffraction on two different sets of planes, and (b) a vector diagram of the lattice spacing in varying directions. N_s is the normal to the surface, N_d is the normal to the diffraction planes, σ_{ϕ} is the applied uniaxial stress, ψ is the angle between N_s and N_d and d is the lattice spacing [8].

For an applied stress σ_{ϕ} , the change of lattice spacing will depend on the orientation of the diffracting lattice planes. Referring to Figure 6.2, where σ_{ϕ} is a tensile stress, the spacing of lattice planes oriented parallel to the surface will become smaller than d_0 , while that of lattice planes oriented perpendicular to the surface will become larger. Thus, the lattice spacing is a function of the measurement direction Ψ , as schematically shown in Figure 6.2 (b). This relationship is very useful for the determination of multi-axial stresses and forms the basis of the $sin^2\Psi$ - method. For a biaxial stress state (Figure 6.3 a), the stress in an arbitrary direction can be found by using the same principle, as is explained in detail by Cullity [8].

$$\frac{d_{\phi\psi} - d_0}{d_0} = \left[\frac{(1+\upsilon)}{E}\right] \sigma_{\phi} \sin^2 \psi + \left[\frac{-\upsilon}{E}\right] (\sigma_1 + \sigma_2) ,$$
or
$$\frac{d_{\phi\psi} - d_0}{d_0} = \frac{1}{2} S_2 \sigma_{\phi} \sin^2 \psi + S_1 (\sigma_1 + \sigma_2) ,$$
(6.4)

The stress in the direction ϕ , σ_{ϕ} , can be determined by measuring the lattice spacing in that direction $(d_{\phi\psi})$ at several measurement angles ψ . If the elastic constants, *i.e.* the Poisson ratio v and the Young's modulus *E*, are known, the stress σ_{ϕ} can be determined from the slope of a $d_{\phi\psi}$ versus $\sin^2\psi$ -plot (Figure 6.3 b).

In order to measure the macro stresses, the volume of material that is exposed to the X-ray beam must be large enough to represent the macroscopic material.



Figure 6.3 a) Definitions of measurement directions for the $\sin^2 \psi$ -method. b) Example of a $d_{\psi\psi}$ versus $\sin^2 \psi$ -plot for a Ag layer fired on top of a silicon wafer.

6.2.2 Experimental Procedure

Residual stress measurements were performed on rectangular $(10 \times 30 \text{ mm}^2)$ neighbouring single crystalline (czochralski silicon - cz) silicon solar cell specimens, which were laser cut from complete solar cells. Stresses in the metallic contact layers of cz-silicon solar cells were measured using conventional XRD with a Bruker D8 diffractometer carried out in reflection mode. The measurement comprises the determination of a (high) 2θ peak at different tilting angles (ψ) of the sample [9]. Using the elastic constants taken from the X'pert stress software database [10] the residual stress was calculated.

The 2 θ peaks were fitted using a Gaussian fit. Usually the type of profile is chosen which gives the best results in peak position and minimum error in the sin² ψ vs *d*-spacing plot.

In this series of measurements the Ag {311) and Al {420} reflections were used. In the calculations the following elastic constants were taken (see equation 6.4): for Ag: $\frac{1}{2} S_2 = 16.53 \text{ 1/TPa}$; for Al: $\frac{1}{2} S_2 = 19.051 \text{ 1/TPa} [10]$. The θ -2 θ (gonio) scans are performed using the Panalytical X'pert Pro MPD system setup as shown in Figure 6.4, with the sample at the goniometer centre. The sample and detector rotate with respect to X-ray beam, allowing sample measurements at different positions.

Cu K α X-ray radiation, 40 kV, 40 mA was used in this work. Data evaluation was performed with the Panalytical software Xpert stress 2.0 [10].



6.4 Panalytical X'pert Pro MPD equipment for stress measurements [11].

Due to the relatively low energy of this laboratory set-up X-rays can only penetrate a few microns into the material, after which the beam is attenuated. For aluminium, the typical penetration depth (τ) of the laboratory X-rays is approximately 20 µm and for silver only 2 µm [11]. Therefore, with this X-ray technique only surface stresses can be measured. It should be pointed out, that synchrotron X-rays have a much higher energy as a result of which they can fully penetrate the thickness of Al and Ag metallic contacts (see section 6.3). However, this low-energy XRD technique was chosen among other non-destructive investigation techniques, because it is the most accurate, in-house and best developed method, and it can be applied to a wide variety of sample geometries.

To investigate the effect of the maximum firing temperature on the residual stress development in the Al and Ag contact layers, three neighbouring wafers were processed under identical conditions, but with different peak temperatures, *i.e.* 750, 850, and 950 °C.

In order to examine the influence of the aluminium layer thickness on the residual stresses of the cells, two different cells with 20 and 40 μ m Al layers were investigated (the commercially available Al paste type B was used). Measurements of the amount of bowing that resulted from metallization were made by an optical method over the full length of the solar cell (156 mm), using a Quick Vision Mitutoyo system (see Appendix A). In order to measure residual stresses in the eutectic layer, the aluminium porous layer was partially removed with Ar⁺ ions using a Gatan precision ion polishing system, normally used for transmission electron microscopy.

Creep tests were performed at a controlled constant temperature and force using a dynamic mechanical analysis (DMA) Q800 setup with a 3-point bending clamp in order to analyze the origin of a stress drop observed during XRD measurements on loaded specimens.



Figure 6.5 In-situ 4-point bending device for XRD: Bending device inside the diffractometer.

Scanning electron microscopy (SEM) was used to analyze the surface and crosssection morphology of the solar cells. XRD was also used to examine the phase and elemental composition.

Specifically for this work, an in-situ 4-point bending device was built to fit inside the X-ray goniometer (Figure 6.5) in order to measure stresses resulting from applied external loads of 1, 2, and 3 N. This bending device is capable of measuring the applied load.

Source to sample distance is constant and equal to the sample to detector distance, limiting measurement of rough and bowed samples. However, these constrains are removed if the incident beam is parallel (*i.e.* does not diverge). A polycapillary collimating optics is used to form an intense X-ray excitation beam resulting in very high X-ray intensities at the sample surface with parallel beam geometry (Figure 6.6). Thus, in this work a parallel beam geometry was used, which excludes the influence of the sample curvature. Different in-situ bending XRD stress experiments were performed and for each loading condition the resulting curvature was measured by an optical method.



Figure 6.6 A comparison between focusing method and parallel beam geometry (where ds is the divergence slit, ss is the scattering slit and rs the receiving slit).

6.2.3 Results and Discussion

6.2.3.1 Residual Stress Determination in Aluminium Rear-Side and Silver Front-Side Contacts

From the investigations discussed in chapter 3, it was found that the porous bulk aluminium rear-side contact has a complex composite-like microstructure, consisting of three main components (see also Figure 6.7):

- spherical (3 5 μm) hypereutectic Al-Si particles, surrounded by a thin aluminium oxide layer (150-200 nm);
- a bismuth-silicate glass matrix (3.3%);
- pores (14%).

It is known that when fired, the aluminium layer creates a large amount of solar cell bowing [12]. However, it is not entirely clear what effect the porous aluminium part has on the strength of and the residual stresses in solar cells. X-ray stress determinations were conducted on two solar cell samples with different thicknesses of the aluminium back contact layers. Results showed that residual stresses in the porous part of the Al back contact layer are very low, *i.e.* in the range of 10 MPa (Table 6.2). It was also found that a 20 µm thick Al layer shows higher stresses than a 40 µm layer. Note that the X-ray penetration depth in Al is about 20 µm. These results could indicate that the Al porous part of the rear-side contact consists of loosely interconnected Al-Si spherical particles and the major part of the solar cell bowing is generated by the Al-Si eutectic reaction layer. It should be pointed out that residual stresses were found to be equal in all directions for Al layer (Figure 6.10). In the experiments discussed in this chapter, the direction ϕ (see Equation 6.4) can be chosen as either longitudinal (L) (direction of the bowing) or the transverse (T). In this work, longitudinal stress will be shown for silicon solar cell samples, because stresses in transverse direction were found to be identical ($\sigma_1 = \sigma_2$).

In order to confirm this hypothesis a part of the aluminium layer was carefully removed, resulting in a cross section, as shown in Figure 6.8. The stress in the remaining layer, which basically is the eutectic layer, was found to be \sim 30 MPa. However, this value is not representative for the entire eutectic layer, because the scan partially covered the edges of the porous part of the Al layer, thus an application of an additional stress measurement method allowing deeper X-ray penetration and stress evaluation is required.



Figure 6.7 Microstructural model of the aluminium rear-side contact of a silicon solar cell.

Specimens with different firing temperatures of the Al back contact, and as a result with different thicknesses of the eutectic layer, showed that higher firing temperatures lead to larger amounts of cell bowing (Table 6.3). As can be seen in Figure 6.9, firing Al contact at 750 °C allows only a small amount of eutectic 'islands' to be formed. Firing at 850 °C and 950 °C gives a much more uniform and thicker eutectic layer, entirely covering the silicon wafer. Thus the bow increase can only be explained by an increased thickness of the eutectic layer, because the total Al layer thickness was the same for all samples.

Table 6.2. Residual stresses in Al layer (penetration depth $\sim 20 \ \mu m$).

Allower thickness	Biaxial stress ($\sigma_1 = \sigma_2$)	Stress
Al layer unickliess,	Al {420},	error,
(μπ)	(MPa)	(MPa)
20	10	1.8
40	3	3.4



Figure 6.8 Removal of Al porous layer: a) Schematic cross section of the layer; b) Micrograph of the resulting "hole" in the porous part of the Al layer.

The XRD patterns of Al layers fired at different temperatures showed that there is an increased amount of Si in the Al layer with increasing firing temperature, indicating a higher diffusion of Si into the liquid Al particles. Furthermore, XRD stress measurements in the Al layer showed that there is only a minor stress increase with increasing firing temperature (Table 6.3). This increase could be the result of a higher fraction of Si phase (shown as grey particle in Figure 6.9) inside the Al particles, leading to a higher degree of aluminium deformation.

Table 6.3. Effect of firing temperature (and thus eutectic layer thicknesses) on residual stresses in porous Al layer (X-ray penetration depth - $20 \mu m$).

Firing Temperature (°C)	Biaxial stress $(\sigma_1 = \sigma_2)$ in porous Al{420}, (MPa)	Amount of bowing, (mm)
750	0.8±1.0	0.48
850	5.5±1.5	1.40
950	4.5±3.0	1.80

Despite the low value of stresses, there is a clear increase of the amount of bowing, which could result from the eutectic layer itself, rather than from the porous part of the aluminium layer (Figure 6.9). It can be concluded, that both thickness and composition of the eutectic layer can be considered as important parameters controlling mechanical stability of silicon solar cells.

XRD stress measurements were also performed on silver front contacts and on the Ag/Al bus bars, Figure 6.10. The stress in the Ag/Al bus bars was found to be lower (42 MPa), compared to the stress in the Ag front side contact (69 MPa). This is possibly related to the different composition of the silver bus bars, which also contain aluminium.



Figure 6.9 Effect of maximum firing temperature on microstructure of Al back contact layers, showing different thicknesses of the eutectic layer.



Figure 6.10 Residual stresses in silver front contact and silver bus bar (X-ray penetration depth ~ 2 μ m; Ag {311} peak) and corresponding longitudinal and transverse stresses ($\sigma_1 = \sigma_2$).

XRD stress determinations in the Ag layer showed that the stresses are higher at 850 °C firing than at 750 °C or 950 °C (Table 6.4). The explanation to this effect can be found in Chapter 3, where the effect of Ag layer firing temperature was studied in respect to microstructure.

