CHARACTERIZATION OF THIN-FILM SILICON MATERIALS AND SOLAR CELLS THROUGH NUMERICAL MODELING

PROEFSCHRIFT

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- Gene Fowler

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Chapter 1

Introduction

In this house, we OBEY the laws of thermodynamics!

- Homer Simpson

1.1 Motivation: thermodynamics, economics and the photovoltaic effect

Strong incentives for the development of technologies for the sustainable production of energy are the limited availability of, and the environmental issues related to the use of fossil and nuclear fuels, i.e., the unsustainable nature of the latter two energy sources. But what exactly do we want to sustain and, consequently, what determines the sustainability of an activity? A limited supply of fossil fuels logically inhibits sustaining the burning of the same, but there is more to consider than sustaining this activity of burning fossil fuels. Isotopic signatures from sulfide and sulfate in Precambrian rocks indicate that more than 2400 million years ago the atmospheric oxygen (O₂) partial pressure was low [1] (less than 10^{-5} times the present atmospheric level [2]). It is generally believed that most of the oxygen in our atmosphere is the product of oxygenic photosythesis [3,4]. As fossil fuels and the oxygen in the atmosphere are both the products of oxygenic photosythesis, the amount of free oxygen is a measure for the amount of fossil fuels. It can be deduced based on the 21 % of oxygen in our atmosphere, that there are still considerable amounts of fossil fuels left [5]. From the same argument it follows we would suffocate before we can burn it all. However, long before the oxygen would be burned, our environment would be drastically changed. The way we live our lives depends strongly on the environment and therefore, in order to sustain ourselves and our way of living, we need to sustain our environment. In light of this we will start the motivation for this work by discussing some fundamental physics at the basis of life itself, and how utilizing solar energy may help us to continue our activities while maintaining an environment capable of sustaining us.

First I have to apologize for the terminology in the first paragraph. Energy can, according to the first law of thermodynamics, not be produced. Instead, in order to do work we produce entropy in accordance with the second law of thermodynamics. That is, we convert available energy, or "exergy", to unavailable energy. This conversion is fundamental to everything we do as it is fundamental to everything, including life itself. A living organism, as any system in nature, tends to equilibrium, the state of maximum entropy. Equilibrium, however, equals death for any organism. The only way the organism can stay sufficiently far away from this final state of maximum entropy is to draw available energy from the surroundings, or as Schrödinger [6] put it, "it [life] feeds on negative entropy". Note that entropy in the classical formulation refers to closed systems only, in which case there can be no such thing as a decrease in entropy or "negative entropy". However, living organisms are "open systems" which can exchange energy and matter with their surroundings. Open systems far from thermodynamic equilibrium are often referred to as "dissipative systems". For such dissipative systems extended concepts of entropy have been developed, see for example the work of Prigogine et al. [7,8]. In these extended concepts, the intake of available energy from the environment by an open system will lead to a decrease in the entropy of that system, and thus this absorption of available energy leads to a negative entropy term.

Just like organisms, earth as a whole can also be seen as an open system far from equilibrium. This global dissipative system receives exergy from the continuous energy current of $1 \cdot 10^{17}$ W which radiates to earth from the sun [5]. Earth in turn radiates heat back into space. Apart form the energy coming from the sun, the system earth also has considerable amounts of available energy present in the system that are gradually dissipated through geothermal activities and tidal dissipation. Note that the tides dissipate the available energy present in the system formed by the rotating earth, moon and sun. Tidal dissipation leads to a slowing of the earth's rotational speed and the receding of the moon. Very little mass is exchanged with space and thus earth can be considered a closed system with respect to mass. The global dissipative system can be subdivided in a wide variety of dissipative systems (living or lifeless such as turbulence in water or air). All these dissipative systems are open systems exchanging matter and energy with their environment. The primary source of exergy for ecosystems and the living organisms in it comes from solar irradiation. Solar irradiation is utilized through the photosynthesis process in plants, bacteria and algae. In this process water (H_2O) and carbon dioxide (CO_2) react to form carbohydrates and oxygen. Other organisms, not capable of photosynthesis, get their exergy in the form of carbohydrates by eating other organisms. In the subsequent dissipation of the available energy in the carbohydrates, the materials are recycled into water and carbon dioxide. This recycling is necessary for the processes to sustain as earth is a closed system with respect to mass.

One of the first to realize the relevance of thermodynamic constraints on economic processes was Georgescu-Roegen [9], who argued that economic processes increase entropy on earth and that this increase is an irreversible degradation of the natural environment. He argues that due to this irreversible degradation of the environment, the resources we use from the environment will eventually become depleted and the economic system is therefore doomed to "run down". To explain this view we consider the economic process as a dissipative system, taking "low entropy" as input and producing "high entropy" waste. With low entropy input we do not only mean exergy or negative entropy, we also mean that the resources we use are usually highly concentrated (low in entropy) as it costs much more energy to utilize a highly dispersed (high in entropy) resource. The economic process generally produces heat and dispersed materials (high entropy waste). A commonly used example to illustrate the highly dispersed nature of some of our waste products is the rubber that is dispersed on roads as it is scraped of car tires.

Our economic systems are closely linked to the ecosystems on earth as the ecosystems provide resources and recycle waste in ecocycles. Before the industrial revolution, economic systems drew almost all their resources, food, materials and energy sources, directly from local ecosystems. Therefore, the productivity of ecosystems (photosynthesis) posed effective (and rather narrow) boundaries to economic development [10]. Generally, the physical and biological impact of economic systems on ecosystems was small[†]. The industrial revolution, however, added large quantities of useful energy from fossil sources to the economic systems. This led to much higher levels of productivity, pushing the limits of producing food, materials and final products far beyond previous (natural) levels. This in turn causes serious disruptions of natural cycles such as pollution, deforestation, loss of biodiversity, climate change, etc. [12] as the ecosystems cannot recycle the large amounts of waste fast enough nor regenerate the resources (e.g., fossil fuels and metals) at the rate they are used.

It can be seen that failure to recycle the materials we use leads to an increase in entropy, hence an entropy increase is an aggregated measure of pollution. Georgescu-Roegen [13] claimed that the degradation of the natural environment by the economic

[†]Nevertheless, as has been documented by several authors (see for instance Jared Diamond [11]), there are examples of economic systems that suffered significantly from over exploiting their natural resource base (eventually significantly contributing to their downfall). For example the society on Easter Island collapsed entirely due to environmental damage caused by mismanagement of natural resources [11].

process is irreversible[‡]. This degradation, however, does not need to be irreversible if a continuous, exogenous flux of exergy is available (e.g., from the sun), which can be used to regenerate the used resources in a "steady-state recycling system" [14]. It is, however, in practice very difficult to reverse the degradation of the environment we cause. Daly [15] argues that, the degradation is *economically* irreversible as the extensive recycling would cost ruinous amounts of available energy and time. This assessment, however, seems to be technology related as the amount of time, and whether a certain amount of energy is "ruinous", are factors that are at least partially determined by technology. However, in the case of exergy sources, recycling costs, according to the second law of thermodynamics, more energy than the amount of energy that was released. Recycling of an exergy source is only needed when materials were "dissipated" during the process (i.e., we do not need to recycle solar irradiation as earth is an open system with respect to this irradiation). In order to be sustainable an exergy source should therefore provide more energy than needed to recycle all the materials that were dissipated in the process. With respect to the sustainability of the economic process as a whole we can conclude that in order to be sustainable, complete recycling of the used materials is required. Furthermore, complete recycling can only be accomplished when the required energy for recycling is provided by sustainable exergy sources.

Currently (predicted for 2008) the total annual amount of available energy we dissipate in our economic processes is about $5.19 \cdot 10^{20}$ J/annum of which $4.47 \cdot 10^{20}$ J/annum comes from fossil fuels, $3.11 \cdot 10^{19}$ J/annum from nuclear fuel (uranium isotope U235), and the use of renewable sources is $4.10 \cdot 10^{19}$ J/annum [16][§]. The bulk (86 %) of our exergy needs are met with fossil fuels. Even though the products of using fossil fuels, CO₂ and H₂O, can in principle be recycled by earth's ecosystems, fossil fuels are not sustainable. The matter of these fossil fuels, and the available energy stored therein, have not been present in the ecosystems for several million years and are now re-introduced at a high rate. The current production of carbon dioxide and water is not compensated by photosynthesis in the ecosystems (i.e., we take the

[‡]Georgescu-Roegen put forward a fourth law of thermodynamics [13] from which the irreversible nature of the degradation follows. His fourth law of thermodynamics states that similarly to available energy, matter also degrades from an available state (concentrated) to an unavailable state (dispersed) and that recycling the dispersed matter will always leads to more dispersion of materials. This fourth law is generally considered to be flawed [14].

[§]In reference [16] there is an error in the data for the global electricity generation (Figure 6), obfuscated by the multitude of units and scales in the document. The reported total annual amount of generated electricity, originally given in Trillion kWh, is larger than the global consumption of energy, originally given in Quadrillion British Thermal Units (Btu). However, reference [16] refers to reference [17] as the source of the electricity generation data, which reports values three orders in magnitude lower, this time measured in Billion kWh. It seems the Billion in reference [17] was erroneously replaced with Trillion in reference [16]. Note that in both references the short scale is used for the numeric names (Billion= 10^9 , Trillion= 10^{12} , and Quadrillion= 10^{15}).

fuels out of the ground at a much higher rate than the ecosystems are putting fuels back). As a result the composition of the earth's atmosphere changes as the amount of CO_2 increases and the amount of O_2 decreases. The changes in the composition of the atmosphere have serious implications through the well known "greenhouse effect" (see the frame for a short explanation of the greenhouse effect). An advantage of the use of nuclear fuels is that it does not involve emissions of CO_2 . However, the use of nuclear fuels is unsustainable as recycling of the fuels (if technically possible) would require more energy than provided by the process. Furthermore, there are several risks involved with the use of nuclear fuels. The use of nuclear fuels requires storage and transportation of particularly hazardous materials, leading to a potential for, possibly severe, radioactive contamination due to accidents or sabotage. The process itself also entails risks, as illustrated by the accidents at Three Mile Island (in 1979) and Chernobyl (in 1986). Eventhough the probability of a repetition of such accidents is strongly reduced due to considerable changes in the way nuclear reactors are designed and operated after these accidents, nuclear safety requires continuous vigilance [18]. Finally we arrive at the renewable sources. The renewable sources are a collection of many different methods to harvest exergy, such as hydro energy, geothermal energy, biofuel, wind energy, solar heat and solar electricity. Note that apart from geothermal and tidal energy all renewable sources are a direct or indirect form of solar energy. This can be no surprise as the main exergy source for the entire global dissipative system is sunlight and consequently solar energy is the most viable source for the long term exergy supply. In this work we will focus on solar cells, which use photovoltaic conversion to convert light directly into electricity.