As described in section 3.6.1.1, at a low firing temperature of 750 °C the Ag layer is porous and there are some discontinuities in the Ag layer coverage of the silicon wafer. Furthermore, the glass layer is thin and only a small amount of silver is expected to be dissolved at this temperature. Furthermore, there is no or very weak Ag crystallite formation at 750 °C, which can be explained by the lack of a reaction between the glass frit and the SiN_x. Hence, the low firing temperature of 750 °C (the actual cell temperature will be ~650 $^{\circ}$ C) is most likely not sufficient to fire though the SiN_x and allow the formation of Ag crystallites, which results in delamination of the weak Ag/Si contact interface. This explains the relatively low amount of cell bowing at 750 °C, which gives lower stresses. Firing the cell at 950 °C results in only local coverage of the silicon surface with glass globules, and hence this non-uniform glass layer could explain low bowing and stresses at 950 °C. A substantial delamination was observed at the edges of the fired cell, indicating a high shear stress at the edges. Edge delamination and poor glass coverage explain a reduction of cell bowing and measured stresses compared to firing at 850 °C, where a more uniform contact with no delamination is created.

Firing Tomporatura	Biaxial stress $(\sigma_1 = \sigma_2)$	Amount of cell		
	Ag {311},	bowing,		
(C)	(MPa)	(mm)		
750	51.8±0.5	1.95		
850	68.9±0.8	2.88		
950	48.6±1.0	1.82		

Table 6.4. Effect of firing temperature on residual stresses in a Ag layer (X-ray penetration depth $\sim 2 \ \mu m$).

6.2.3.2 Stress Determination in Combination with Bending Tests

In-situ loading was performed on the Ag layer, using the bending device installed inside the diffractometer, in order to measure the actual bending stresses induced in the Ag layer. Loading of the specimen showed an increase in bending stresses in the Ag layer (Figure 6.11), indicating that it is possible to determine bending stresses by X-ray diffraction using an in-situ bending clamp. The stress in the Ag layer was found to be 87 MPa after loading to 3 N. Furthermore, it was found that holding the sample at a load of 3 N during 8 h resulted in a 10 MPa stress drop, while no significant change in

deflection could be observed (Figure 6.12), which confirmed by direct optical curvature measurements.

In Table 6.5, the bending stress determined with XRD resulting from loading the specimen is compared with the stress calculated from equation 4.4. used for 4-point bending.

Table 6.5. Comparison	of stress	measured	with XF	D and	l calculated	on	the	basis	of 4-
point bending.									

	XRD stress, (MPa)	4-point bending	
Stress Type	(loading over a few	stress at 3 N,	
	hours)	(MPa)	
Residual stress at 0 N load	60 ± 1.4	-	
Residual stress + stress resulting			
from applying 3 N bending load	87 ± 2.3	-	
(close to failure)			
Stress resulting from applying 3 N	27	38	
bending load	27		

The XRD stress is lower than the calculated stress, however it is in the same order of magnitude. The difference can be explained by the following factors:

1. differences in the 4-point loading devices used in the in-situ XRD measurement and the testing machine in terms of loading rate;

2. a low penetration depth in combination with a gradient of stress in the Ag layer, resulting from the roughness profile of the Ag layer. It should be noted that in these stress measurements the X-ray penetration depth in the Ag is only 2 μ m.

Despite the discrepancy in the measured and calculated stresses the composite beam theory is still considered appropriate for bending stress calculations in silicon solar cell samples.

Creep tests were performed at a controlled constant temperature in order to analyze the origin of the time dependant stress drop shown in Figure 6.11. A bending sample with a Ag layer on the tensile side was loaded to 1.8 N load at 50 °C and kept in a dynamic mechanical analysis chamber for 8 hours, while displacement changes were measured with an accuracy up to a few hundred nm (Figure 6.13).



Figure 6.11 Bending stresses in Ag front contact as a function of loading and holding time.



Figure 6.12 Deflection of the sample with Ag front contact as a function of loading and holding time of 8 hours.



Figure 6.13 DMA creep bending test on a sample with Ag front contact at constant temperature with 8 h holding time.

It was found that there is only a minor displacement change of $\sim 5 \ \mu m$ after 8 h, which obviously cannot explain the 10 MPa stress drop observed during the XRD measurements.

It is concluded that stresses do not relax in the bulk of the Ag layer during the 8 h holding, but that some relaxation effect takes place, at least in the near-surface part (upper few μ m) of the Ag layer. This could be due to creep and/or cracking of the Ag top layer.

An in-situ bending test on the diffractometer with the aluminium layer loaded in tension did not result in a significant stress increase in the Al porous layer. This result indicates that the porous part of the Al back contact is too loose to show any build-up of residual or bending stresses and consequently will not give any contribution to the fracture strength of solar cells. The data obtained are consistent with results previously discussed in chapter 4.

It should be pointed that due to the low penetration depth of ~20 μ m in Al and only ~2 μ m in Ag, this laboratory XRD technique can determine only near-surface residual stresses. Furthermore, it was found that it is impossible to measure stresses in each individual layer, especially in the eutectic layer, which from discussions in previous chapters was considered as the most important parameter controlling mechanical stability of silicon solar cells. Hence, high energies (30-80 keV) and small beam sizes (~50×50 μ m²) are required in order to achieve the above mentioned specific objective. Therefore, the use of synchrotron X-ray diffraction measurements was sought.

6.3 Residual Stresses Determined by Synchrotron Diffraction Analysis

6.3.1 Background and Experimental Conditions

Synchrotrons, provide very intense beams of high energy X-rays (hard X-rays), with a high penetration depth (~50 mm in Al), potentially providing a high spatial resolution and three-dimensional maps of the strain distribution to 10 mm depth in engineering components [13-14]. Narrow beams of 1 mm - 10 μ m in size are possible, this leads to spatial resolutions that are limited by the crystallite size within the sample, but not by the instrument. Measurements are also much quicker than by conventional X-ray diffraction.

In order to measure possible stress gradients across Al and Ag contact layers, as well as exclude effects of surface roughness of these layers, a series of synchrotron Xray diffraction residual stress measurements were performed at beam line ID11 at the European Radiation Synchrotron Facility in Grenoble, France (ESRF).

A schematic overview of the diffraction set-up is given in Figure 6.14, while Figure 6.15 shows a picture of the experimental arrangement [15], consisting of a synchrotron source that passes a monochromator to produce a 60 keV X-ray beam. The size of the incoming beam is defined by the horizontal and vertical incoming beam slits. The beam is directed towards the sample, which is mounted on a translation and rotation system. The diffracted beam passes an analyzer crystal, which eliminates the effects of out-of-plane displacements of the sample on the measurement result. An outgoing beam slit, together with the ingoing beam slits, is used to define the gauge volume. The detector is mounted on a rotating disk, in order to scan the 2θ range.



Figure 6.14 Schematic configuration for the synchrotron X-ray diffraction measurements at the ESRF [15].



Figure 6.15 Overview of the diffraction set-up at beam line ID11 at the ESRF in Grenoble.

Solar cell samples were clamped with the help of a system especially designed for thin silicon wafers (see insert in Figure 6.15). This system allows an accurate and repeatable positioning of the samples. The clamping was applied such that the thin Si samples were mounted firmly with minimal clamping forces and stresses in the samples were not affected.

The specimens were irradiated by a monochromatic beam of 44.4 keV photons (corresponding to a wavelength of 0.27924 Å) with a size of $50 \times 100 \ \mu\text{m}^2$ incident on the centre of the sample along the sample's thickness direction. The diffracted X-rays from the samples were recorded in transmission mode using a FreLon 2D area detector. The 2D diffraction rings were recorded based on the saturation intensity of the detector for the Al and Ag contact layers with an exposure time of 10 s at 0.5° rotation step. After subtracting the detector background and distortion statistics, the 2D diffraction patterns were integrated using *Fit2D* software [16].

A reference powder sample (W) was affixed to the specimen to monitor any drift in the diffraction peaks as a result of changes in the beam energy profile and to detect the sample position relative to the detector. W powder was chosen, because its diffraction rings do not overlap those of Al, Si or Ag (Figure 6.16).



Figure 6.16 An example of the calibration (fitting) procedure using W powder with known lattice parameters (red lines represent fitted W rings).

The diffraction peaks were obtained by integrating the diffraction rings and subsequently fitting the result using a Gaussian profile. The internal strain for each reflection was then calculated using:

$$\varepsilon_1 = \frac{d_1 - d_0}{d_0} \quad , \tag{6.5}$$

where d_0 is the "unstressed" lattice parameter and ε_1 the strain in certain direction (longitudinal or transverse).

This approach requires that the stress free lattice spacing (d_0) is known. Note that this value is not necessarily constant over the whole sample. For example, variations in composition or microstructure can affect d_0 .

Estimations for the stress-free lattice parameters for Al and Ag layer were obtained by removing powder from the metalized Si wafer. Residual stresses were calculated using Hook's law:

$$\sigma = (\varepsilon_1 + v\varepsilon_2)(\frac{E}{1 - v^2}), \text{ where for biaxial stress state } \varepsilon_1 = \varepsilon_2$$

thus

$$\sigma_1 = \sigma_2 = \frac{E\varepsilon}{1 - v} = \frac{E\left(\frac{d_i - d_0}{d_0}\right)}{(1 - v)}$$
(6.6)

where *E* is the Young's modulus ($E_{Al} = 72$ GPa, $E_{Ag} = 83$ GPa) and υ is Poisson's ration ($\upsilon_{Al}=0.334$; : $\upsilon_{Ag}=0.37$)

6.3.2 Results and Discussion

2D Diffraction patterns of as-fired (850 °C) Ag paste on a silicon wafer were compared with as-received original Ag powder (here assumed to be stress free material) (Figure 6.17). It was found that the integrated measured profile of the as-fired Ag layer exhibits a significant peak shift (Figure 6.18 a). It should be noted that the compositions of the as-fired Ag layer and removed/stress-free reference Ag powder are identical, thus the peak shift can only result from a residual stress. As can be seen from Figure 6.18, all four Ag peaks shift towards lower 2 θ angles, corresponding to a larger *d*-spacing. This indicates a tensile stress, which is expected after the firing process in view of the higher thermal expansion coefficient of silver as compared to silicon.

Furthermore, there is a peak splitting of Ag {111}, indicating strain variations along the thickness of the Ag layer. The results show that there are two different stress levels in the Ag layer (see Figure 6.18 b):

• peak 1, corresponding to a tensile stress (54 MPa) similar to that obtained via conventional XRD;



• peak 2, corresponding to a much higher tensile stress value (390 MPa).

Figure 6.17 2D diffraction patterns obtained from a) as-fired silver layer diffraction pattern b) Ag powder before the firing process.

The relatively broad width of the two peaks suggests that there is a rather smooth strain change over the entire Ag layer thickness. It can be suggested, that the first lower stress comes from the outer surface of the Ag layer (due to a good agreement with


laboratory X-ray results with 2 microns penetration depth in Ag layer), whereas the second stress represents the rest of the thickness of the Ag layer.

Figure 6.18 a) Diffraction spectrum of the reference Ag layer and as-fired silver layer, showing peak splitting for Ag $\{111\}$ in the layer; b) Corresponding d-spacing and stresses for 2 $\{111\}$ peaks of Ag.

Figure 6.18 represents the synchrotron diffraction spectrum of the as-fired Al layer, showing peak splitting for Al {111} and Al {200}. The splitting of the peaks and their sharpness suggest a relatively abrupt strain change over the thickness of the Al layer. The lower stressed peak, giving a stress value of ~3 MPa, is similar to that obtained by the conventional XRD with a low penetration depth (Table 6.2). This peak results from the porous part of the Al layer. The second much higher stressed peak ($\sigma = 156$ MPa) could originate from the eutectic layer underneath the porous Al layer. This result further proves that the eutectic layer can be considered as an important factor controlling mechanical stability of silicon solar cells.