1.2 Scope and outline of this thesis

At present most commercially available solar cells are made of crystalline silicon (c-Si). With this type of solar cell efficiencies up to 24.7 % have been obtained for unconcentrated light [20]. However, the disadvantage of crystalline silicon solar cells are the high material cost and energy consumption during production. Crystalline silicon is usually produced in the form of an ingot which is subsequently mechanically sawn into slices with a typical thickness of 0.3 mm. A cheaper alternative can be found in thin-film silicon solar cells. Thin-film silicon solar cells are usually deposited from a gas phase on a substrate such as glass. The thin-film silicon used in this type of solar cells is in a different phase than *c*-Si and usually alloyed with hydrogen. The most common thin-film silicon phases are hydrogenated amorphous silicon (*a*-Si:H) and hydrogenated micro-crystalline silicon (μc -Si:H). Thin-film silicon solar cells can be made very thin, typically thin film solar cells are 300 – 2000-nm thick, resulting in less material consumption. Furthermore, the production of thin-film silic

Aside: The greenhouse effect

The greenhouse effect can be understood through a simple radiative model. The temperature on earth will be constant when the energy current earth absorbs is equal to the energy current earth emits in the form of thermal radiation. Due to the high temperature of the sun the solar spectrum has the highest spectral power density around a wavelength of 500 nm (light with a turquoise color). The lower temperature of earth leads to a maximum in spectral power density around 10 μ m (infrared) of earth radiation. Carbon dioxide and other "greenhouse gasses", such as water-vapor and methane, are good absorbers for infrared light. As a result most solar irradiation has no problem reaching the surface, however, the radiation of the surface is partly absorbed in the atmosphere by greenhouse gasses. The atmosphere in turn emits thermal radiation in all directions, toward earth and toward space. As not all radiation that is emitted by the atmosphere is radiated to space, an increase in absorption of earth radiation in the atmosphere will lead to a relative decrease in radiation toward space and, therefore, leads to the warming of earth until the balance between incoming and outgoing radiation is restored. This way an increase in the concentration of greenhouse gasses in the atmosphere can lead to a global warming effect. However, in reality the climate is, apart from the effects in this simple radiative model, also determined by the atmospheric circulation and by its interactions with the large-scale ocean currents and land [19]. As a result of these complicating factors, projections on the climate change are uncertain.

con solar cells consumes less energy than crystalline silicon solar cell technologies.

Thin-film solar cells are usually deposited at low temperatures (typically 150 - 300 °C), which allows for the use of low cost substrates like glass and even some plastics. Furthermore, as the solar cells are very thin, flexible solar cells can be made by depositing the solar cell on a flexible substrate, such as a metal film or plastic foil. The deposition techniques allow for large area deposition of solar cells (solar cell production lines using glass panels up to 5.7 m^2 are being sold by Applied Materials, Inc.). A drawback to the thin-film silicon technologies are the relatively low efficiency and the light induced degradation of *a*-Si:H (μc -Si:H is generally stable). The light induced degradation leads to an initial efficiency decrease of *a*-Si:H solar cells, after which the efficiency stabilizes. For thin-film silicon solar cells, stabilized cell efficiencies up to 13 % [21] have been reported and for modules record stable efficiencies of 10.4 % have been reported [22]. However, present day commercially available modules have stabilized efficiencies in the range of 4.5 - 8.5 % [23]. Thin-film silicon modules are a good candidate for those photovoltaic applications where low cost is more important than high efficiency. In particular building integration,

where a sufficient surface area is available without extra cost.

The title of this work is "Characterization of thin-film silicon materials and solar cells through numerical modeling". In this case modeling refers to the development and application of detailed mathematical models to describe the physics relevant to the operation of a semiconductor device. In the case of solar cells these models should describe both the optical and the electronic processes in the device. There are several reasons to work on device modeling. An important reason is to enhance our understanding of the operation of the device. Generally, device models can simulate measurable external quantities, such as electric currents and voltages. In order to simulate the external quantities most models use a detailed description of internal quantities that are generally not directly measurable (e.g. carrier densities, recombination rates, etc.). This way modeling can give insight in the internal functioning of a device. However, one can also find the device models failing to accurately reproduce observed behavior of a device. In this case the failure to describe the device accurately indicates that the model needs refinement (or even replacement). The refinement of the models potentially leads to a better understanding of the relevant physical processes for device operation. Apart from modeling leading to a better understanding of the physics in a device, modeling may also be useful in the design and optimization of a device. For the latter it is necessary, however, that the model is *predictive*.

In practice, the predictive power of models describing disordered semiconductors, such as a-Si:H and μc -Si:H, is limited. One limitation is that the material properties of disordered materials may vary over a broad, continuous range. These variations in material properties do not only occur from sample to sample, also samples are generally found to be inhomogeneous. Due to these variations the exact properties of a device are often not known. A second limitation arised from the complex electronic characteristics of the materials, requiring complex physical models and hampering the interpretation of measurements. Note that the interpretation of measurements of material characteristics relies on the same models that are used to describe the material and the devices. Ideally, measurement techniques for the characterization of materials are sensitive only to the measured quantity itself and not to other material properties, unless those properties are well known. If this is not the case the measurements become sensitive to errors in the assumed or measured value of other material properties. In such cases the detailed and consistent modeling of several different experiments on a device or devices may help to obtain a more accurate estimate of the model parameter values in question.

In this work we use a "device simulator" to solve numerically a set of mathematical models describing the electronic and optical properties of a semiconductor device. The device simulator we used in this work is Advanced Semiconductor Analysis (*ASA*). The *ASA* program is designed for modeling of (thin-film) solar cells, i.e., the program is specifically designed to model both electrical and optical properties of multi-layered heterojunction device structures. Furthermore, *ASA* is equipped with several models which are specific for disordered semiconductors in general and *a*-Si:H in particular.

We have used ASA for the characterization of a-Si:H and μ c-Si:H materials by self consistently modeling various experiments. In several instances we have added models to ASA in order to accommodate the simulation of certain experiments or certain materials for which the appropriate models were lacking in ASA. Chapter 2 gives an overview of the properties of a-Si:H and its implications for the design of thin-film silicon solar cells. The chapter discusses the deposition and structure of a-Si:H and the related electronic and optical properties of a-Si:H, such as the band structure, the metastable behavior of a-Si:H upon illumination and the optical absorption coefficient. Furthermore, the chapter introduces basic characterization techniques for both material and solar cells and the the general structures used in thin-film silicon solar cells. Chapter 3 gives an overview of the models used for the simulation of thinfilm silicon devices. It describes electronic transport in thin-film silicon materials. models for the density of states and the calculation of space-charge and recombination. In Chapter 4 we present Charge Deep-Level Transient Spectroscopy (Q-DLTS) as a measurement technique to determine the density of states distribution in a-Si:H. We developed and implemented a model for Q-DLTS in ASA. Using simulated and measured Q-DLTS spectra we characterized the defect distribution in a-Si:H Metal-Insulator-Semiconductor structures. In Chapter 5 we discuss the modeling of μc -Si:H solar cells in detail. We first discuss the structure of μc -Si:H and its implications for the modeling of electronic transport in a-Si:H solar cells. Furthermore, based on our analysis of the relevant device models we developed a method to determine the mobility gap in μ c-Si:H. A calibrated parameter set for the 1-D simulation of μ c-Si:H solar cells is presented. Finally Chapter 6 summarizes the main conclusions of this work.

Chapter 2

Properties of *a***-Si:H and thin-film silicon solar cells**

2.1 Introduction

This chapter gives an introduction in modeling and characterization of a-Si:H and thin-film silicon solar cells. We will start with an introduction in material properties of a-Si:H in Section 2.2. This Section deals with structural and optical properties of a-Si:H, and the growth of a-Si:H and related materials. In Section 2.3 we discuss the structure and design of a-Si:H based solar cells. We briefly introduce basic characterization techniques for a-Si:H and for solar cells in Section 2.4.

2.2 Material properties of *a*-Si:H

2.2.1 Band structure of *a*-Si:H

Amorphous materials are materials where the lattice has some degree of disorder. Contrary to its crystalline counterpart, which exhibits a strict periodic repetition of a unit cell, variations in bond lengths and angles in amorphous materials lead to a lack in long range order. However, in many amorphous materials the variations in bond lengths and angles are small and therefore the local arrangement of atoms in the lattice resembles the local arrangement of atoms in the crystalline phase. The lack of long range order will inevitably lead to a situation where the bonding requirements are not met for all atoms, leading to "dangling bonds". To illustrate the difference in structural properties crystalline semiconductors and their amorphous counterparts,



Figure 2.1: Schematic drawing of the lattice of: (a) crystalline silicon; (b) hydrogenated amorphous silicon.

Figure 2.1.a and Figure 2.1.b shows a schematic drawing of the atomic structure of c-Si and a-Si:H respectively.

It was long believed that amorphous materials could not behave as semiconductors as the band theory of conduction was strongly identified with the interaction of an electronic waveform with a strict periodic lattice. In the mid-1950s, however, semiconducting behavior was discovered in various chalcogenide glasses [24]. This means that the local order in amorphous semiconductors is sufficiently high to give rise to bands of electronic states. However, the lack of long range order and the resulting random variations in potential influence the behavior of electrons in the valence and conduction band. The random potential fluctuations give rise to so called "Anderson localization" [25]. For materials with moderate disorder Anderson localization leads to localized wave-functions at both sides of a band. These localized band states at the extremities of an energy band are generally referred to as "band tails". In addition to the presence of band tails, defects, such as dangling bonds or lattice vacancies, give rise to additional localized electronic states. In general electronic states arising from a particular type of defect do not have identical energy levels in amorphous semiconductors. The random nature of amorphous semiconductors lead to a blurring of the energy levels of electronic states associated with a particular type of defect [24].

In a-Si:H the atomic hydrogen present in the material can passivate dangling



Figure 2.2: Schematic representation of the density of states in a-Si:H

bonds. This passivation with hydrogen greatly reduces the dangling bond concentration from $10^{25} - 10^{26}$ m⁻³ to $10^{21} - 10^{22}$ m⁻³ [26]. Figure 2.1.b also illustrates the passivation of dangling bonds with hydrogen in *a*-Si:H.

The schematic density of states in a-Si:H is shown in Figure 2.2. Indicated are the extended states in the valence and conduction band, the valence and conduction band tails and the states originating from dangling bonds. Due to the localized nature of band tail states and states from structural defects, the mobility of electrons and holes at these states is much lower as compared to the non-localized states in the valence and conduction band, where the carriers are considered free. The energy separation of localized and non-localized states is rather sharp [24, 27] and, consequently, this dividing energy has been termed "mobility edge". The energy difference between the valence-band mobility-edge and conduction-band mobility-edge is the so called "mobility gap". As the energy separation of localized and non-localized states is sharp, electronic transport in a-Si:H is dominated by the carriers in the states just below the valence-band mobility-edge and just above the conduction-band mobilityedge, hence for electronic transport, the mobility gap is the amorphous equivalent of the bandgap. In Figure 2.2 the mobility edges of the valence and conduction band are indicated by E_v and E_c respectively. A typical value of the mobility gap in *a*-Si:H is 1.75 eV [26].

It was long assumed that *a*-Si:H could not be doped and that the doping atoms would be incorporated with their optimal valency. In 1969 Chittick *et al.* [28] reported a doping effect in *a*-Si:H. However, the change in conductivity reported by Chittick *et al.* was small. Six years later, in 1976, Spear and LeComber reported about significant changes in conductivity of *a*-Si:H upon doping with boron and phosphorus,

albeit with a low doping efficiency [29]. Shortly after Spear and LeComber demonstrated that doped *a*-Si:H could be obtained, Carlson and Wronski [30] reported the first *a*-Si:H solar cell. The doping efficiency in *a*-Si:H is low and declines with increasing doping levels [31,32]. In heavily doped *a*-Si:H only about 1 % of the dopant atoms occupy a fourfold-coordinated location [31]. Furthermore, the presence of a large number of localized band states makes it difficult to move the Fermi-level close to the mobility edges.

2.2.2 Metastability in *a*-Si:H: The Staebler-Wronski effect

Shortly after the first reports on *a*-Si:H solar cells, Staebler and Wronski reported their findings on metastability in *a*-Si:H [33]. Under illumination the conductivity of *a*-Si:H degrades but can be restored by annealing at temperatures of about 425 K. This degradation effect is known as the Staebler-Wronski effect (SWE). The metastable behavior is ascribed to the light-induced creation of additional defects. It is generally accepted that these metastable defects are additional dangling bonds that act like recombination centers in the material and that these dangling bonds are created by the breaking of weak or strained Si–Si bonds. Hydrogen plays an important role in the metastable behavior of *a*-Si:H, however, there is no consensus on the exact mechanisms involved and the role of hydrogen in the SWE [34–37]. The creation of additional recombination centers affects *a*-Si:H based solar cells to such a degree that the SWE is a severe limitation for the application of *a*-Si:H in single junction solar cells.

2.2.3 Optical absorption and the optical bandgap in *a*-Si:H

When comparing the band structure of different semiconductors, one can distinguish between semiconductors with a direct bandgap and an indirect bandgap. For materials with a direct bandgap, the maximum of the valence band and the minimum of the conduction band have approximately the same wave-vector, \vec{k} . A semiconductor in which the minimum of the conduction band occurs at a different \vec{k} value than the maximum of the valence band, is called an indirect bandgap semiconductor. Crystalline silicon has an indirect bandgap. In general, semiconductors with a direct bandgap are better light absorbers than indirect bandgap semiconductors. Because photons have a relatively small momentum, indirect optical transitions require the absorption of an additional phonon to conserve momentum, reducing the probability of indirect transitions. Due to the lack of long range order in *a*-Si:H the crystal momentum is not a proper quantum number [38] and as a result *a*-Si:H acts like a quasi-direct semiconductor.

In Figure 2.3 the optical absorption of a-Si:H and c-Si are shown. Often the absorption spectrum is used to determine the "optical bandgap" of amorphous semiconductors. As most filled electron states available for optical absorption are in the valence band and most empty electron states are located in the conduction band, the optical bandgap is a measure of the distance between the extended states in the valence and conduction band. Several definitions exist for the optical bandgap. In crystalline semiconductors the optical absorption coefficient is nearly zero for photons with an energy below the bandgap. For photons with an energy larger than the bandgap the absorption follows a square-root dependency on energy due to the parabolic shape of the valence- and conduction-band. In amorphous semiconductors the absorption coefficient for photon energies below the bandgap is non zero due to dangling-bond states and band-tail states. If we assume the bands in a-Si:H to be parabolic, we would expect a square-root dependency of the absorption coefficient, α , for photon energies above the bandgap. We can therefore define an optical bandgap by assuming parabolic bands and fitting the following expression to the absorption data [39]:

$$\sqrt{E_{ph}}\alpha(E_{ph})n(E_{ph}) \propto (E_{ph} - E_{tauc}),$$
 (2.1)

where E_{ph} is the photon energy, $n(E_{ph})$ is the refractive index, and E_{tauc} is the "Taucgap", the bandgap determined for the optical absorption data under the assumption of parabolic bands. In Figure 2.3 a fit of the expression in Eq. (2.1) to the absorption coefficient of *a*-Si:H is illustrated.

As mentioned several other definitions for the optical bandgap exist, such as the "iso-absorption bandgap", E_{04} , which is defined as the photon-energy for which the absorption coefficient equals 10^4 cm⁻¹. According to Klazes *et al.* [40] the absorption spectra of *a*-Si:H fit better when in Eq. (2.1) a cubic-root is used instead of the square root. However, the Tauc gap corresponds well to the mobility gap in *a*-Si:H [26], and, furthermore, corresponds best to the separation of the beginning of the exponential tails of the valence and conduction band [38] (note, however, that there is no principle reason why the mobility gap should be equal to the separation of the beginning of the Tauc-gap are in the range of 1.75 - 1.85 eV for *a*-Si:H, for the Klazes-gap is typically in the range of 1.55 - 1.65 eV, and the iso-absorption bandgap is in the range of 1.80 - 1.90 eV.

As mentioned the absorption coefficient of amorphous semiconductors for photon energies below the optical bandgap is non zero due to dangling-bond states and band-tail states. As in *a*-Si:H the tail state distributions decay exponentially into the bandgap, the tail-states give rise to an exponential relation between photon energy and absorption coefficient due to optical transitions between extended states and the band-tails. The exponential part of the absorption spectrum is called the "Urbach



Figure 2.3: Absorption spectra of a-Si:H and c-Si

edge" and for a-Si:H can be found in the in the energy range of 1.4 eV and 1.7 eV. As the valence band-tail is broader than the conduction band tail in a-Si:H, the slope of the Urbach edge, the Urbach energy, is usually identified with the characteristic energy of the valence band tail. Absorption below 1.4 eV is mostly due to mid-gap states.

2.2.4 Plasma enhanced chemical vapor deposition of *a*-Si:H and *a*-Si:H alloys

Ratio-Frequency Plasma Enhanced Chemical Vapor Deposition (rf-PECVD) is a common technique to deposit *a*-Si:H and related materials. In this technique a plasma is used to decompose a source gas. The radicals thus created in the plasma can give rise to the growth of a film on a substrate. In case of *a*-Si:H deposition, the source gas is usually silane (SiH₄). In order to dope or alloy the material other gasses can be added to the source gas. To grow doped *a*-Si:H layers usually phosphine (PH₃) is added to obtain n-type material, or diborane (B₂H₆) is added to obtain p-type material.

Properties of PECVD grown *a*-Si:H like sub-bandgap density of states, band mobilities, hydrogen content, optical bandgap and growth rate, depend strongly on the deposition conditions like the temperature, gas pressure, plasma power density and dilution of the process gasses by hydrogen.

It has been found that diluting the process gasses during deposition can lead to more stable *a*-Si:H based materials with respect to the SWE [41,42]. The enhanced stability of these materials has been attributed to a "medium range order" in the material [43], as opposed to the long range order of crystals and the short range order of regular *a*-Si:H films. The supposed medium range order has lead to the name "protocrystalline silicon" (*pc*-Si:H). At a certain threshold of hydrogen dilution, a transition from amorphous to micro-crystalline growth takes place. Micro-crystalline silicon

(μ c-Si:H) contains two solid phases, volumes of crystalline material embedded in an amorphous network. The structure and composition of μ c-Si:H is discussed in more detail in Section 5.2.

It is also possible to make *a*-Si:H alloys by adding other gasses to the source gas. Alloying amorphous silicon is an effective way to adjust the optical bandgap. Two commonly used *a*-Si:H alloys in solar cells are:

- **Hydrogenated amorphous silicon-germanium** (*a*-SiGe:H) *a*-SiGe:H is often applied because it has an optical gap in the range of 1.35 eV to 1.80 eV, depending on germanium content. The reduced optical bandgap leads to an enhanced absorption of the red and near infrared part of the spectrum and thus can be used to obtain a higher red response of *a*-Si:H based solar cells. To deposit *a*-SiGe:H usually germane (GeH₄) is added to the source gas.
- **Hydrogenated amorphous silicon-carbide** (*a*-SiC:H) Alloying *a*-Si:H with carbon leads to an increase of the optical gap to 1.75 2.2 eV. To deposit *a*-SiC:H usually methane (CH₄) is added to the source gas. The main application of *a*-SiC:H in *a*-Si:H based solar cells is as a p-type window layer.

2.3 *a*-Si:H based solar cells

2.3.1 The solar spectrum

Before we discuss the structure and design of a-Si:H solar cells it is important to discuss the solar spectrum. The most widely used standardized spectrum is the Air Mass 1.5 Global (AM1.5G) spectrum. The AM1.5G spectrum is shown in Figure 2.4. Air mass is a measure of the optical path length through Earth's atmosphere of light from a celestial body. Usually air mass is given relative to the zenith (i.e. relative to the situation where the earth's surface normal points toward the light source). The AM1.5G spectrum corresponds to an optical path length through the earth's atmosphere of 1.5 times the optical path length at the zenith. The AM1.5G spectrum represents the solar spectral irradiance with an air mass of 1.5 (both direct and diffuse components) on a 37° tilted surface facing the sun under an idealized standard atmosphere [44]. The atmospheric conditions used to define the standard can be found in reference [45]. Despite the term "Global" in the name of the spectrum, the AM1.5G spectrum is de facto an American standard developed for the continental United States of America (not including Alaska). The atmospheric conditions represent an average of reasonably cloudless conditions in the 48 contiguous United States over the period of a year and the slope of the sun-facing surface was chosen to represent the average latitude of



Figure 2.4: Spectral irradiance of the AM 1.5G spectrum [44].

the continental United States of America [44]. The AM1.5G spectrum is normalized to give a power-density of 1000 Wm^{-2} .