Figure 6.19 a) Diffraction spectrum of the as-fired Al layer, showing peak splitting for Al {111} and Al {200}; b) Corresponding d spacing and stresses.

6.4 Stress Determined by Raman Spectroscopy

Laboratory X-ray and synchrotron diffraction were successfully used for stress measurement in Al and Ag metallic contacts, however, unfortunately these methods are difficult to apply to multicrystalline silicon material, due to its coarse grain microstructure. To circumvent this problem, Raman spectroscopy was proposed as a stress characterization technique suitable for single and multicrystalline Si wafers. The goal of measurements was to characterise stresses and their relation to the microstructure, defects and processing conditions of the silicon substrate itself.

6.4.1 Background and Experimental Conditions

The physical principle of Raman spectroscopy is based on characteristic spectroscopic features when illuminated by light, that allow materials to be uniquely identified. When a monochromatic light beam, such as a laser, hits a molecule, three

phenomena can occur: absorption, emission, or scattering. Raman spectroscopy relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down (Figure 6.20) [17]. The shift in energy gives information about the vibrational modes in the system. The Raman effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. For the spontaneous Raman effect a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength.

If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency in order for the total energy of the system to remain balanced. This shift in frequency is designated as a Stokes shift. If the final vibrational state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an anti-Stokes shift (Figure 6.20).

A plot of intensity of scattered light versus energy difference is a Raman spectrum. The scattered light contains components (Raman peaks) with frequencies equal to the ones of the lattice vibrations/rotations. The intensity of Raman scattering depends on the wavelength of radiation used to excite the sample [17].



Figure 6.20 Energy level diagram showing the states involved in a Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions [18].

When load is applied to an elastic crystalline material, then the equilibrium separation between the constituent atoms is altered in a reversible manner. As a result, the interatomic force constants that determine the atomic vibrational frequencies will also change since they are related to the interatomic separation. In general, as the bond lengths increase with tensile load, the force constants, and hence the vibrational frequencies, decrease, whereas the reverse effect is present when the material is subjected to mechanical compression [17].

Various properties of a sample can be characterized by Raman spectroscopy, which is sensitive to crystal structure, composition, stress, and temperature. Raman spectroscopy has been utilized to investigate stresses and phase transformations in semiconductors [19]. Stress maps of Si generated around indentations have been quantified [20]. Quantification of residual stress in a silicon wafer has also been reported [21], as well as internal stress in semiconductors induced by machining [22, 23]. Perhaps, the biggest advantages of Raman spectroscopy are its non-destructive character, the simplicity of the experimental set-up and the short time required to obtaining data, with essentially no sample preparation process required and no surface damage resulting. It is also attractive, because it can detect both organic and inorganic species and measure the crystallinity of solids. In addition, it is free from charging effects that can influence electron and ion beam techniques.

The Stoke Raman peak shift expressed in wavenumber ($\Delta \omega$) corresponds to lower energy scattered photons λ_1 than the incident ones λ_0 . In colloquial usage, Raman shifts are typically in wavenumbers, which have units of inverse length. In order to convert between spectral wavelength and wavenumbers of shift in the Raman spectrum, the following formula can be used (the formula accounts for conversion from nm to cm⁻¹) [18, 25]:

$$\Delta\omega(cm^{-1}) = \left(\frac{1}{\lambda_0(nm)} - \frac{1}{\lambda_1(nm)}\right) 10^7 \tag{6.7}$$

The Stokes peak shifts broaden and become asymmetric for microcrystalline Si with grain sizes below 100 Å. The lines become very broad for amorphous semiconductors, allowing a distinction to be made between single crystal, polycrystalline, and amorphous materials. A shift in frequency can be observed due to stress in the material, where a frequency increase can be found with compressive stress and a decrease with tensile stress (Figure 6.21).

In this work rectangular silicon specimens were laser cut from complete p-type block-cast multicrystalline (mc) wafers in order to perform stress measurements and to study the effect of grain boundaries as well as inclusions on the stress field. All tested neighbouring wafers were chosen from one cast block, taken from the middle position, assuring a lower defect density.

Furthermore, single crystalline Si (100) wafers were used to study the effect of Al and Ag metallization in cross section samples. It should be pointed that in order to exclude possible effects, no SiN_x as well as emitter doping was applied on the samples studied. The samples were mechanically polished to a 0.25 µm finish in order to reduce uncontrolled reflections from rough facets.



Figure 6.21 Raman spectroscopy peaks of pure and stressed Si [17].

The Raman stress measurement was carried out at room temperature in the backscattering configuration using a Renishaw InVia Raman spectrometer, equipped with a He-Ne laser with an excitation wavelength of 633 nm and a 100× objective, resulting in a focused spot with a diameter of ~1 μ m and a penetration depth of a few μ m in silicon. The measurements were performed in steps of ~1 cm⁻¹. The peak position of the (crystalline) c-Si peak is determined by fitting a Lorentzian distribution through the data. The accuracy of the position depends on the spectrum intensity and the fit accuracy, and is between 0.1 and 0.01 cm⁻¹, under the assumption that the TO peak follows a Lorentzian distribution [24]. The system was calibrated using Si (100) reference material. The relative stress level $\Delta \sigma$ and its sign can be evaluated from the shift $\Delta \omega$ of the Raman peak by the equation for:

uniaxial stress (for cross-sectional samples) [25]:

$$\Delta \sigma (MPa) = -500 \Delta \omega (cm^{-1})$$
(6.8)

or biaxial state (for planar samples) [24]:

$$\Delta \sigma (MPa) = -250 \Delta \omega (cm^{-1}),$$
(6.9)

where, $\Delta \omega = \omega_s - \omega_0$ with ω_0 being the peak position of the stress-free state and ω_s the peak position of the stressed state. Internal stress with a resolution of $\sim \pm 0.1$ cm⁻¹ = ± 20 MPa can be evaluated [25]. The shift of the Si Raman peak towards lower wave numbers corresponds to a tensile stress, while the shift in the direction of higher wave numbers indicates a compressive stress.

To investigate the effect of grain boundaries and to reveal the metallic inclusions on stress, mc-Si samples were etched by Secco-etchant for 20 seconds. In order to study the effect of saw-damage removal, specimens without a metal layer were etched for 30 s in a $HF(10\%) + HNO_3(30\%) + CH_3COOH(60\%)$ solution. The effects of saw-damage removal were analyzed by comparing results from as-cut wafers with those from chemically etched specimens using Raman spectroscopy. Three types of specimens were prepared in order to analyze the effect of surface treatment on stress state. Surface states included: the as-cut state (with saw-damaged layer), a textured surface (a real in-line process, which serves for two main purposes: to remove the damaged layer and to create a highly textured silicon surface in order to trap the light), and a chemically polished surface (15 μ m removal from both wafer sides). Furthermore, defect imaging was performed by electroluminescence (EL) scanning of complete screen-printed solar cells. Electroluminescence was used to locate areas of high defect concentration.

In order to evaluate effects on the stress development in the silicon, six neighbouring single crystalline cz-Si (100) wafers were processed to a cell using identical conditions, but using different peak firing temperatures. Samples covered with only Al and both Ag and Al metallic contacts were embedded into Epofix resin in order to perform Raman scanning along the metallization interfaces of solar cells. The cross sections of Si (100) with Al and Ag metallic contacts were polished to $0.25\mu m$ finish in order to exclude any possible effect of surface inhomogeneities. Measurements of the amount of bowing, that resulted from metallization, were made by an optical method over the full length of the solar cell (156 mm), using a Quick Vision Mitutoyo system.

Specifically for this work, a bending device was built to fit inside the Raman spectrometer (Figure 6.22). This device was used to investigate Raman shifts of loaded and unloaded polished mc-Si samples at grain boundaries and within the grains. The investigated surfaces were subject to a tensile load.



Figure 6.22 Bending clamp used for external loading during Raman spectroscopy measurements.

6.4.2 Results and Discussion

6.4.2.1 Effect of Sawing Process and Surface Treatment of Multicrystalline Silicon Wafers on Stress State

Silicon is a hard and brittle material and in order to cut Si ingots into thin wafers, a multi-wire sawing process is used, which creates a highly stressed and damaged layer.

During the cutting process when abrasive particles are big, the damage of the Si surface is large and there are several large grooves across the surface. The region near the cutting lines shows a large amount of damage and high stresses. Figure 6.23 shows an SEM micrograph of a typical surface of an as-cut multicrystalline silicon wafer. The samples were analysed with a Raman spectrometer in order to check for phase transformations in the damaged layer.

The Raman spectrum shown in Figure 6.24 indicates the presence of amorphous Si (a-Si) beside polycrystalline Si on the as-cut surface. Measurements were made at many different locations on the wafer surface and for many locations an a-Si peak was visible.



Figure 6.23 Micrograph of a typical surface of an as-cut multicrystalline silicon wafer.



Figure 6.24 Representative Raman shift for the as-cut wafer, showing a local indentation-induced transformation of Si into a-Si.

It is known that when indented or scratched at low load, silicon shows a local phase transformation from cubic diamond (Si-I) into a metallic (ductile) β -tin structure (Si-II) leading to a 22% volumetric reduction [26]. During fast unloading this ductile phase in not stable and transforms into a layer of amorphous silicon, or if the unloading is slow enough, a mixture of amorphous and metastable phases (*i.e.* Si-XII a rhombohedral phase with 8 atoms per unit cell and Si-III, a body-centred cubic phase with 16 atoms per unit cell) is formed [27-29]. This new phase transformation in unloading gives a sudden volumetric increase in the transformed material.

In this study, amorphous silicon was found only in the smooth grooves (Figure 6.23). The rough parts of as-cut silicon wafers, where material is chipped off instead of indented, mainly consist of stable crystalline silicon.

As can be seen from Figure 6.25 there is a significant positive shift $\Delta \omega$ of 2 cm⁻¹ of the Raman peak for as-cut samples (with respect to the damage-free etched samples), corresponding to a compressive stress of 500 MPa.

This shift could be caused by a high degree of silicon transformation of the top layer of the silicon surface (due to the cutting process) resulting in a volume change. Note, the resulting Raman shift is representative only for the top few μ m of the damage layer, as this is the penetration depth in silicon.

From these results and from our previous investigations discussed in chapter 4, it is suggested that applying the etching process reduces the depth of surface microcracks, that some cracks disappear completely and some crack tips become more blunted, and that the layer of transformed a-Si is removed. Both of these effects reduce the risk of macrocrack initiation, making the material less susceptible to failure.



Figure 6.25 Representative Raman shift for as-cut, textured and polished neighbouring wafers.

6.4.2.2 Effect of Mc-Silicon Microstructure

A specific crystal grain configuration, featuring a grain boundary in the middle (Figure 6.26), was investigated using Raman spectroscopy in order to see the effect of grain boundaries on the stress state development during the application of an external load.



Figure 6.26 A specific crystal grain configuration featuring a grain boundary in the middle.

First of all, Raman stress measurements showed that there are different residual stresses at the grain boundaries and inside the grain (Table 6.6). The Raman shift difference changed when going from the grain boundary to a location inside the grain by $+0.15 \text{ cm}^{-1}$, corresponding to a stress change of -37 MPa (compressive stress).

The Raman shift differences between the unloaded and tensile loaded conditions are (Table 6.6):

- at the grain boundary: -0.16 cm^{-1} (+40 MPa)
- in the grain: -0.09 cm^{-1} (+22 MPa)

Table 6.6. Raman shifts of unloaded and tensile loaded polished mc-Si samples at grain boundaries and inside the grains.

Raman shift, (cm^{-1}) at:			
No Load		Loaded	
At grain boundary	In the grain	At grain boundary	In the grain
521.54 ± 0.03	521.69± 0.01	521.38 ± 0.05	521.60 ± 0.02

These results indicate that grain boundaries, when tensile loaded, experience higher stresses than areas inside the grains. This could result from both materialintrinsic properties, such as elastic anisotropy of the individual grains causing stress concentration at grain boundaries and from extrinsic variables such as defects (metallic inclusions) distributed along the grain boundaries. It is concluded that grain boundaries are the most probable sources of mechanical strength degradation of mc-Si wafers.