2.3.2 Structure of *a*-Si:H solar cells

In crystalline silicon solar cells typically consist of a p-type wafer with a thin n-type layer. The electron-hole pairs are separated in the depletion region between the p and n regions. The optically generated minority carriers diffuse from the quasi-neutral doped regions to the pn-junction. In a-Si:H the diffusion length is much lower than in crystalline silicon. The diffusion length in intrinsic a-Si:H is typically in the order of 100 nm, for doped a-Si:H material the diffusion length is even lower. Therefore, instead of a pn-junctions, a-Si:H solar cells usually consist of *pin* junctions. In a *pin* junction an intrinsic layer is sandwiched between a p-doped layer and a n-doped layer. This way the depletion region is made thicker and, due to the relatively low defect density in intrinsic *a*-Si:H, the charge carriers in the depletion region have relatively long lifetimes. The intrinsic layer in single junction a-Si:H solar cells is in the order of several hundreds of nanometers thick. Because of the poor electronic properties of doped a-Si:H, most of the optically generated electron-hole pairs in the doped layers do not contribute to the photo-current. Therefore, the doped layers are kept thin (in the order to 10-30 nm thick). The total thickness of the *pin* junction can be kept low as a-Si:H is a good absorber of light.

A single junction *a*-Si:H *pin* solar cell is schematically shown in Figure 2.5.a. A typical *a*-Si:H solar cell is deposited on a glass substrate coated with a transparent conductive oxide (TCO). The TCO forms the top electrode and the back contact is made of aluminium or silver. As TCO material SnO_x : F and ZnO:Al are commonly



Figure 2.5: Schematic drawing of: (a) an *a*-Si:H *pin* solar cell, and (b) an *a*-Si:H based tandem solar cell. For each layer a typical thickness is indicated.

used. The TCO layer is often textured to scatter the entering light and thus increase the average optical path length through the solar cell. The average optical path length through the solar cell is further increased by using a highly reflective back contact.

The mobility of holes is lower than the mobility of electrons. It is therefore beneficial when the distance over which holes have to be transported is minimized. To minimize this distance the p-layer, where the holes are collected, should be close to the location where most optically generated charge carriers are. As the optical generation rate is highest where the light enters the solar cell, the p-layer is usually the layer through which light enters the cell. The doped layer where the light enters the *pin* junction is often made from *a*-SiC:H, which has the advantage that the optical bandgap is higher, reducing the optical absorption in this doped layer.

As briefly mentioned before, light induced degradation of a-Si:H also affects the performance of a-Si:H solar cells. The light induced additional defects reduce the carrier lifetime in the solar cell and affect the space-charge distribution in the solar cell. As the defects act as trapping centers, more charge is trapped in the intrinsic layer near the doped layers, causing more pronounced band bending in this region and a reduction of the electric field in a large portion of the intrinsic layer. Both the reduction of carrier lifetime and the reduction of the electric field degrade the performance of the solar cell.

There are two ways to enhance the stability of the solar cells with respect to SWE. One way is to search for a more stable material, the other way is to reduce the

thickness of the intrinsic layer. When the thickness of the intrinsic layer is reduced, the electric field in the intrinsic layer is increased, making the solar cell less sensitive to the light induced changes in the space-charge distribution. However, when the intrinsic layer is too thin, the efficiency of the solar cell is limited by the amount of absorbed light. One way to overcome this problem is to use multi-junction cells. In a multi-junction solar cell two or more *pin* junctions are stacked. The multi-junction solar cell concept is illustrated by Figure 2.5.b with a tandem (two junctions) solar cell. This has the advantage that the thickness of the component cells and thus the degradation can be reduced and at the same time the thickness of the total structure can be kept thick enough to absorb most of the light. Further advantages are that the open-circuit voltage is increased and the current is reduced, leading to less losses due to series resistance. However, as the two component cells are connected in series, the current through the device is usually limited by one component cell. Thus, to a first order approximation, the conversion efficiency is maximized when the thickness of each individual component cell is such that the photo-current for all component cells is the same. This matching of the thicknesses of the component cells is generally referred to as "current matching".

In addition to a reduced degradation, multi-junction concept also allows for a better utilization of the solar spectrum by using different bandgaps for the absorber layers of the component cells. There are two major limitations in the utilization of the solar spectrum for solar cells using a single bandgap for the absorber layer:

- 1. Most photons with energy less than the mobility gap are lost for power generation as few of these photons are absorbed.
- 2. Photons with an energy higher than the bandgap create electron and hole pairs with an energy in excess of the mobility gap. This energy in excess of the mobility gap is lost as the photo-generated charge carriers thermalize toward the mobility edges.

As a result a solar cell with a low-bandgap absorber layer generally generates a high short-circuit current and a low open circuit voltage, where a solar cell with a highbandgap absorber layer generally generates a low short circuit current and a high open circuit voltage. The first limitation determines the maximal short circuit current that can be generated in the cell under a given illumination spectrum and intensity and the second puts an upper limit to the open circuit voltage. Therefore a better utilization of the solar spectrum can be obtained by using multi-junction solar cells where the absorber layers of the component cells, each have a different bandgap. In order to make sure that the component cells with a low bandgap only receive light with low photon energies, the component cells should be arranged such that, from the top, each subsequent component cell has a lower bandgap than the previous component cell. This way the light enters through the component cell with the highest bandgap where only the photons with a photon energy higher than this bandgap are absorbed. The remaining photons are transmitted to the underlying component cells with lower bandgaps. A disadvantage of using more than one optical bandgap in a multi-junction solar cell is that current matching becomes sensitive to the illumination spectrum [46].

2.4 Basic material and solar cell characterization

2.4.1 Material characterization

Dark conductivity In general the conductivity (σ) of a semiconductor can be described by:

$$\sigma = q\left(\mu_n n + \mu_p p\right),\tag{2.2}$$

where *n* and *p* are the electron and hole concentration,. respectively, μ_n and μ_p are the electron and hole mobilities, respectively, and *q* is the electron charge. Furthermore, in equilibrium and using the Maxwell-Boltzmann approximation for the carrier concentrations as a function of the Fermi-level, the carrier concentrations can be written as:

$$n = N_c \exp\left(\frac{E_f - E_c}{kT}\right) \tag{2.3}$$

$$p = N_{\nu} \exp\left(\frac{E_{\nu} - E_f}{kT}\right), \qquad (2.4)$$

where N_{ν} and N_c are the effective density of states in the valence and conduction band, respectively, E_f is the Fermi-level, E_{ν} and E_c are the valence band and the conduction band mobility edges, respectively.

From Eqs. 2.3 and 2.4 it can be seen that the dark conductivity, σ_d in Eq. (2.2) is dominated by either electrons, when the Fermi-level is above mid-gap, or by holes, when the Fermi-level is below mid-gap. Thus, the dark conductivity provides information on the product of $\mu_n n$ or $\mu_p p$.

The activation energy of the dark conductivity, E_a , can be determined from:

$$\sigma_d = \sigma_0 \cdot \exp\left(\frac{-E_a}{kT}\right),\tag{2.5}$$

where, σ_0 is a temperature independent term, and *k* is Boltzmann's constant, and *T* is the temperature. Under the condition that the temperature dependency of the mobility is small compared to the temperature dependency of the

majority carrier density, the dark current activation energy equals the energy separation between the Fermi-level and the mobility edge corresponding to the majority carriers.

- **Reflection and transmission** Reflection-Transmission (RT) measurements are carried out to determine both the thickness of thin films as well as the wavelength dependent complex refractive index, $\tilde{n} = n \kappa i$, of which the real part, *n* is the refractive index and the imaginary part, κ is the extinction coefficient, which is related to the absorption coefficient, α as: $\kappa = \frac{\lambda}{4\pi} \alpha$. From the absorption spectrum the Tauc gap can be determined by fitting Eq. 2.1 to the measured absorption.
- Sub-bandgap absorption The sub-bandgap absorption is often measured as it provides much information about the density of states in the mobility gap of *a*-Si:H. As mentioned in Section 2.2 the sub bandgap absorption can be related to band tails and defect states. From the sub bandgap absorption we can determine the Urbach energy, which is generally identified with the characteristic energy of the valence band tail in *a*-Si:H. The RT measurement is not sensitive enough to measure the sub bandgap absorption of *a*-Si:H and related materials accurately. A common technique for measuring sub-bandgap absorption is the dual beam photo-conductivity (DBP). With this technique the conductivity is measured with a bias light beam and a superimposed monochromatic modulated light beam. The change in conductivity due to the modulated monochromatic light beam is a measure of the absorption at that wavelength.