6.4.2.3 Effect of Silicon Defects on Raman Shift and Stress State

A combination of Raman spectroscopy and electroluminescence was performed for characterization of defect-rich areas in solar cells. The results show that there are tensile stresses in these areas of 275 MPa compared to defect-free areas (Figure 6.27).

Samples featuring metallic inclusions were prepared from metallurgically refined silicon in order to investigate the local effect of metallic inclusions on stress distribution (Figure 6.28 *).

Figure 6.27 shows Raman measurements taken at several areas of interest: inside the bulk silicon (as a reference point), close to an Al inclusion and close to a $CaSi_2$ inclusion. It should be pointed out, that each line scan includes at least 5 Raman measurements.



Figure 6.27 Combination of Raman spectroscopy and electroluminescence for characterization of defect areas in solar cells: a) Electroluminescence image of solar cell with defect areas marked in red and defect-free areas marked in blue; b) Representative Raman shifts between defect and non-defect areas.



Figure 6.28 Defects in multicrystalline silicon: SEM micrograph of CaSi₂ and Al inclusions at the grain boundary of mc-Si (blue lines correspond to Raman scans shown in Table 6.7) and representative phases in the SEM micrograph (marked in red)*. *Courtesy to Dr. Yulia Meteleva-Fischer, Materials innovation institute M2i.

Table 6.7 shows the average Raman shift for the line scans designated in Figure 6.28 a. It can be seen that the Al particle (line scans A and B) is accompanied by a local compressive stress field of ~450 MPa (compared to bulk Si). Such localized thermal stresses are produced during cooling of the silicon ingot to room temperature because of the thermal expansion coefficient mismatch (CTE) between the inclusion and the silicon matrix ($\alpha_{Si} = 3 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_{Al} = 23 \cdot 10^{-6} \text{ K}^{-1}$). It should be noted that the Raman shift is smaller for the CaSi₂ inclusion because of the lower CTE difference, resulting in compressive stresses up to ~150 MPa.

Scanning position	Raman shift, (cm^{-1})
Si bulk	520.57 ± 0.01
Line scan A (near Al)	521.36 ± 0.04
Line scan B (further along Al inclusion)	521.31 ± 0.06
Line scan C (upper part of the CaSi ₂)	520.95 ± 0.04

Table 6.7. Raman shift close to Al and CaSi₂ inclusions.

6.4.2.4 Effect of Metallization Process on Stress State in Silicon Wafers

In order to measure the residual stress distribution along metallization interfaces, Raman spectroscopy scanning was performed on cross-sections (Figure 6.29 and Figure 6.31). There were at least 10 measurements taken along each interface and the middle in order to have a better impression of the stress distribution.

In Table 6.8 results are shown for a wafer covered with both Ag front and Al back contacts. There is a clear distribution of compressive and tensile stress across the silicon wafer thickness.



Figure 6.29 Microstructure of silicon solar cell cross-sections: mc-Si wafer covered with both Ag and Al contacts.

This stress distribution is the result of the metallization process, where residual stresses are created due to the thermal expansion coefficient mismatch. Applying both

Al and Ag contacts, results in higher tensile stress (~250 MPa higher) at the Al/Si interface than the sample with only an Al contact, which can be explained by a much denser Ag layer as compared to the porous Al layer, that causes higher stresses at both Ag/Si and Al/Si interfaces.

Wafers with only an Al back contact fired at different firing temperatures, *i.e.* without a Ag front contact were also examined. The different firing temperatures used for the Al back contact, result in different thicknesses of the eutectic layer (Figure 6.30). Measurements show that higher firing temperatures lead to higher residual stresses at the Al/Si interface and larger amounts of bowing.

It is concluded, that both thickness and uniformity of the eutectic layer are important parameters controlling mechanical stability of silicon solar cells. Furthermore, it should be noted, that increasing the firing temperature results in a positive Raman shift along the Al/Si eutectic interface, indicating a further increase of compressive residual stresses with increasing firing temperature (Table 6.9, Figure 6.31). However, there are many other possible effects, such as silicon doping profile, samples preparation, crystallinity, surface roughness that might influence the Raman spectrum.

Table 6.8. Raman shift across the cross section of a silicon solar wafer covered with both Ag front and Al back contacts (Figure 6.28).

Scanning position	Raman shift, (cm^{-1})	
At Al/Si eutectic interface	520.48 ± 0.07	▲ Tension
Middle of Si wafer	520.62 ± 0.03	
At Ag/Si interface	520.70 ± 0.05	♦Compression



Figure 6.30 a) Effect of maximum firing temperature on microstructure of Al back contact layers, showing different thicknesses of the eutectic layer; b) Resulting amount of bowing.

As can also be seen from Table 6.8, the Al/Si eutectic interface shows higher stress levels compared to the outer Si edge, which can be explained by bowing as a result of Al shrinkage during the firing process and could also be affected by the formation of the BSF (back surface layer) and Si doping with Al.



Figure 6.31 Microstructure of silicon solar cell cross-section with Al paste B fired at 950 °C, showing Raman line scans performed at the Al/Si eutectic and silicon wafer interface, in the middle of the Si wafer and at the Si wafer outer edge.

Table 6.9. Effect of maximum firing temperature of Al back contact on the resulting Raman shift and compressive/tensile uniaxial stress in the solar cell cross-section (for visual example see Figure 6.31).

Max firing	Raman shift, (cm^{-1})			Compressive	Tensile
temperature, (°C)	At Al/Si	Middle of	At the Si	stress at the	stress at
	eutectic	the Si wefer	outer edge	Al/Si interface,	Si edge,
	interface	the SI water		(MPa)	(MPa)
950	520.47	520.40	520.19	75	65
	± 0.05	± 0.06	± 0.04	-75	
850	520.40	520.36	520.23	40	45
	± 0.01	± 0.05	± 0.03	-40	43
750	520.37	520.32	520.29	25	15
	± 0.04	± 0.03	± 0.01	-23	15
Reference Cz-Si	520.32 ± 0.02		-		

6.5 Conclusions

The X-ray diffraction technique, in combination with bow measurements and bending tests, proved to be a powerful non-destructive qualitative and quantitative experimental technique that provides information about fracture behaviour and stress states of silicon solar cells. The results presented in this chapter showed a connection between silicon microstructure, processing conditions, defects and mechanical stress.

The residual stresses and stresses resulting from bending in silicon solar cells were investigated using conventional and synchrotron X-ray diffraction measurements, bowing measurements and bending tests. The study showed that:

- It is necessary to combine conventional XRD, synchrotron diffraction and bow measurements in order to obtain a representative picture of the stress distribution in Al and Ag metallic contacts.
- The thickness of the eutectic layer as well as the composition of the aluminium rear-side contact layer have an important influence on the mechanical stability of silicon solar cells.
- There is a strong correlation between maximum firing temperature, amount of bowing and residual stress level of solar cells, *i.e.* the higher the firing temperature the higher the residual stresses and the amount of bowing.
- It is possible to determine applied bending stresses by X-ray diffraction using an in-situ bending clamp specially designed for thin solar cell specimens.
- Applied stresses determined using XRD and calculated using expressions for 4point bending are comparable in magnitude, thus composite beam theory (used in chapter 4) can be considered appropriate for bending stress calculations in silicon solar cells.
- Holding samples at a load of 2 3 N results in a stress relaxation effect, possibly due to creep or cracking of the Ag layer.
- Synchrotron diffraction analysis showed that there is a stress gradient in both Ag and Al layers.

Furthermore, it was found that conventional and synchrotron X-ray diffraction methods are not appropriate for stress measurement in the coarse-grained silicon substrates studied in this thesis. Thus, residual and bending stress in the silicon substrate was investigated using Raman spectrometry, bowing and 4-point bending tests. The Raman study showed that:

- Residual stresses at the grain boundaries are 37 40 MPa higher than within the grain;
- Grain boundaries are the most probable sources of mechanical strength degradation of mc-Si wafers;
- The saw-damaged layer contains tensile stresses of ~500 MPa;

- An amorphous Si phase was found only in smooth grooves of the as-cut wafer.
- The presence of transformed amorphous Si could also affect mechanical stability of the as-cut wafers (which was already discussed in chapter 4).
- It was found that it is possible to determine bending stress in silicon wafers and solar cells by Raman spectroscopy using an in-situ bending clamp specially designed for thin solar cell specimens.
- An Al inclusion at the grain boundary of mc-silicon creates a local compressive stress field of ~450 MPa (as compared to bulk Si), due to CTE mismatch between the inclusion and the silicon matrix.

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CHAPTER 7

Conclusions and Recommendations

"Follow the evidence to where it leads, even if the conclusion is uncomfortable." Steven James, The Knight

The overall demand to reduce solar energy costs gives a continuous drive to reduce the thickness of silicon wafers. Handling and bowing problems associated with thinner wafers become more and more important, as these can lead to cracking of the cells and thus to high yield losses. Hence, it is very important to find a compromise between electrical properties, strength and costs of the solar cell, which in terms requires a better understanding of microstructure, stress development and mechanical properties of the cell.

This PhD research focuses on aspects related to the microstructure, defects, strength and stress state of crystalline silicon solar wafers and cells, as well as the effect of solar cell processing conditions on these aspects. Discussion and conclusions were given at the end of each chapter, while general conclusions from the investigation are presented below.

Microstructure of Aluminium and Silver Electrical Contacts

- The aluminium layer has a porous composite-like microstructure, consisting of three main components: 1) spherical (3 - 5 μm) hypereutectic Al-Si particles, surrounded by a thin aluminium oxide layer (150-200 nm); 2) a bismuth-silicate glass matrix (3.3 vol.%); 3) pores (14 vol.%).
- 2. The thickness of the Al-Si eutectic layer depends on the Al particle size, the amount of Al paste and the surface roughness of the textured silicon wafers. Furthermore, all these parameters affect the fracture strength of metallised solar cells.
- 3. Drying Al paste at a lower temperature (250 °C) gives smaller process induced cavities and thus a denser Al layer structure, improving the strength of solar cells.
- 4. An alternative mechanism for Ag contact formation was proposed, where under an oxidizing environment Ag dissolves as Ag⁺ ions into the molten glass and there is a redox reaction between diffused Ag and silicon substrate, which creates inverted pyramidal pits on the Si surface. The Ag atoms reduced by the reaction with the Si substrate can precipitate as Ag particles in the molten glass during

firing or as Ag crystals in the inverted pyramidal pits during the subsequent cooling process. This model competes with the previously proposed one, where metal oxides contained in the glass interact with silicon wafer.

5. Furthermore, it was found that there are two main processing parameters affecting the uniformity of the Ag/Si interface, namely the peak firing temperature and the silicon surface roughness.

Fracture Strength of Crystalline Wafer Based Solar Cells

- 1. The ring-on-ring test combined with finite-element (FE) modelling has been developed within this research to provide a new biaxial fracture strength test method for thin solar cell samples. The FE model was validated by digital image correlation. The use of this ring-on-ring test can be recommended for those applications where the surface properties of solar cells are of interest, such as the effects of crystallinity and the impurity concentrations on fracture strength.
- 2. Damage-layer removal by etching significantly increases the strength of both multicrystalline (mc) and single crystalline silicon wafers.
- 3. It was found that mc-silicon wafer crystallinity has a significant effect on the mechanical strength, *i.e.* the more grain boundaries, the weaker the silicon wafer.
- 4. Samples taken from the bottom of the multicrystalline silicon ingot are up to 30% stronger than those taken from the top. This effect was most significant for samples with many grain boundaries. The decrease in strength for the top ingot location could be related to a high concentration of oxygen and other non-metallic impurities.
- 5. There is a significant decrease in fracture strength when an anti-reflective coating is applied. The high application temperature of this SiN_x coating, 375 °C, induces high thermal stresses in the SiN_x layer, which are thought to be the cause of the decrease in the stress at fracture.
- 6. The composition of the aluminium rear side contact paste has an effect on the mechanical strength of a cell through the total thickness of the Al layer, the thickness of the eutectic layer, the porosity and the bismuth glass concentration. The highest strength was observed for the paste with smaller aluminium particle size. Furthermore, both eutectic layer uniformity and microcrack removal contribute to the improvement of mechanical strength of solar cells.
- 7. A strong correlation was found between the maximum firing temperature of the Al rear contact and the amount of bowing and the fracture strength of solar cells, *i.e.* the higher the firing temperature, the higher the bowing and the stronger the cell, which is related to the thickness of Al-Si eutectic layer.
- 8. The silver contact etches the silicon wafer during the firing process creating small etch pits, which negatively affect the strength of the solar cell.

9. Samples where the Si-wafer surface is polished prior to applying a Ag layer show higher strengths because of the stronger Ag-Si contact interface resulting from a good glass wetting of the silicon surface. Non-uniformity of the glass layer and large voids at the Ag/Si interface, observed for textured and as-cut wafer-surface conditions, have a negative effect on the mechanical strength of the solar cells.

Stress Characterization in Silicon Solar Cells

- 1. A combination of laboratory X-ray and synchrotron diffraction together with Raman spectroscopy is required in order to obtain a realistic picture of the residual stress distribution in Al and Ag metallic contacts and crystalline silicon wafers.
- 2. It was shown that there is a stress gradient along the thickness direction in both the Ag and Al layers, resulting from complex composite-like microstructures of the contacts.
- 3. Residual stresses at the grain boundaries of multicrystalline silicon wafers were found to be higher than within the grain. Grain boundaries are therefore considered the most probable sources of mechanical strength degradation of mc-Si wafers.
- 4. An amorphous Si phase was found in the layer damaged by the wafer-cutting process and it is thought that the presence of this transformed amorphous Si also affects the mechanical stability of as-cut wafers.

Recommendations for Future Research

The current project was mainly focused on fundamental aspects of microstructure and fracture strength in crystalline silicon solar cells and on processing conditions affecting these aspects. Implementing the knowledge obtained in this PhD research in a thermo-mechanical model should be one of the main goals for future research in this area. Such a model would allow prediction of the stress state resulting from each processing step during the manufacturing of solar cells. In order to realize this objective, it is recommended to further investigate the following aspects:

Characterization of the effect of silicon crystal orientation on fracture strength of silicon solar cells

By means of electron back-scatter diffraction techniques in combination with ring-on-ring tests it should be possible to evaluate the effect of silicon crystal orientation on fracture strength.

> Further investigation into the electrical contact firing process - understanding the effect of cooling rate on electrical contact formation and resulting properties

In order to further understand the Al and Ag contact formation, it is recommended to carry out fracture strength and stress state evaluations after firing in different atmospheres and using different cooling rates. Furthermore, it would be interesting to include different types of metallization patterns (such as metal wrap-through solar cells) in this research.

> A more precise characterization of the effect of metallic inclusions and SiC needle precipitates on fracture strength and stress state of silicon solar cells

It is recommended to use intentionally contaminated mc-Si block cast from scrub material, containing known high amounts of metallic inclusions, and compare it in terms of fracture strength and stress state with a reference uncontaminated mc-Si block cast (with 99.99% purity) using identical processing conditions. The use of photoluminescence and etching techniques is advised in order to locate different defect areas.

> Effect of soldering on the strength of solar cells and the mechanical behaviour of soldered solar cell interconnections

The influence of making a soldered joint on the mechanical strength of a solar cell should be quantified by comparing test results from specimens covered by a silver layer with results from specimens that are exposed to a local heat input comparable with soldering. Furthermore, the strength of soldered joints themselves and also of conductive adhesives should be evaluated. Because of the more complex geometry, a FE model is required to determine the relationship between the applied load during mechanical testing and the stresses in the different layers.

> Evaluating the effect of different metallization and soldering conditions on the stress state in silicon solar cells

In the present work it is found that metallization conditions have a significant influence on fracture strength of solar cells. It is recommended to extend this work to the effect of soldering time and temperature. Furthermore, it should be possible to develop a set of metallization and soldering parameters leading to the most mechanically stable solar cell.

> Investigation into the origin of failure of silicon solar cells

One of the important questions in the investigation of fracture behaviour of silicon solar cells is where the crack initiates. It is relevant to understand whether there is any delamination at interface layers or microcracking that leads to this initiation.

By means of an in-situ combination of DIC and SEM with a bending test it should be possible to evaluate the crack initiation and crack path in relation to the microstructural features and strain field.

Stress state characterization and the effect of solar cell processing conditions

It is important to further develop stress measurement procedures, allowing accurate evaluation of the effect of different processing parameters on stress state in silicon. A combination of the in-situ bending device with Raman spectroscopy and synchrotron stress characterization methods is recommended.

APPENDIX A

Bow Measurement Procedure

A1: Bow Measurements Details

The bow of cells was measured using a Mitutoyo Quick Vision measuring system [1]. The measurement arrangement and wafer position is shown in Figure A-1. The bow is measured using the focal plane – a plane perpendicular to the optical axis of an imaging system, which contains the focal point of the imaging system. Bow is obtained at the centre point of the wafer with respect to a reference plane determined by three points equally spaced on a circle.



Figure A-1 Measurement positioning.

The bow profile is measured using a 5x5 grid over the centerline of the wafer. The absolute value of the bow is then determined from the bow profile. The measurement grid is shown in Figure A-2.

The bow profile was extracted from the measurement using QVPAK Version 7 Software [1] and a 3D representation of the deformed wafer is shown in Figure A-3.



Figure A-2 Measuring grid for bow measurement.



Figure A-3 Bow results: left, the extracted profile; right a 3D representation of the bow profile.

A2: Data Processing

The deformation profile of the wafers after production is characterized by a bow in one direction. The profile has a circular shape, thus the bow radius can be calculated from the bow measurements. The bow radius can be found using the depth on an arc, Sagitta [2]. The radius of the bow profile can be calculated using A1 and is shown in Figure A-4.

$$s = r - \sqrt{r^2 - l^2} \tag{A1}$$

where *s* is the sagitta, *r* is the radius and , *l* is half the length of the cord spanning the base of the arc. Inversely the radius can be calculated using A2:



Figure A-4 Schematic representation of the sagittal [2].

The bow from the simulations is used to calculate the bow radius of the produced wafers. The bow is measured over a width of 144 mm of the wafer.

APPENDIX B

Data Processing of the Ring-on-ring Test Results

B1: Data Fitting of the Ring-on-ring Test Results

The measurement results from the ring-on-ring experiments have been processed to remove the start-up nonlinear behaviour. The curve has also been translated moving the start point of the force/deflection curve to the origin. This is needed for the comparison with the digital image correlation (DIC) results and the finite element model (FEM).

The start-up behaviour is excluded by fitting the data points from 0.7 N up to 8 N. On these selected points a 3^{rd} order polynomial function is used. The third order function does not fit the curve as a whole, but for the selected points (Force = 0.7-8 N) this gives a good fit as can be seen in Figure B-1.

The 3^{rd} order polynomial fit is used to calculate the intersection for F=0 on the xaxis so the curve can be translated to the origin as can be seen in Figure B-1. The repositioned raw data (green) is fitted with a 4^{th} order polynomial (purple) which is used for later comparison of the ring-on-ring bending results



Figure B-1 Curve fitting of ring-on-ring test data.

B2: Ring-on-ring Calculations

The deflection and stress for a ring-on-ring test can be calculated using the calculations suggested by Roark for a simple supported round plate loaded by a line load [3]. The notations used and the assumed geometry are shown in Figure B-2.



Figure B-2 geometry and notations used. For ring-on-ring calculations [3].

The deflection of the centre of the specimen, y_c , can be calculated using Eq. B1

$$y_c = \frac{-w \cdot a^3}{2 \cdot D} \left(\frac{L_9}{1 + \nu} - 2 \cdot L_3 \right), \tag{B1}$$

where w is the applied line load, a is the sample radius and v is the Poisson ratio. It should be noted that the sample radius is the same as the loading ring radius since no overlap is assumed for this analytical solution. The effective stiffness D of the sample can be calculated using Eq. B2.

$$D = \frac{E \cdot t^3}{12 \cdot \left(1 - \nu^2\right)},\tag{B2}$$

where *E* is the Young's modulus and *t* is the sample thickness

The geometric constants L_3 and L_9 can be calculated using Eq. B3 and Eq. B4.

$$L_3 = \frac{r_0}{4 \cdot a} \left\{ \left(\left(\frac{r_0}{a}\right)^2 + 1 \right) \ln \left(\frac{a}{r_0}\right) + \left(\frac{r_0}{a}\right)^2 - 1 \right\},$$
(B3)

$$L_{9} = \frac{r_{0}}{a} \left\{ \frac{1+\nu}{2} \ln\left(\frac{a}{r_{0}}\right) + \frac{1-\nu}{4} \left(1 - \left(\frac{r_{0}}{a}\right)^{2}\right) \right\},$$
 (B4)

where r_0 is the location of the load in this case it is the loading ring diameter.

The deflection can be calculated for any position of the specimen using Eq. B5.

$$y(r) = y_c + \frac{w \cdot a \cdot L_9 \cdot r^2}{2 \cdot D \cdot (1 + v)} + \frac{-w \cdot r^3}{D} G_3 .$$
(B5)

The geometrical constant G_3 is obtained from [3] of Roarks formula's for $a/r_0 = 0.5$, which gives $G_3=0.014555$.

The stress at the outer fibre of the bottom of the sample can be calculated using Eq. B6:

$$\sigma = \frac{6 \cdot w \cdot a \cdot L_9}{t^2} . \tag{B6}$$

The results presented in the chapter 5 are obtained using the constants shown in Table B-1 [3].

Table B-1. Constants used for ring-on-ring calculations.

Symbol	Description	Value	Unit
t	Sample thickness	180	μm
a	Sample radius	10	mm
r	Loading ring radius	5	mm
E	Young's modulus	163	GPa
v	Poisson ratio	0.29	-

APPENDIX C

Digital Image Correlation Details and Fitting Procedure

C1: Details of Digital Image Correlation Measurements

A Limess 3D Digital Image Correlation System (DIC) with two 5MPixel cameras was used for all DIC experiments. The camera and analog signals were collected using a Limess DAQhw data acquisition box. The load and displacement of the tensile machine have been acquired on a 10 V signal, corresponding to a load of 250 N and the displacement of 5 mm. The data acquisition was synchronized to that of the images and collected on a laptop using the Istra 4D software package [4].

The DIC cameras used lenses with a 50 mm focal length and the diaphragm was set to 20. The calibration was performed using a Limess A12 $10x10 \text{ mm}^2$ calibration grid and a 3D residuum (a quality parameter of the correlation algorithm, which set a maximum acceptable deviation of the pixel position found by the correlation and the back projected object point in pixel [5]) of 0.25 or lower was achieved for every calibration file used. The shutter time were set depending on the sample type for the best image quality.

The Istra 4D software was used to correlate the image and to measure the deflection of the complete image acquired by the two cameras. The correlation algorithm requires a starting point in both images, which was obtained using the correlation parameters shown in Table C-1. If the speckle pattern or image were of poor quality the accuracy (sets maximum acceptable value for the residuum of the correlation algorithm in grey values [5]) and 3D residuum were increased so that the correlation algorithm would detect the start point selected manually.