2.4.2 Solar cell characterization

- **Illuminated J-V characteristics.** There is an obvious interest in determining the conversion efficiency of solar cells and thus the illuminated J-V characteristics is probably the most common measurement technique in the field of photovoltaics. Usually the measurement is carried out under illumination with the AM1.5G spectrum (see Section 2.3.1). Figure 2.6 shows a typical J-V measurement under illumination. In the figure the open circuit voltage (V_{oc}), the short circuit current density (J_{sc}), the voltage at the maximum power point (V_{mpp}), and the current density at the maximum power point (J_{mpp}) are indicated. The maximum power (P_{max}) is indicated by the gray area. The fill factor (*FF*) of the solar cell is defined by the ratio $P_{max}/(V_{oc} \cdot J_{sc})$.
- **Dark J-V characteristics.** The dark current characteristics of a solar cell can provide qualitative information about the device. Figure 2.7 shows typical J-V



Figure 2.6: Typical J-V characteristics of an *a*-Si:H cell under illumination. Indicated are the open circuit voltage (V_{oc}), the short circuit current density (J_{sc}), the maximum power (P_{max}), the voltage at the maximum power point (V_{mpp}), and the current density at the maximum power point (J_{mpp}).

characteristics of a *a*-Si:H *pin* device. Three regimes can be distinguished, namely:

- Between 0.4 V and 0.7 V the forward bias through a typical *a*-Si:H *pin* device can be approximated with the expression $J(V) = J_0 \exp(qV/nkT)$, where J_0 is the reverse bias saturation current density and *n* is the diode ideality factor (sometimes referred to as quality factor). Typically diode ideality factors of *a*-Si:H *pin* devices range from 1.4 to 2.
- The deviation from the exponential J-V characteristics for bias voltages below 0.4 V is often referred to as "shunting". This shunting is usually caused by current spreading [26]. Current spreading is the effect that at low bias voltages the current is collected from the periphery of the contact as at these low bias voltages the collected current is very small. As a result the lateral currents through the n-layer do not cause a significant potential drop. Thus the effective contact area increases for low bias voltages. The effect of current spreading is illustrated by Figure 2.8.
- In the region above 0.8 V deviations from the exponential J-V characteristics are observed that are ascribed to Space Charge Limited Current (SCLC) and series resistance.
- **External Quantum Efficiency.** The spectral sensitivity of a solar cell is usually measured by the External Quantum Efficiency (EQE). Usually the EQE is measured by illuminating the solar cell with probe light that consists of a chopped



Figure 2.7: Typical dark J-V characteristics of an *a*-Si:H cell.



Figure 2.8: Illustration of the contribution of the periphery of the contact to the dark current at low current levels.



Figure 2.9: Typical external quantum efficiency spectrum for an *a*-Si:H solar cell. The measurement was carried out with a 0 V bias voltage and no bias illumination.

monochromatic light source of wavelength, λ , and measuring the photo-current through the solar cell with a lock-in amplifier. The external quantum efficiency, η_{eqe} , is then determined as:

$$\eta_{eqe}(\lambda) = \frac{J_{ph}}{q\phi_{ph}} \tag{2.6}$$

where J_{ph} is the photo-current due to the probe light, ϕ_{ph} is the photon flux of the probe light incident on the solar cell. The external quantum efficiency is thus the ratio between the number of incident photons and the number of collected electron-hole pairs for one particular wavelength. As the photo-current is strongly influenced by the applied bias voltage, the bias voltage must be fixed. In addition to a bias voltage, bias illumination can be applied (in this case usually an approximation of the AM1.5G spectrum is used). The number of photons per second of the probe light incident on the solar cell is generally determined by measuring the EQE of a calibrated diode in the same system. A typical measurement of the EQE is shown in Figure 2.9.

When a 0 V bias voltage is applied, the integral of the product of the AM1.5G photon flux spectrum and the EQE gives the short circuit current. When a reverse bias voltage is applied one can, in most cases, assure that nearly all photo-generated charge carriers in the intrinsic layer are collected, thus this measurement can be used to asses the effectiveness of the optical design of the cell, i.e., light trapping and light absorption in inactive layers (like the TCO layer, doped layers and back reflector). At higher bias voltages the collection efficiency of the cell will be reduced due to recombination losses. As the penetration depth of photons is strongly wavelength dependent, the spectral re-

sponse contains information about the spatial properties of the solar cell, e.g. in a *pin* device the blue response is strongly influenced by the reflection losses, absorption in the front TCO layer and p-layer and the quality of the p-i interface region. However, it is often difficult to distinguish between the various loss mechanisms.

Chapter 3

Modeling of *a*-Si:H devices: *ASA*

There's all different types of models, and there are also plus models as well. But the majority is skinny.

- Heidi Klum

In this chapter we will give a short introduction in modeling of *a*-Si:H devices. Section 3.1 introduces the models we use for steady-state simulations of the electrical characteristics of *a*-Si:H devices. In Section 3.2 we will briefly discuss optical models for the simulation of the optical properties of *a*-Si:H solar cells.

3.1 Electrical modeling of *a*-Si:H devices

Semiconductor equations

The semiconductor equations consist of the Poisson equation (Eq. (3.1)) and the continuity equations for electrons and holes (Eq. (3.2) and Eq. (3.3), respectively):

$$\nabla \cdot (\varepsilon \nabla \Psi_{vac}) = -\rho \tag{3.1}$$

$$\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot \vec{J}_n + G - R \tag{3.2}$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot \vec{J}_p + G - R, \qquad (3.3)$$

where Ψ_{vac} is the potential related to the local vacuum level, ρ is the space charge density, *n* and *p* refer to electron and hole concentrations in the extended conduction and valence band, respectively, $\vec{J_n}$ and $\vec{J_p}$ are, respectively, the electron and hole current density, *t* is time, *G* is the generation rate, and *R* is the recombination rate.

The electron and hole current densities are described by:

$$\vec{J}_n = \mu_n n \nabla E_{fn} \tag{3.4}$$

$$\vec{J}_p = \mu_p p \nabla E_{fp}, \qquad (3.5)$$

where E_{fn} and E_{fp} are the quasi-Fermi levels for electrons and holes, respectively.

Using the Maxwell-Boltzmann approximation for the carrier concentrations as a function of the quasi-Fermi levels and the effective density of states in the valence (N_v) and conduction (N_c) band we can write:

$$n = N_c \exp\left(\frac{E_{fn} - E_c}{kT}\right) = N_c \exp\left(\frac{E_{fn} - (E_{vac} - q\chi)}{kT}\right)$$
(3.6)

$$p = N_{\nu} \exp\left(\frac{E_{\nu} - E_{fp}}{kT}\right) = N_{\nu} \exp\left(\frac{(E_{\nu ac} - q\chi - E_{\mu}) - E_{fp}}{kT}\right), \quad (3.7)$$

where E_{vac} is the vacuum potential, χ is the electron affinity, and E_{μ} is the mobility gap.

In equilibrium the product of *n* and *p* is equal to:

$$n_i^2 = N_c N_v \exp\left(\frac{E_v - E_c}{kT}\right) = N_c N_v \exp\left(-\frac{E_\mu}{kT}\right),$$
(3.8)

where n_i is the intrinsic carrier concentration.

In *a*-Si:H the tail states and dangling bond states act as charge trapping and recombination centers and greatly influence the electrical properties of the material. We will first discuss the description of the density of tail and dangling bond states in *a*-Si:H followed by a discussion on recombination and charge trapping on these states.

Tail states

In Section 2.2 we already mentioned the existence of localized band tail states in disordered semiconductors. The localized tail states are single electron states, meaning they can be occupied by either 0 or 1 electrons. Tail states belonging to the conduction band exhibit acceptor-like behavior, meaning the states are neutral when unoccupied and negatively charged when occupied by an electron. Tail states belonging to the valence band, on the other hand, exhibit donor-like behavior and are positively charged when unoccupied and neutral when occupied by an electron. The tail state densities of the conduction and valence band decay exponentially into the gap [47]. The density of tail states can be described by the following equations:

$$N_{cbt} = N_{c0} \exp\left(\frac{E - E_c}{E_{c0}}\right)$$
(3.9)

$$N_{vbt} = N_{v0} \exp\left(\frac{E_v - E}{E_{v0}}\right),$$
 (3.10)

where $N_{\nu 0}$ and N_{c0} are the density of tail states at the mobility edges of the valence and conduction band, respectively, and $E_{\nu 0}$ and E_{c0} are the characteristic energies of the valence and conduction band tails, respectively. In *a*-Si:H the valence band tail is much broader than the conduction band tail. Typical values of the characteristic energies of the tail states in device quality *a*-Si:H are 45 meV for the valence band tail and 30 meV for the conduction band tail.

Dangling bond states

Defect states arising from dangling bonds are *amphoteric* in nature, meaning the dangling bond is in one of three charged states, namely, positively charged when the state is unoccupied by electrons, neutral when the dangling bond is occupied by one electron and negatively charged when the dangling bond is occupied by two electrons. A dangling bond therefore has two energy levels: the $E^{+/0}$ level related to the transition between the positively and neutrally charged states of the dangling bond, and the $E^{0/-}$ level related to the transition between the neutrally and negatively charged states of the dangling bond. The energy difference between the $E^{+/0}$ and $E^{0/-}$ levels of the dangling bond is the correlation energy, U. It is generally accepted that in *a*-Si:H the correlation energy is positive, i.e. the $E^{0/-}$ level is higher than the $E^{+/0}$. In device modeling the amphoteric states are sometimes modeled by two single electron states, one for the $E^{+/0}$ level and one for the $E^{0/-}$ level. This can lead to errors in the computation of the electron occupation of dangling bond states as the two single electron states are both independently capable of trapping an electron, whereas the $E^{0/-}$ level can never be occupied by an electron when the $E^{+/0}$ is not.

For the distribution of dangling-bond states in the mobility gap of a-Si:H and related materials the most used models are the standard model and the defect-pool model. The standard model is a simple approach where the distribution of dangling bond states is assumed to be Gaussian. The distribution of dangling bond states as

characterized by their $E^{+/0}$ transition level is:

$$N_{db}^{+/0} = N_{db} \frac{1}{\sigma_{db} \sqrt{2\pi}} \exp\left(-\frac{(E - E_{db0}^{+/0})^2}{2\sigma_{db}^2}\right),$$
(3.11)

where $N_{db}^{+/0}$ is the distribution of energy levels arising from the $E^{+/0}$ transition level, N_{db} is the total dangling bond concentration of which the $E^{+/0}$ are distributed around the energy level $E_{db0}^{+/0}$ with a standard deviation of σ_{db} . Note that Eq. 3.11 can easily be transformed to describe the distribution of $E^{0/-}$ transition levels by replacing $E_{db0}^{+/0}$ with $E_{db0}^{0/-} = E_{db0}^{+/0} + U$

The defect-pool model, of which several versions exist [48–51], is an elaborate thermodynamical model that describes chemical equilibrium reactions where weak Si-Si bonds break to form two dangling bonds and the reverse reaction (the weakbond-dangling-bond conversion model [52]). Hydrogen plays a key role in the equilibration processes in a-Si:H. At normal deposition temperatures of a-Si:H, the hydrogen in the material is mobile. The establishment of a chemical equilibrium between weak-bonds and dangling-bonds requires structural changes in the material, for which the mobile hydrogen provides the required atomic motion [53, 54]. The central idea behind the defect-pool models is that the concentration of dangling bond states depends on the formation energy of the dangling bonds. Furthermore the formation energy of a dangling bond depends on charged state of the dangling bond [55] and thereby on the position of the Fermi-level and the energy levels of the amphoteric dangling bond state. In defect-pool models the energy distribution of the dangling bond states is computed such that the free energy of the system is minimized [50], resulting in equilibrium defect-state distributions that depend strongly on the position of the Fermi-level in the material. An important result is that the defect-pool model can account for the observed differences in energy distribution of defect-states in undoped and doped a-Si:H [51].