Parameter	Value/Setting	Unit
Facet size	25	pixels
Image levels	two levels	-
Outlier tolerance	low	-
Maximum permissible values	0.5	pixels
Residuum	20	grey values
3D Residuum	10	pixels
Grid spacing	29	pixels

Table C-1. Instra 4D correlation parameters.

C2: Digital Image Correlation Fitting Procedure

The DIC camera system is used to measure the deflection and the deformed shape of the samples. The DIC system acquired an image every 2 second during the ring-onring bending test, which has a displacement rate of 0.2 mm/min. The analog signals of the loads and deflections are simultaneously measured during the images recording. The correlation was performed using the Istra 4D software package using the parameters described in Appendix C1. The data extracted from the software is a number of points, n, for which the position in space is given by their x, y and z-coordinate. The coordinate system of the DIC data has the x and y axis in plane of the sample and z out of plane.

The data is fitted by finding a mathematical description for the deformed profile in the form of a 4th order surface polynomial (see Eq. C1). The fitting was also performed using lower order surfaces, however it did not allow to fit the entire deformed profile.

$$z(x, y) = C_1 \cdot x^4 + C_2 \cdot x^3 \cdot y + C_3 \cdot x^2 \cdot y^2 + C_4 \cdot x \cdot y^3 + C_5 \cdot y^4 + C_6 \cdot x^3 + C_7 \cdot x^2 \cdot y$$
(C1)
+ $C_8 \cdot x \cdot y^2 + C_9 \cdot y^3 + C_{10} \cdot x^2 + C_{11} \cdot x \cdot y + C_{12} \cdot y^2 + C_{13} \cdot x + C_{14} \cdot y + C_{15}$

where x and y are the coordinates and C_1 to C_{15} constants that define the shape of the fitted surface.

The output of the Istra 4D correlation algorithm are three vectors with the x, y and z value for every point measured.

$$\underline{x} = \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix} , \underline{y} = \begin{bmatrix} y_1 \\ \vdots \\ y_n \end{bmatrix} , \underline{z} = \begin{bmatrix} z_1 \\ \vdots \\ z_n \end{bmatrix}$$

The following procedure was used to calculate the constants C_1 to C_{15} for Eq. C1, which are the components of C.

$$\underline{C} = \begin{bmatrix} C_1 \\ \dots \\ C_{15} \end{bmatrix}$$

The vector *C* is calculated using the following matrix operations:

$$\underline{C} = inv(F^T \times F) \times F^T \times \underline{z}$$
(C2)

The matrix F is shown below:

The first step of the data fitting for all the loading steps, for which images are acquired, is to find the peak of the fitted surface profile at the maximum load. This is needed because the x and y-values are only relative values and can vary from sample to sample. The peak is found by fitting the profile at the peak load so the x and y coordinate can be extracted. The x and y values for the peak are used to re-position all the data points so the peak intersects at the origin of the x-y plane. After the repositioning all measured steps are fitted and the constants C_1 to C_{15} are calculated for every step. An example of the measured and the fitted profile is shown in Figure C-1.



Figure C-1 a) DIC raw data; b) DIC fitted data.

The difference between the raw data and fitted surface is plotted in C-2. The largest fluctuations are visible near the edge of the measured surface. This is a result of the edges areas being further from the focal place of DIC cameras. There can also be peaks at arbitrary positions, which are a result of a badly fitted group of pixels in the Istra 4D software.



Figure C-2 Typical example of the distribution of the deviation of the fitted surface profile relative to the measured surface profile.

APPENDIX D

Finite Element Model (FEM) Description and Validation

D1: Finite Element Model Validation on Digital Image Correlation Results

The load data from the tensile measurements is combined with the load obtained from the DIC measurements described in Appendix C. The mathematical description can be used to calculate the bow profiles for every cross section. The data of 4 sections is used for the processing of the results. The profiles are depicted in Figure D-1.

The profile shape and deformed profile can be compared to the result from the FE model for a specific sample geometry and load.



Figure D-1 Sections along which the deflection profiles are extracted from the DIC results.

The data extracted has been compared to the FE model results in two ways:

- Firstly the shape of the deformed profile has been compared to FE results. This can only be done for a specific load and geometry.
- Secondly the deflections at the position of the loading ring can be compared. The deflection of the loading ring can be extracted from the FE model as a function of the load. The profile shape has only been compared for several specific samples. The comparison between the deflection of the loading ring of the DIC measurement and FE model has been done for all successful DIC measurements.

Deformed Profile Shape

The DIC test results have been compared with the test results of the FE model. The comparison has not been performed on all samples but only samples with a bow profile deviating from most results. The deflection profile comparison is shown for a low load in Figure D-2, which shows an almost circular bow profile. The bow profile comparison between the DIC and FE model for a high load is shown in Figure D-3. The model and FE model show the change of the bow profile that occurs at high loads. The best orientation is the bow profile extracted for y=0 because this area is best in focus for the camera positioning used.



Figure D-2 Comparison between DIC profile and FE model results (shown on example of textured cz-Si with ARC, load = 21.6 N).



Figure D-3 Representative example of a comparison between adjusted DIC test results and FE model results (shown on example of polished cz-Si with an aluminium layer type B, load=96.3 N).

The FE model has a lower deflection as the DIC deflection measured for nearly all samples. This difference becomes larger as the applied load is increased up to 10-15% of the measured deflection. There are several reasons which could cause this. The first one is the boundary condition where the frictionless contact is modelled as a free moving support. The material properties are taken as isotropic and a theoretical equivalent of the Young's modulus of silicon is used which could be underestimated. The set-up could show deformation which would result in a difference in the absolute displacement measured using the DIC system. For metallization samples the aluminium or silver layer could deform significantly which is not taken into account in the FE model. All of these reasons could have an effect on this difference.

Loading Ring Deflection

The model can also be correlated to the average value for all 8 points of the position of the ring to compare the DIC load/deflection curve with the result from the FE model. The comparison of the FE model and the DIC measurement for several samples is shown in Figure D-4.



Figure D-4 Comparison of the deflection of the loading ring from FE model and measured points from the DIC results.

D2: Details of the Finite Element Model

To validate the FE model several simulations have been performed to assure convergence of the solutions and prevent errors.

Comparison of an Axisymmetric Simulation with a 3D Simulation

The axisymmetric simulation was compared with a more complex 3D model to validate the accuracy of the calculated stresses and the deformation profile. The accuracy of the 3D model was limited by the mesh size that was achievable in view of the processing power of the available computer. The 3D model has been simulated using ANSYS research licence [6] to allow for such a complex simulation (further details can be found in [7]).

Detailed Options of the Finite Element Model

The specific model options used for the ring-on-ring FE model are shown in Table D-1. All other options and values used are the default settings and values used in ANSYS 11.0 Academic introductory [6].

Option	Settings	Comments
Element type	Plane 182	Linear 4-node element used for solid 2D modelling. The elements are well suited for meshing of rectangular shaped geometries.
Keyoption (1)	2	Enhanced strain to prevent shear locking of the elements and improve the accuracy for bending dominant simulations [8].
Keyoption (3)	1	Axisymmetric boundary condition is used.
Solution method	Static	The problem is simulated using a static analysis.
Non-linear geometries	ON	Non-linear geometries are turned on to allow for effects due to large deflections and this option is needed to calculate effects due to plasticity.
Auto time stepping	ON	The step defines the number of steps in which the solution is calculated. The auto time stepping function is turned on in order to allow Ansys to alter the solution step size to assure convergence of the model.
Time step start/min/max	100/15/1000	The start step size is 1/100 th to ensure an initial small step size without any non-linear effects. The minimum step size was chosen to be 15 to have enough data points to create a plot of stress and displacement as a function of the load. The maximum step size of 1000 is chosen to stop the simulation if no convergence of the simulation is achieved after 1000 time steps.

Table D-1. Ring-on-ring model specifications.
D3: Solution Convergence

Mesh size

The 2D simulation was checked for convergence as a function of the number of elements used. The calculated stresses and deflections for coarse and fine meshes were compared by increasing the number of elements and checking the difference in the obtained solutions. The mesh is determined by the number of divisions of the lines of the model and is shown in Table D-2.

Model	N, divisions width	N, divisions along the thickness of Si	N, divisions along the thickness of Ag	N, divisions along the thickness of Eutectic layer	N, divisions along the thickness of Al
Silicon	800	8	-	-	-
Silver metallization	800	8	5	-	-
Aluminium metallization	800	8	-	4	4

Table D-2. Mesh size used for ring-on-ring finite element model.

Nodal and Elemental Solution

The nodal and elemental solutions have been compared to ensure convergence of the calculated stresses. The concept of a nodal solution and an elemental solution is schematically shown in Figure D-5. The nodal solution averages the stress from all elements to which node is connected. The elemental solution averages the stress calculated at the nodes of a specific element. When the nodal and elemental solutions deviate, this usually suggests that the mesh is too coarse and a finer mesh should be used. In the performed simulations the nodal and elemental solutions converge within 0.2 %, which is well below the value of 10 % suggested in practice [8] and [9].



Figure D-5 Examples of a) FEM calculation; b) nodal and c) elemental stress solutions.

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Summary

Due to pressure from the photovoltaic industry to decrease the cost of solar cell production, there is a tendency to reduce the thickness of silicon wafers. Unfortunately, wafers contain defects created by the various processing steps involved in solar cell production, which significantly reduce the strength of the wafers and cells. Therefore, a higher breakage rate is to be expected if thinner wafers are produced with identical fracture strength in combination with the same forces applied during processing. It should be noted that if identical displacements are applied to thinner wafers, the breakage rate will be decreased.

Wafer breakage has become an important issue in the photovoltaic silicon industry, since it limits production yield and results in a further price reduction. Microflaws generated during wafer sawing, as well as impurity precipitations, structural defects, and residual stresses are the leading sources of crack initiation/propagation and mechanical strength degradation of silicon wafers and solar cells. In this work aspects related to microstructure, defects and stress state of crystalline silicon solar wafers and cells were studied. The aim of this work is to determine which stage during the manufacturing process, from wafer to a complete cell, is critical with respect to the introduction of stresses or cell damage, both potentially resulting in premature failure. Emphasis is placed on fundamental understanding of the microstructure and of defect and stress development and the resulting fracture strength at all stages during the production process from wafer to solar cell. The results presented in this thesis may be applied to enhance production yields, improve solar cell reliability and help to establish mechanical criteria, which all lead to a reduction in cell production costs.

Microstructure and Mechanical Properties of Aluminium and Silver Contacts

The research presented in this thesis provides a deeper understanding of the microstructure and mechanical properties of screen-printed and fired aluminium and silver contacts of solar cells. Furthermore, new models are proposed for the Al and Ag contact formation.

It is shown that the Al layer has a porous outer part with a complex compositelike microstructure, consisting of three main components: 1) spherical $(3 - 5 \mu m)$ hypereutectic Al-Si particles, surrounded by a thin aluminium oxide layer (150-200 nm); 2) a bismuth-silicate glass matrix (3.3 vol.%) 3) and pores (14 vol.%). As a result of a reaction between the porous Al and the Si wafer, a eutectic layer develops. The thickness of this eutectic layer depends on the Al particle size, the amount of Al paste and the surface roughness of the textured silicon. Smaller Al particles preferentially fill the bottom of the textured surface, while interdiffusion and alloying are facilitated by a lower melting temperature of the finer particles, resulting in a thicker and more uniform eutectic layer. Larger Al particles sinter more slowly and require higher sintering temperatures and/or longer sintering times, resulting in a wavy eutectic layer.

It is also found that the drying process of the aluminium paste layer needs special attention, otherwise volatilizing solvent can cause cavities to develop in the fired layer, which affect mechanical stability and most likely electrical performance of the entire solar cell. Drying aluminium paste at a temperature of 250 °C gives small cavities and a dense Al layer structure; hence it can be recommended as an appropriate drying temperature.

The Young's modulus of the Al back contact layer, measured by nanoindentation, is found to be 44 GPa, which is in good agreement with the Young's modulus, calculated on the basis of bowing data and a bilayer strip model.

In this work the formation of fired Ag front contact layers was studied and an alternative "ionic reduction" mechanism is proposed. It is suggested, that under an oxidizing environment (atmosphere) Ag dissolves as Ag^+ ions into the molten glass and there is a redox reaction between diffused Ag^+ ions and the silicon substrate, which creates inverted pyramidal pits on the Si surface. The Ag atoms reduced by the reaction with the Si substrate can precipitate as Ag particles in the molten glass during firing or as Ag crystals in the inverted pyramidal pits during the subsequent cooling process.

There are two main processing parameters affecting the uniformity of the Ag/Si interface, namely the peak firing temperature and the silicon surface roughness. Silicon surface polishing gives a better wetting of the silicon wafer by the glass layer, resulting in a good contact and a lower incidence of large voids, compared to the case of highly textured surfaces. In the case of such a textured surface, non-uniformity of the glass layer and large voids at the Ag/Si interface have a negative effect on the mechanical strength of the solar cell.

The Young's modulus of the bulk layer of Ag agglomerates was measured by nanoindentation and found to be \sim 54 GPa.

Mechanical Stability of Crystalline Silicon Solar Wafers and Solar Cells

Special fracture strength tests suitable for thin specimens, to be used in combination with Weibull statistics, were developed within this study in order to investigate the influence of the industrial processing steps on the mechanical stability of silicon wafers and solar cells.

It is concluded that a combination of a 4-point bending and a ring-on-ring test method allows a more accurate evaluation of the effects of different processing conditions on the fracture strength of silicon wafers and solar cells than each test individually. In the analysis of the stresses developing during 4-point bending tests, silicon solar cell samples were treated as composite beams, consisting of two or three layers, namely a wafer and either a silver layer or aluminium porous and eutectic layers.

In the ring-on-ring test stresses were analysed with a finite-element (FE) model, which was validated using digital image correlation. The combination of ring-on-ring test and FE modelling provides a new biaxial fracture strength test method for thin solar cell samples. The use of this method can be recommended for those applications where surface properties of solar cells have to be investigated, such as the effects of crystallinity and impurity concentrations on fracture strength. The results of both types of fracture tests (ring-on-ring and 4-point bending) are in good agreement.

The fracture strength of crystalline silicon wafers was measured by means of both 4-point bending and ring-on-ring tests. The results show that removal of the layer containing saw damage through etching significantly increases the strength of both multicrystalline (mc) and single crystalline silicon wafers. Furthermore, the effect of mc-silicon crystallinity on fracture strength shows similar trends for both types of mechanical testing, indicating that weak grain boundaries are more detrimental than edge defects that possibly affect results from 4-point bending tests. It is found that this crystallinity has a significant effect on the strength of polished wafers, *i.e.* a lower strength if more grain boundaries are present, for samples taken from the middle of an mc-Si cast ingot where the impurity concentrations are low.

The location where the wafer is extracted from the mc-Si cast ingot also has an effect on mechanical strength, namely samples taken from the bottom of the ingot are 30% stronger than those taken from the top. This observation was most significant for samples with many grain boundaries. This could be related to a higher carbon concentration at the bottom of the ingot.

The study shows that there is a significant decrease in fracture strength when an anti-reflective coating is applied. It is thought that this is caused by high thermal stresses in this SiN_x layer, which result from the high application temperature (375 °C). These high stresses probably cause fracture in the SiN_x layer (before and/or during wafer loading), which consequently results in early failure of the complete wafer.

The composition of the aluminium rear side contact paste has an effect on the mechanical strength of a solar cell through the total thickness of the Al layer, the thickness of the eutectic layer, the amount of porosity and the bismuth glass concentration. It was found that the larger the Al particle size, the more porous the aluminium layer is and consequently the less uniform the resulting eutectic layer is. This leads to a reduction of fracture strength, due to a non-uniform stress distribution (stress concentrations within the thinner areas of the 'wavy' eutectic layer). The Al-Si eutectic layer appears to show some plasticity and possibly serves to shield critical microcracks at the silicon wafer surface, thus improving the strength. Furthermore, both eutectic layer uniformity and microcrack removal contribute to the improvement of mechanical strength of Si wafers. Both the ring-on-ring and the 4-point bending test results indicate that an aluminium paste with a fine particle size can be considered the most optimal from a mechanical point of view. A strong correlation is found between

the maximum firing temperature of the Al rear contact and the amount of bowing and the fracture strength of solar cells. The higher the firing temperature, the higher the bowing and the stronger the cell, effects that are related to the thickness of Al-Si eutectic layer. Aluminium contact firing temperatures between 800 °C to 850 °C are the most optimal with respect to the amount of bow and the fracture strength.

Conversely, the silver paste type showed no significant influence on the fracture strength of solar cells. Samples where the Si-wafer surface is polished prior to applying a Ag layer show higher strengths, because of the stronger Ag-Si contact interface resulting from a good glass wetting on the silicon surface. Non-uniformity of the glass layer and large voids at the Ag/Si interface, observed for as-cut and textured wafer-surface conditions, have a negative effect on the mechanical strength of the solar cell and result in a lower Weibull modulus.

Stress Characterization in Silicon Solar Cells

Stress measurements through X-ray diffraction, in combination with bow measurements and bending tests, proved to be a powerful non-destructive qualitative and quantitative experimental technique that provides information about the stress state in the metal contact layers of silicon solar cells. Results reveal the relationship between silicon microstructure, processing conditions, defects and residual stress. The study shows that it is necessary to combine conventional X-ray diffraction, synchrotron diffraction and bow measurements in order to obtain a complete picture of the residual stress distribution in Al and Ag contacts.

There is a strong correlation between maximum firing temperature, amount of bowing and the residual stress level in a solar cell, *i.e.* the higher the firing temperature the higher the residual stresses and the amount of bowing. Furthermore, synchrotron diffraction analysis revealed that there is a stress gradient along the thickness direction in both the Ag and Al layers.

Laboratory and synchrotron X-ray diffraction methods are not appropriate for a complete stress analysis of the coarse-grained mc-silicon substrates studied in this thesis. Therefore, residual and bending stresses in the silicon substrate were investigated using Raman spectroscopy in combination with 4-point bending loading. This Raman study shows that residual stresses at the grain boundaries are higher than within the grains. The presence of grain boundaries is therefore considered the most probable reason for the lower mechanical strength of mc-Si wafers relative to sc-Si wafers.

An amorphous Si phase was found in the layer damaged by the wafer-cutting process and it is thought that the presence of this transformed amorphous Si also affects the mechanical stability of as-cut wafers, caused by a transformation-induced volume change resulting in high stresses.

The studies reported in this thesis provide the photovoltaic industrial and academic audience with a more fundamental understanding of the microstructure and mechanical property development during industrial multicrystalline silicon solar cell processing. On the basis of this work it can be concluded that wire-sawing, texturing, applying a SiN_x antireflection coating and firing of metallic contacts are the most critical solar cell processing steps. Recommendations for the most suitable processing parameters are proposed in this thesis.

Samenvatting

Door druk vanuit de fotovoltaïsche industrie om de kosten van de productie van zonnecellen te verlagen, bestaat een tendens om de dikte van silicium-wafers te verminderen. Helaas bevatten wafers defecten, gevormd door de verschillende processtappen tijdens de productie van zonnecellen, die de sterkte van wafers en cellen aanzienlijk verminderen. Daarom zal vaker breuk te verwachten voor cellen die op basis van dunnere wafers worden geproduceerd, uitgaande van dezelfde breuksterktes en uitgeoefende krachten tijdens het productieproces. Opgemerkt moet worden, dat als dezelfde verplaatsingen worden uitgeoefend op dunnere wafers, breuk minder vaak zal voorkomen.

Wafer-breuk is een belangrijk onderwerp geworden in de industrie voor fotovoltaïsch silicium, omdat het het productierendement en daarmee verdere prijsdaling beperkt. Microscheuren die ontstaan tijdens het zagen van de wafers, maar ook uitscheidingen van verontreinigingen, structuurdefecten en restspanningen zijn de belangrijkste oorzaken voor scheurinitiatie/-groei en de achteruitgang van de mechanische sterkte van silicium-wafers en zonnecellen. In dit werk zijn aspecten gerelateerd aan microstructuur, defecten en spanningstoestand van kristallijne siliciumwafers en zonnecellen bestudeerd. Het doel van dit werk is om te bepalen welke stap van het productieproces, van wafer tot complete cel, kritisch is met betrekking tot het veroorzaken van spanningen of celschade, beide mogelijk leidend tot vroegtijdig bezwijken. De nadruk wordt gelegd op fundamenteel begrip van de microstructuur en van defectvorming en spanningsontwikkeling en de resulterende breuksterkte tijdens alle stappen van het productieproces van wafer tot zonnecel. De resultaten die in dit proefschrift worden gepresenteerd kunnen worden gebruikt om het productierendement te verhogen, de betrouwbaarheid van zonnecellen te verbeteren en mechanische criteria helpen vast te stellen, die alle leiden tot een verlaging van de productiekosten van zonnecellen.

Microstructuur en mechanische eigenschappen van aluminium- en zilvercontacten

Het in dit proefschrift gepresenteerde onderzoek geeft een meer diepgaand inzicht in de microstructuur en mechanische eigenschappen van gezeefdrukte en gesinterde aluminium- en zilvercontacten van zonnecellen. Verder worden nieuwe modellen voorgesteld voor de vorming van deze Al- en Ag-contacten.

Het is aangetoond dat de aluminiumlaag een poreus buitenste deel heeft met een complexe composietachtige microstructuur bestaande uit drie hoofdcomponenten: 1) bolvormige (3 - 5 μ m) hypereutectische Al-Si-deeltjes, omringd door een dunne aluminiumoxidelaag (150-200 nm); 2) een matrix van bismutsilicaatglas (3.3 vol.%) 3) en poriën (14 vol.%). Als gevolg van een reactie tussen het poreuze Al en de Si-wafer,

ontwikkelt zich een eutectische laag. De dikte van deze eutectische laag hangt af van de Al-deeltjesgrootte, de hoeveelheid aluminiumpasta en de oppervlakteruwheid van het getextureerde silicium. Kleinere Al-deeltjes vullen bij voorkeur de dalen van het getextureerde oppervlak, terwijl onderlinge diffusie en legeren bevorderd worden door een lagere smelttemperatuur van de kleinere deeltjes, resulterend in een dikkere en een meer gelijkmatige eutectische laag. Grotere Al-deeltjes sinteren langzamer en vereisen hogere sintertemperaturen en/of langere sintertijden, met als resultaat een golvende eutectische laag.

Het is ook vastgesteld dat het droogproces van de laag aluminiumpasta speciale aandacht vereist, omdat anders het vluchtige oplosmiddel holtevorming kan veroorzaken in de gesinterde laag, zodanig dat de mechanische stabiliteit en waarschijnlijk het elektrisch gedrag van de hele zonnecel wordt beïnvloed. Het drogen van de aluminiumpasta bij een lagere temperatuur (250 °C) geeft kleinere holtes en een dichtere structuur van de Al-laag, zodat dit als de meest geschikte droogtemperatuur kan worden aanbevolen.

De elasticiteitsmodulus van de aluminiumcontactlaag aan de achterzijde, gemeten met nanoindentatie, is bepaald op 44 GPa, wat in goede overeenstemming is met de elasticiteitsmodulus berekend op basis van krommingsdata en een dubbele-stripmodel.