In the following section we will briefly introduce the defect-pool model as it was formulated in 1996 by Powell and Deane [50] (in 1993 a similar defect-pool model was published by Powell and Deane [49]). In the model it is assumed that weak Si-Si bonds correspond to states in the valence band tail. Furthermore, the defect-pool function, P(E), is the energy distribution of *potential* defects, and is assumed to be a Gaussian distribution:

$$P(E) = \frac{1}{\sigma_{dp}\sqrt{2\pi}} \exp\left(-\frac{(E - E_{dp})^2}{2\sigma_{db}^2}\right),\tag{3.12}$$

where σ_{dp} is the standard deviation of the Gaussian defect-pool and E_{dp} is the mean

energy of the Gaussian defect-pool. Using this Gaussian defect-pool function and taking into account the influence of the formation energy of dangling bonds on the equilibrium concentration thereof, Powell and Deane derived the following expression for the energy distribution of dangling bond defect states:

$$N_{db}^{+/0}(E) = \gamma \left(\frac{2}{F_{eq}^{0}(E)}\right)^{kT/2E_{v0}} P\left(E + \frac{\sigma_{dp}^{2}}{2E_{v0}}\right), \quad (3.13)$$

$$\gamma = N_{\nu 0} \left(\frac{H}{N_{SiSi}}\right)^{kT/4E_{\nu 0}} \left(\frac{2E_{\nu 0}^2}{2E_{\nu 0} - kT}\right) \exp\left(-\frac{1}{2E_{\nu 0}}\left[E_p - E_\nu - \frac{\sigma_{dp}^2}{4E_{\nu 0}}\right]\right), \quad (3.14)$$

where F_{eq}^0 is the equilibrium occupation function for neutral dangling-bond states, N_{SiSi} is the concentration of electrons in Si-Si bonding states; taking four electrons per Si atom N_{SiSi} is approximately $2 \cdot 10^{29}$ m⁻³ [50], *H* is the concentration of hydrogen in the *a*-Si:H and is approximately $5 \cdot 10^{27}$ m⁻³ [50]. The thermal equilibrium occupation functions for amphoteric dangling-bond states are given by [56, 57]:

$$F_{eq}^{+} = \frac{1}{1 + 2\exp\left(\frac{E_f - E^{+/0}}{kT}\right) + \exp\left(\frac{2E_f - E^{+/0} - E^{0/-}}{kT}\right)}$$
(3.15)

$$F_{eq}^{0} = \frac{2\exp\left(\frac{E_{f} - E^{+/0}}{kT}\right)}{1 + 2\exp\left(\frac{E_{f} - E^{+/0}}{kT}\right) + \exp\left(\frac{2E_{f} - E^{+/0} - E^{0/-}}{kT}\right)}$$
(3.16)

$$F_{eq}^{-} = \frac{\exp\left(\frac{2E_f - E^{+/0} - E^{0/-}}{kT}\right)}{1 + 2\exp\left(\frac{E_f - E^{+/0}}{kT}\right) + \exp\left(\frac{2E_f - E^{+/0} - E^{0/-}}{kT}\right)},$$
(3.17)

where F_{eq}^+ and F_{eq}^- are the equilibrium occupation function for positively charged and negatively charged dangling-bond states, respectively.

Figure 3.1 shows the defect state distributions computed with the 1996 defectpool model for three positions of the Fermi-level (as indicated by the arrows). In the case the Fermi-level is around mid-gap ("i-type") the total dangling bond concentration is lower than when the Fermi level is close to the conduction band ("n-type") or close to the valence band ("p-type").



Figure 3.1: Defect-state distributions in *a*-Si:H according to the 1996 defect-pool model for three positions of the Fermi-level, close to the conduction-band mobility edge ("n-type"), around mid-gap ("i-type"), and close to the valence-band mobility edge ("p-type").



Figure 3.2: Schematic illustration of capture and emission processes on a single electron trap state.

Recombination statistics for single electron states: Shockley-Read-Hall recombination

Shockley-Read-Hall (SRH) recombination considers two capture and two emission processes as illustrated in Figure 3.2. Recombination occurs when a trap state occupied by an electron captures a hole or vice versa. The capture and emission rates can be described by the equations in Table 3.1 for both single electron trap states. In Table 3.1 N_t is the concentration of traps with electron occupation probability f, σ_n and σ_p are the electron and hole capture cross-sections, respectively, and e_n and e_p are the electron and hole emission coefficients, respectively.

In thermal equilibrium there is no net recombination and the principle of detailed
Process		Rate
electron capture	r_1	$n \cdot v_{th} \cdot \sigma_n \cdot N_t \cdot (1-f)$
electron emission	r_2	$e_n \cdot N_t \cdot f$
hole capture	r_3	$p \cdot v_{th} \cdot \sigma_p \cdot N_t \cdot f$
hole emission	r_4	$e_p \cdot N_t \cdot (1-f)$

Table 3.1: Capture and emission rates of single electron trap states.

balance applies, meaning $r_1 = r_2$ and $r_3 = r_4$. Furthermore, in thermal equilibrium the electron occupation probability of a trap at energy E_t is described by the Fermi-Dirac distribution, $f = (1 + \exp\left(\frac{E - E_f}{kT}\right))^{-1}$. Applying the principle of detailed balance and using the Fermi-Dirac distribution for the occupation probability function, yields for the emission coefficients:

$$e_n = v_{th} \sigma_n N_c \exp\left(\frac{E_t - E_c}{kT}\right)$$
(3.18)

$$e_p = v_{th} \sigma_p N_v \exp\left(\frac{E_v - E_t}{kT}\right), \qquad (3.19)$$

where v_{th} is the thermal carrier velocity.

The recombination efficiency, η_R , is defined as the net recombination rate per trap state. In non-equilibrium steady-state conditions, the recombination efficiency is equal to the net rate at which electrons are captured by a trap state. Under steady-state conditions the net electron capture rate must be equal to the net capture rate of holes (i.e., the average charged state of trap states is not changed), therefore it follows that:

$$\eta_R = r_1 - r_2 = r_3 - r_4 \tag{3.20}$$

Using the equations from Table 3.1 and Eq. 3.20, the electron occupation function can be determined as:

$$f = \frac{nv_{th}\sigma_n + e_p}{nv_{th}\sigma_n + pv_{th}\sigma_p + e_n + e_p}.$$
(3.21)

The recombination efficiency of single electron trap states is then determined as:

$$\eta_R = v_{th}^2 \sigma_n \sigma_p \frac{np - n_i^2}{nv_{th}\sigma_n + pv_{th}\sigma_p + e_n + e_p}.$$
(3.22)

The total recombination on single electron trap states can now determined as the integral over all the single electron trap states in the bandgap:

$$R = \int_{E_v}^{E_c} N(E) \eta_R(E) \mathrm{d}E.$$
(3.23)

For the modeling of *a*-Si:H the donor-like trap states of the valence band and the acceptor-like states of the conduction band not necessarily have the same capture cross-sections. In that case the integral of Eq. 3.23 should be computed for both tail state distributions separately. When we refer to capture cross-sections of trap states we usually distinguish between the charged states of the trap. Acceptor-like traps that capture an electron must be empty, and thus positively charged and acceptor-like traps that capture a hole must be filled and thus neutral. Therefore we refer to the capture cross-sections of donor-like states as σ_n^+ and σ_p^0 , for the electron and hole capture cross-sections respectively. Likewise, for acceptor-like states, the capture cross-sections are referred to as σ_n^0 and σ_p^- , for the electron and hole capture crosssections, respectively.

Although it is not relevant for computer modeling, the Taylor and Simmons approximation [58] provides an elegant approximation for SRH statistics in the presence of materials with a continuum of gap states. The Taylor and Simmons approximation is particularly useful for understanding device operation and deriving analytical approximations of device characteristics. From Eq. (3.18) and Eq. (3.19) we observe that the emission coefficient of a trapped carrier to its corresponding band decreases exponentially as a function of the energy distance of the trap to the corresponding band. Therefore, we can define the intrinsic trap-level[†] as the energy level, E_0 , for which the emission coefficient of electrons and holes is equal. Solving $e_n = e_p$ for Eq. (3.18) and Eq. (3.19) we find for E_0 :

$$E_0 = \frac{E_v + E_c}{2} - \frac{kT}{2} \ln\left(\frac{\sigma_n N_c}{\sigma_p N_v}\right)$$
(3.24)

From Eq. (3.24) it can be seen that E_0 lies close to mid-gap

For traps located more than 3kT above E_0 , the emission coefficient of electrons is much higher than the emission coefficient for holes, and similarly the emission coefficient of holes is much higher than the emission coefficient of electrons for traps

[†]Taylor and Simmons referred to this energy level as the intrinsic Fermi-level. However, we follow the terminology as introduced by Willemen [26] to avoid confusion with the normal meaning of the intrinsic Fermi-level.

located more than 3kT under E_0 . Thus we can rewrite Eq. (3.21) to:

$$f = \frac{nv_{th}\sigma_n}{nv_{th}\sigma_n + pv_{th}\sigma_p + e_n}.$$
(3.25)

And simularly we can write for the hole occupation function, or 1 - f:

$$1 - f = \frac{p v_{th} \sigma_p}{n v_{th} \sigma_n + p v_{th} \sigma_p + e_p}.$$
(3.26)

Rearrangement of terms in Eq. (3.25) gives:

$$f = \frac{n\sigma_n}{n\sigma_n + p\sigma_p} \left[1 + \frac{e_n}{nv_{th}\sigma_n + pv_{th}} \right]^{-1}, \qquad (3.27)$$

where the term between brackets is in fact a Fermi-Dirac function as the emission coefficient depends exponentially on the energy level. We can therefore define a quasi-Fermi level for trapped electrons, E_{fn_t} , by solving $e_n = nv_{th}\sigma_n + pv_{th}$:

$$E_{fn_t} = E_c + kT \ln\left(\frac{n\sigma_n + p\sigma_p}{N_c\sigma_n}\right)$$
(3.28)

Substitution of Eq. (3.28) in Eq. (3.27) gives:

$$f = \frac{n\sigma_n}{n\sigma_n + p\sigma_p} \left[1 + \exp\left(\frac{E_t - E_{fn_t}}{kT}\right) \right]^{-1},$$
(3.29)

which is essentially a scaled Fermi-Dirac function. Analogously we can write for the hole occupation function:

$$1 - f = \frac{p\sigma_p}{n\sigma_n + p\sigma_p} \left[1 + \exp\left(\frac{E_{fp_t} - E_t}{kT}\right) \right]^{-1}, \qquad (3.30)$$

where the quasi-Fermi level for trapped holes, E_{fp_t} , equals:

$$E_{fp_t} = E_v - kT \ln\left(\frac{n\sigma_n + p\sigma_p}{N_v\sigma_p}\right)$$
(3.31)



Figure 3.3: The recombination efficiency according to the Taylor and Simmons approximation (Eq. (3.32)). Model parameters used for this graph are: $E_{\mu} = 1.8 \text{ eV}$, $v_{th} = 10^5 \text{ m/s}$, $\sigma_n = \sigma_p = 10^{-20} \text{ m}^2$, $N_c = N_v = 4 \cdot 10^{26} \text{ m}^{-3}$, $E_c - E_{fn} = 0.6 \text{ eV}$, and $E_{fp} - E_v = 0.6 \text{ eV}$.

Similarly the recombination efficiency can be approximated by:

$$\eta_{R} = \begin{cases} v_{th} \frac{\sigma_{n} \sigma_{p} np}{\sigma_{n} n + \sigma_{p} p} \left[1 + \exp\left(\frac{E_{t} - E_{fn_{t}}}{kT}\right) \right]^{-1} & E_{t} > E_{0} \\ v_{th} \frac{\sigma_{n} \sigma_{p} np}{\sigma_{n} n + \sigma_{p} p} \left[1 + \exp\left(\frac{E_{fp_{t}} - E_{t}}{kT}\right) \right]^{-1} & E_{t} < E_{0} \end{cases}$$
(3.32)

The relation in Eq. (3.32) is illustrated in Figure 3.3 for $E_{\mu} = 1.8 \text{ eV}$, $v_{th} = 10^5 \text{ m/s}$, $\sigma_n = \sigma_p = 10^{-20} \text{ m}^2$, $N_c = N_v = 4 \cdot 10^{26} \text{ m}^{-3}$, $E_c - E_{fn} = 0.6 \text{ eV}$, and $E_{fp} - E_v = 0.6 \text{ eV}$. From Eq. (3.32) it can be seen that the traps located between the quasi-Fermi levels for trapped charge are most active in recombination and the recombination efficiency is approximately constant in this energy range.

Recombination statistics for amphoteric states

Sah and Shockley [59] developed a model that can describe recombination and trapping statistics on amphoteric states. Figure 3.4 illustrates an amphoteric trap level and the capture and emission processes that can occur for an amphoteric trap level. Table 3.2 lists the rates for each capture or emission process of an amphoteric trap level. The symbols $F^{+,0,-}$ denote the occupation functions and represent the probability that the trap is empty, F^+ , the trap is occupied by a single electron, F^0 , or the trap is occupied by two electrons F^- .

In a similar fashion as for single electron states the emission coefficients can be derived from the equilibrium electron, n_{eq} , and hole, p_{eq} , concentrations and the



Figure 3.4: Schematic illustration of capture and emission processes on an amphoteric trap state.

Process		Rate
electron capture	r_1	$n \cdot v_{th} \cdot \sigma_n^+ \cdot N_{DB} \cdot F^+$
electron emission	r_2	$e_n^0 \cdot N_{DB} \cdot F^0$
hole capture	r_3	$n \cdot v_{th} \cdot \sigma_n^0 \cdot N_{DB} \cdot F^0$
hole emission	r_4	$e_n^- \cdot N_{DB} \cdot F^-$
electron capture	r_5	$p \cdot v_{th} \cdot \sigma_p^0 \cdot N_{DB} \cdot F^0$
electron emission	r_6	$e_p \cdot N_{DB} \cdot F^+$
hole capture	r_7	$p \cdot v_{th} \cdot \sigma_p^- \cdot N_{DB} \cdot F^-$
hole emission	r_8	$e_p \cdot N_{DB} \cdot F^0$

Table 3.2: Capture and emission rates of amphoteric states.

equilibrium occupation probabilities, F_{eq}^+ , F_{eq}^0 , and F_{eq}^- , (see Equations 3.15, 3.16, and 3.17). The emission coefficients are found as:

$$e_n^0 = v_{th} \sigma_n^+ n_{eq} \frac{F_{eq}^+}{F_{eq}^0} = \frac{1}{2} v_{th} \sigma_n^+ N_c \exp\left(\frac{E^{+/0} - E_c}{kT}\right)$$
(3.33)

$$e_n^- = v_{th} \sigma_n^- n_{eq} \frac{F_{eq}^0}{F_{eq}^-} = 2 v_{th} \sigma_n^0 N_c \exp\left(\frac{E^{0/-} - E_c}{kT}\right)$$
(3.34)

$$e_{p}^{+} = v_{th} \sigma_{p}^{0} p_{eq} \frac{F_{eq}^{0}}{F_{eq}^{+}} = 2v_{th} \sigma_{p}^{0} N_{v} \exp\left(\frac{E_{v} - E^{+/0}}{kT}\right)$$
(3.35)

$$e_p^0 = v_{th} \sigma_p^- n_{eq} \frac{F_{eq}^-}{F_{eq}^0} = \frac{1}{2} v_{th} \sigma_p^- N_v \exp\left(\frac{E_v - E^{0/-}}{kT}\right).$$
(3.36)

In steady-state situations the net recombination rate is zero and therefore the rate equation of the occupation functions should be zero. The rate equations of the occupation functions are given by:

$$\frac{\partial F^+}{\partial t} = -nv_{th}\sigma_n^+F^+ + e_n^0F^0 + pv_{th}\sigma_p^0F^0 - e_p^+F^+ \qquad (3.37)$$

$$\frac{\partial F^{-}}{\partial t} = n v_{th} \sigma_n^0 F^0 - e_n^- F^- - p v_{th} \sigma_p^- F^- + e_p^0 F^0.$$
(3.38)

By further taking into account that the sum of the occupations functions should be unity, $(F^+ + F^0 + F^- = 1)$, the occupation functions are obtained as:

$$F^{+} = \frac{P^{0}P^{-}}{N^{+}P^{-} + P^{0}P^{-} + N^{+}N^{0}}$$
(3.39)

$$F^{0} = \frac{N^{+}P^{-}}{N^{+}P^{-} + P^{0}P^{-} + N^{+}N^{0}}$$
(3.40)

$$F^{-} = \frac{N^{0}N^{+}}{N^{+}P^{-} + P^{0}P^{-} + N^{+}N^{0}},$$
(3.41)

where, for readability the terms P^0 , P^- , N^0 , and N^+ are introduced, which are defined

as:

$$P^0 = pv_{th}\sigma_p^0 + e_n^0 \tag{3.42}$$

$$P^- = pv_{th}\sigma_p^- + e_n^- \tag{3.43}$$

$$N^0 = n v_{th} \sigma_n^0 + e_p^0 \tag{3.44}$$

$$N^{+} = nv_{th}\sigma_{n}^{+} + e_{p}^{+}. ag{3.45}$$

The recombination efficiency is given by $\eta_R = r_1 - r_2 + r_3 - r_4$. Using the derived occupation functions we obtain:

$$\eta_R = v_{th}^2 (pn - n_i^2) \frac{\sigma_n^+ \sigma_p^0 P^- + \sigma_n^0 \sigma_p^- N^+}{N^+ P^- + P^0 P^- + N^+ N^0}.$$
(3.46)

The total recombination rate can be obtained by integration of the recombination efficiency over all dangling bond states.

3.2 Optical modeling of *a*-Si:H devices

The optical generation rate in a solar cell is also an important input parameter for electrical modeling. It is determined from the absorption profile of the photons in the solar cell. When assuming that every photon generates one and only one electron-hole pair the generation rate profile is equal to the absorption profile. Calculation of the absorption profile in *a*-Si:H based solar cells is complicated by the commonly used light trapping techniques making *a*-Si:H based solar cells complex optical systems.

For flat solar cells the multi-layer thin-film optics model can be used. The multilayer thin-film optics model uses the complex refractive indices of the media and the effective Fresnel's coefficients to calculate the optical generation rate profile. This model includes multiple internal reflections and interference. See for details e.g. references [60, 61]. Though all practical solar cells use textured substrates and therefore their interfaces are rough, solar cell structures with flat interfaces are a very useful experimental tool for examining the optical models, extracting unknown optical parameters and showing the trends in optical behavior.

To model the optical properties of a-Si:H based solar cells utilizing textured interfaces to enhance light absorption, the light scattering properties of textured interfaces must be taken into account for each interface. For this the multi rough-interface model can be used [60, 62–64]. The multi rough-interface model assumes a rough interface reflects (transmits) the same *amount* of light as a flat interface. When light is reflected (transmitted) at a rough interface a certain amount of light is scattered where the remainder to the reflected (transmitted) light will continue in the specular (non-scattered) direction. In the multi rough-interface model the light is assumed to be incoherent as the scattering is random. The ratio between scattered and specular light is the haze, H. The haze for the reflectance can be described by [65]:

$$H_R = 1 - \exp\left[-\left(\frac{4\pi\delta_{rms}n_0}{\lambda}\right)^2\right],\tag{3.47}$$

where n_0 is the refractive index of the medium of incidence, and δ_{rms} is the root-meansquare (rms) roughness of the interface. It has been found that for the transmission the haze can be described by [64]:

$$H_T = 1 - \exp\left[-\left(\frac{4\pi\delta_{rms}C|n_0 - n_1|}{\lambda}\right)^3\right],\tag{3.48}$$

where *C* depends on the two media. In this work we will assume *C* to be 1 unless otherwise specified. The amount of scattered light at a rough interface is incident angle dependent and has an angle distribution. This means that the reflected and transmitted scattered light, R_{scatt} , and T_{scatt} respectively, are proportional to:

$$R_{scatt} = H_R f_R^{in}(\theta^{in}) f_R^{out}(\theta^{out}) R_{tot}$$
(3.49)

$$T_{scatt} = H_T f_T^{in}(\theta^{in}) f_T^{out}(\theta^{out}) T_{tot}, \qquad (3.50)$$

where $f_{R,T}^{in}$ describes the dependence of scattering on incident angle for reflection and transmittance, $f_{R,T}^{out}$ is the angular distribution of the scattered reflected or transmitted light, θ^{in} and θ^{out} are the incident angle, and the angle of the outbound reflected or transmitted light, respectively, and R_{tot} and T_{tot} are the total reflectance and transmittance of the interface (scattered and specular) respectively. For both angle distribution functions, $f_{R,T}^{in}$ and $f_{R,T}^{out}$, we will assume a cos² distribution unless otherwise specified.