In dit werk is de vorming van gesinterde zilvercontactlagen aan de voorzijde bestudeerd en wordt een alternatief "ionenreductiemechanisme" voorgesteld. Gesuggereerd wordt dat in een oxiderende omgeving (atmosfeer) Ag in het gesmolten glas oplost als Ag⁺-ionen en dat een redoxreactie plaatsvindt tussen gediffundeerde Ag⁺-ionen en het siliciumsubstraat, waardoor op het siliciumoppervlak omgekeerde piramidevormige putten worden gevormd. De zilveratomen, gereduceerd door de reactie met het siliciumsubstraat, kunnen tijdens het sinteren als zilverdeeltjes in het gesmolten glas uitscheiden of tijdens de daarop volgende afkoeling als zilverkristallen in de omgekeerde piramidevormige putten.

Er zijn twee belangrijke procesparameters die de gelijkmatigheid van het Ag/Sigrensvlak beïnvloeden, te weten de pieksintertemperatuur en de oppervlakteruwheid van het silicium. In vergelijking met sterk getextureerde oppervlakken geeft polijsten van het siliciumoppervlak een betere bevochtiging door de glaslaag van de siliciumwafer, met als gevolg een goed contact en een kleiner aantal grote poriën. In het geval van een getextureerd oppervlak, hebben ongelijkmatigheid van de glaslaag en grote poriën aan het Ag/Si-grensvlak een negatief effect op de mechanische sterkte van de zonnecel.

De elasticiteitsmodulus van de bulklaag van zilveragglomeraten is met nanoindentatie bepaald op ~54 GPa.

Mechanische stabiliteit van kristallijne silicium-wafers en -zonnecellen

In deze studie zijn specifieke breuksterktetesten ontwikkelt voor dunne proefstukken, te gebruiken in combinatie met Weibullstatistiek, teneinde de invloed van de industriële processtappen te onderzoeken op de mechanische stabiliteit van siliciumwafers en -zonnecellen.

De conclusie wordt getrokken, dat een combinatie van een 4-puntsbuig- en een ring-op-ring-testmethode een nauwkeuriger bepaling mogelijk maakt dan iedere testmethode afzonderlijk van de effecten van de verschillende procescondities op de breuksterkte van silicium-wafers en -zonnecellen. In de analyse van de spanningen die ontstaan tijdens 4-puntsbuigtesten, zijn de silicium-zonnecelproefstukken beschouwd als samengestelde balken bestaand uit twee of drie lagen, te weten een silicium-wafer in combinatie met een zilverlaag of met een poreuze aluminiumlaag én een eutectische laag. In de ring-op-ring-test zijn de spanningen geanalyseerd met een eindigeelementenmodel, dat is gevalideerd met behulp van digitale beeldcorrelatie. De combinatie van ring-op-ring-test en eindige-elementenmodellering levert een nieuwe twee-assige breuksterktetestmethode op voor dunne zonnecelproefstukken. Het gebruik van deze methode kan worden aanbevolen voor die toepassingen waar oppervlakteeigenschappen van zonnecellen moeten worden onderzocht, zoals de effecten van kristalliniteit en gehalte aan verontreinigingen op de breuksterkte. De resultaten van beide typen breuktesten (ring-op-ring en 4-puntsbuiging) laten een goede overeenkomst zien.

De breuksterkte van kristallijne silicium-wafers is gemeten met behulp van zowel 4-puntsbuig- als ring-op-ring-testen. De resultaten laten zien dat het verwijderen van de door zagen beschadigde laag via etsen de sterkte significant verhoogd van zowel multikristallijne (mk) en éénkristallijne silicium-wafers. Verder toont het effect van de kristalliniteit van mk silicium op de breuksterkte overeenkomstige trends voor beide typen mechanische beproeving, wat aangeeft dat zwakke korrelgrenzen schadelijker zijn dan randeffecten die mogelijkerwijs de resultaten van 4-puntsbuigtesten beïnvloeden. Er is gevonden dat deze kristalliniteit een significant effect heeft op de sterkte van gepolijste wafers, dat wil zeggen een lagere sterkte als er meer korrelgrenzen zijn, voor proefstukken genomen uit het midden van een gegoten mksilicium-ingot waar de concentraties aan verontreinigingen laag zijn.

De plaats waar de wafer uit de gegoten mk-silicium-ingot is gehaald, heeft ook een effect op de mechanische sterkte, namelijk proefstukken die uit de onderzijde van de ingot zijn gehaald zijn 30% sterker dan die uit de bovenzijde. Dit was het meest significant voor proefstukken met veel korrelgrenzen. Dit kan te maken hebben met een hogere koolstofconcentratie aan de onderzijde van de ingot.

De studie laat zien, dat er een significante afname in breuksterkte is als een antireflectie-coating wordt aangebracht. Het idee bestaat dat dit veroorzaakt wordt door hoge thermische spanningen in deze SiN_x -coating, die het gevolg zijn van de hoge temperatuur waarbij deze wordt aangebracht (375 °C). Deze hoge spanningen veroorzaken waarschijnlijk breuk in de SiN_x -laag (voor en/of tijdens belasten van de wafer), die vervolgens resulteert in vroegtijdig bezwijken van de wafer als geheel.

De samenstelling van de aluminiumpasta voor het contact aan de achterzijde heeft een effect op de mechanische sterkte van een zonnecel via de totale dikte van de Allaag, de dikte van de eutectische laag, de mate van porositeit en de bismutglasconcentratie. Het is gevonden dat hoe groter de Al-deeltjesgrootte, hoe poreuzer de aluminiumlaag en, als gevolg hiervan, hoe minder gelijkmatig de resulterende eutectische laag. Dit leidt tot een afname van de breuksterkte als gevolg van een ongelijkmatige spanningsverdeling (spanningsconcentraties in de dunnere delen van de 'golvende' eutectische laag). De eutectische Al-Si-laag blijkt enige plasticiteit te vertonen en beschermt mogelijkerwijs kritische microscheuren aan het oppervlak van de silicium-wafer, waardoor de sterkte wordt verhoogd. Verder dragen zowel een gelijkmatige eutectische laag als verwijdering van microscheuren bij aan verbetering van de mechanische sterkte van silicium-wafers. Zowel de ring-op-ring- als de 4puntsbuigtestresultaten geven aan, dat een aluminiumpasta met een kleinere deeltjesgrootte vanuit een mechanisch perspectief als het meest optimaal kan worden beschouwd. Er is een sterk verband gevonden tussen de maximum sintertemperatuur van het Al-contact aan de achterzijde en de mate van kromming en de breuksterkte van zonnecellen. Hoe hoger de sintertemperatuur, hoe meer kromming en hoe sterker de cel, effecten die zijn gerelateerd aan de dikte van de eutectische Al-Si-laag. Sintertemperaturen voor het aluminiumcontact tussen 800 en 850 °C zijn het meest optimaal met betrekking tot de mate van kromming en de breuksterkte.

In tegenstelling tot aluminiumpasta, laat het type zilverpasta geen significante invloed zien op de breuksterkte van zonnecellen. Proefstukken waarvan het oppervlak van het silicium is gepolijst voordat een zilverlaag is aangebracht vertonen hogere sterktes, vanwege het sterkere Ag-Si-grensvlak dat een gevolg is van een goede bevochtiging van het glas op het siliciumoppervlak. Ongelijkmatigheid van de glaslaag en grote poriën aan het Ag/Si-grensvlak, waargenomen voor gezaagde en getextureerde wafer-oppervlakken, hebben een negatief effect op de mechanische sterkte van de zonnecel en leiden tot een lagere Weibullmodulus.

Spanningskarakterisering in silicium-zonnecellen

Spanningsmetingen met behulp van Röntgendiffractie, in combinatie met krommingsmetingen en buigtesten, blijkt een krachtige non-destructieve kwalitatieve en kwantitatieve experimentele techniek te zijn, die informatie verschaft over de spanningstoestand in de metalen contactlagen van silicium-zonnecellen. Resultaten onthullen het verband tussen siliciummicrostructuur, procesomstandigheden, defecten en restspanningen. De studie laat zien dat het nodig is om conventionele Röntgendiffractie, synchrotrondiffractie en krommingsmetingen te combineren ten einde een volledig beeld te krijgen van de restspanningsverdeling in aluminium- en zilvercontacten.

Er is een sterk verband tussen maximum sintertemperatuur, mate van kromming en het restspanningsniveau in een zonnecel, namelijk hoe hoger de sintertemperatuur, hoe hoger de restspanningen en de mate van kromming. Verder heeft de analyse van de synchrotrondiffractie laten zien dat er een spanningsgradiënt is in de dikterichting in zowel de zilver- als de aluminiumlagen.

Laboratorium- en synchrotronmethoden voor Röntgendiffractie zijn niet toereikend voor een complete spanningsanalyse van de grofkorrelige mk siliciumsubstraten die in dit proefschrift worden bestudeerd. Daarom zijn rest- en buigspanningen in het siliciumsubstraat onderzocht met Ramanspectroscopie in combinatie met 4-puntsbuigbelastingen. Deze Ramanstudie laat zien dat restspanningen bij de korrelgrenzen hoger zijn dan binnen de korrels. Daarom wordt de aanwezigheid van korrelgrenzen beschouwd als de meest waarschijnlijke oorzaak voor de lagere mechanische sterkte van mk-silicium-wafers ten opzichte van éénkristallijne siliciumwafers.

Er is een amorfe Si-fase gevonden in de laag die beschadigd is door het waferzaagproces en veronderstelt wordt dat de aanwezigheid van dit getransformeerde amorfe Si ook de mechanische stabiliteit van gezaagde wafers beïnvloedt. Dit als gevolg van de hoge spanningen veroorzaakt door de volumeverandering die met deze transformatie gepaard gaan.

De studies waarvan in dit proefschrift verslag worden gedaan, geven de photovoltaïsche industrie en het academisch publiek een meer fundamenteel begrip van de ontwikkeling van de microstructuur en de mechanische eigenschappen tijdens de industriële vervaardiging van multikristallijne silicium-zonnecellen. Op basis van dit werk kan geconcludeerd worden dat draadzagen, textureren, aanbrengen van een SiN antireflectiecoating en sinteren van metallische contacten de meest kritische processtappen zijn voor zonnecellen. In dit proefschrift worden aanbevelingen gedaan voor de meest geschikte procesparameters.

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CURRICULUM VITAE

Vera Popovich

Born on 17th of May, 1983 in Vladivostok, Russia

1/2013 – Present	Postdoctoral Researcher, Materials Innovation Institute (M2i), Delft, The Netherlands.
2008 – 2013	PhD Researcher at Delft University of Technology. Project: Microstructure and Mechanical Aspects of Multicrystalline Silicon Solar Cells, a collaboration project between ECN (Energy Research Centre of the Netherlands), ADEM (Advanced Dutch Energy Materials) and TUDelft.

- 2005 2007 Msc in "Joint European Master Materials Science" (Germany – Technical University Hamburg - Harburg, Portugal – University of Aveiro, University of Aalborg, Denmark). Msc thesis: "Fabrication and Mechanical Properties of Al₂O₃-TiC-Mo Composites".
- 9/2004 9/2006 Msc in "Materials Science and Technology of New Materials", Department of Metals and Materials science, Far Eastern National Technical University, Vladivostok, Russia. Msc thesis: "Investigation of Silver Coatings Prepared by Electrochemical Method".
- 9/2000 6/2004 Bsc in "Materials Science and Technology of New Materials", Department of Metals and Materials science, Far Eastern National Technical University, Vladivostok, Russia. Bsc thesis: "Characterization of Silver Coating Technologies Applied on Metallic Alloys".
- 9/2004 5/2005 Chinese Language and Culture Studies, Zhong Shan (Sun-Yat Seng) University, Guangzhou, China.
- 8/2000 6/2005 Engineer in "Translation and Translation science", Qualification: "Linguist and Interpreter"; Specialization: "Chinese language"; Oriental institute, Far Eastern National Technical University, Vladivostok, Russia.