In practical thin film solar cells interference effects are often observed despite the application of surface texture. In order to account also for these interference effects, coherent nature of specular light has to be included in the simulation. In this case a semi-coherent model is required, where specular light is assumed to be coherent and scattered light is incoherent. A semi-coherent model can be obtained by combining the multi-layer thin-film optics model, to analyze the specular light propagation, with the multi rough-interface model, to analyze the scattered light propagation.

3.3 The ASA program

In this section we introduce our device simulator *Advanced Semiconductor Analysis* (*ASA*). The *ASA* program is designed for modeling of (thin-film) solar cells, i.e. the program is specifically designed to model both electrical and optical properties of multi-layered heterojunction device structures. The *ASA* program has been continuously developed at the Delft University of Technology since 1987. Due to the continuous development over a long period of time, the program could evolve to a full featured and versatile program for the simulation of solid state solar cells in general and thin film silicon based solar cells in particular. The *ASA* program simultaneously solves the Poisson equation and the continuity equation for electrons and holes (Eqs. 3.1, 3.2 and 3.3) in one-dimension (1-D) and in steady-state ($\frac{\partial}{\partial t} = 0$). In addition to simulation models for the electrical properties of a device, the *ASA* program has several optical models available to compute the optical generation rate profile in a device. In this section we will give a summary of the capabilities of the, commercially available, *ASA* program.

For the simulation of planar devices such as solar cells, 1-D simulations are in most cases sufficient and have the advantages of short computation times and simple device specification. Device structures in *ASA* are limited to two terminal devices. Devices in *ASA* are defined by *layers* with various properties. The electrically active part of the device can be defined by one or more layers of semiconductor material. In addition, layers that are only relevant to the optical properties of the device may be added at the front and the back of the device. Most model parameters can be defined for each layer individually. In addition many location dependent parameters may be graded linearly within a layer.

As the ASA program was developed with thin film silicon devices in mind, it is equipped with all the models described in Section 3.1. In addition models are available for:

- Tunnel recombination junctions: For the simulation of multi-junction solar cells additional models are required to model the properties of tunnel recombination junctions. For the modeling of tunnel recombination junctions *ASA* includes the following models: the Trap Assisted Tunneling (TAT) model [66] and the field enhanced mobility model [26]. The combination of these models allow for the simulation of tunnel recombination junctions [26].
- · Recently models for direct recombination and Auger recombination were added.
- Models describing the field, temperature, and doping dependencies of the mobility in various crystalline materials.

The core of the ASA program is a command-line application which takes an ASCII text input file as input. However, a graphical user interface for the ASA program exists for ASA versions up to 4.x. This graphical user interface generates the appropriate ASA input file and makes calls to the command-line core program. The graphical user interface does not support all the features of the ASA 5.x versions (yet). The ASA program is designed to carry out a batch of simulations in one run. Furthermore the command-line version of the ASA program can easily be used in conjunction with (mathematical) script languages like GNU Octave [67] and MATLAB® [68]. Using the ASA program from within such a script language has the advantage that input parameters for the simulations can be calculated in a flexible way, enabling the user to extend upon the models in ASA without modifying ASA itself. A nice example of this is the simulation of organic bulk-heterojunction solar cells with Octave and ASA, where the input parameters for the previous ASA simulation [69]. An example input file for the ASA program is shown in Appendix A.

Simulation modes

The ASA program has the following simulation modes:

- *Thermal equilibrium*. This simulations mode solves the equilibrium state of the device. The current is thus zero through the device and hence only the Poisson equation needs to be solved.
- Steady-state current-voltage (J-V). In this simulation mode the Poisson equation is solved simultaneously with the transport equations for various bias voltages. Furthermore, in order to be able to simulate the illuminated J-V characteristics an optical generation rate profile may be used.
- *Optical generation rate.* Several models are available for the calculation of the optical generation rate in a device. The optical generation rate can be computed using the multi-layer thin-film optical model (*GENPRO1*), the recently added multi rough-interface model (*GENPRO2*), and a recently developed semi-coherent model (*GENPRO3*), obtained by combining the *GENPRO1* and *GENPRO2* models.
- *Reflection-transmission*. Reflection and transmission according to the *GEN-PRO1* model.
- *External quantum efficiency (EQE). ASA* can simulate the EQE by computing $\Delta J/q\Delta \phi_{ph}$ as a function of wavelength, where J is the steady-state current

through the device and $\Delta \phi_{ph}$ is the differential photon flux of the probe light. The EQE can be computed with or without bias illumination.

- Quasi steady-state capacitance-voltage. In this simulation mode the capacitance is simulated as $\frac{\Delta Q}{\Delta V}$ in the device, where ΔQ is the change in total charge in the device and ΔV is a user specified perturbation voltage. Note that this value of the capacitance is a theoretical value as capacitance cannot be measured at 0 Hz.
- *Metal-Insulator-Semiconductor (MIS) structure.* A separate simulation mode is added for the simulation of MIS structures. In this simulation mode the user can specify the geometrical capacitance of the insulator $(\frac{\varepsilon_0\varepsilon_r}{d})$, where ε_0 the permittivity of vacuum, ε_r the relative permittivity of the insulator and *d* the thickness of the insulator). As there is no current through the MIS structure only the Poisson equation is solved.
- Capacitance Metal-Insulator-Semiconductor structure. This simulation mode computes the quasi steady-state capacitance-voltage for MIS structures.
- Charge Deep Level Transient Spectroscopy Metal-Insulator-Semiconductor structure. The simulation mode Charge Deep Level Transient Spectroscopy (Q-DLTS) was recently developed and added to the ASA program and is discussed in detail in Chapter 4.

Chapter 4

Deep Level Transient Spectroscopy

4.1 Introduction

The density-of-states distribution in intrinsic *a*-Si:H is of central importance for the understanding and modeling of *a*-Si:H devices. The aim of this work is to develop a tool to extract the density-of-states distribution in *a*-Si:H. Deep-Level Transient Spectroscopy (DLTS), developed by Lang [70], is a widely accepted technique for characterizing deep-levels in crystalline semiconductors. In this technique the change in capacitance of a Schottky barrier upon a voltage pulse is measured. The voltage pulse is used to empty the traps within the bandgap occupied by electrons. The probability that a trapped electron escapes to the conduction band strongly depends on the energy level at which it is trapped. The emission rate is much higher for electrons trapped at shallow states than for electrons trapped at deep states. As a result the evolution of the space-charge width in response to a voltage pulse shows a transient that reflects the density-of-states distribution. A fast capacitance meter is used to monitor the space-charge width.

For the characterization of intrinsic *a*-Si:H with DLTS, usually current or charge DLTS (C-DLTS, Q-DLTS, respectively) are used, which are measured on Metal-Insulator-Semiconductor (MIS) structures. Q-DLTS has been successfully applied to characterize defects in *a*-Si:H both in as-deposited state and after light-induced degradation [71]. Furthermore, Nádaždy *et al.* [72] provided evidence for the defect-pool model by monitoring the change in the energy distribution of defect states upon the application of a bias voltage during annealing using Q-DLTS. Nádaždy and Thurzo

[73] developed a small-signal model for the Q-DLTS signal from a MIS structure that can be used for the extraction of the density-of-states in intrinsic *a*-Si:H in spatial and energy coordinates.

The small-signal model for Q-DLTS developed by Nádaždy and Thurzo [73], uses the depletion approximation to estimate the width and amount of band bending in the MIS structure. However, without ionized doping atoms as the dominant factor in the space-charge, the local space-charge density in both the extended states and the localized trap states depends strongly on the Fermi-level. Therefore the space-charge profile in intrinsic materials shows a large variation over a space-charge region. This seriously limits the application of this model for intrinsic materials because an accurate description of the space-charge density is required to obtain an accurate description of the spatial distribution of trap states. Because it is a small-signal model, it only describes the response of a MIS structure to a voltage pulse of small amplitude (approximately $\frac{kT}{a}V$). When voltage pulses with a small amplitude are used in Q-DLTS measurements, many measurements are needed to extract the complete defect-state distribution in energy and spatial coordinates [73]. A more accurate model that can also be used for large-signal Q-DLTS and for intrinsic materials is obtained when instead of using the depletion approximation the Poisson equation is solved numerically for the investigated device.

As a tool to extract the density-of-states distribution in *a*-Si:H we developed a new model for Q-DLTS. To model Q-DLTS spectra we have extended our device simulator *ASA* with a simulation mode for MIS structures. With this simulation mode it is possible to simulate Q-DLTS measurements taking into account the spatial distribution of defect and tail states. Unlike previous work on DLTS [70,73–75] we model dangling bonds, being the dominant defect in *a*-Si:H, as amphoteric states [59] and not as two single electron states. When two single states are used for an amphoteric state this will lead to errors in the occupation function [26] and thus also in the discharging characteristics. By fitting experimental Q-DLTS spectra with simulated Q-DLTS spectra, the density-of-states distribution in *a*-Si:H can be estimated.

When the Fermi level is shifted in *a*-Si:H by the application of a bias voltage, the defect-state distribution will re-equilibrate to the new bias condition [72, 76]. The applied bias voltage during a Q-DLTS measurement can therefore also affect the defect-state distribution during the measurement. For this reason we have developed a biasing scheme to minimize the change in defect-state distribution and we developed a method to estimate the amount of change in the defect-state distribution during a Q-DLTS measurement.

In this chaqpter we first introduce the theoretical background of the DLTS technique and derive our model for DLTS in Section 4.2. Next, we describe the sample preparation and DLTS measurement setup in Section 4.3. In Section 4.4 we discuss a method for estimating the amount of change in the density of states distribution during the Q-DLTS measurement and the biasing scheme we developed to minimize the change in the density of states distribution during a Q-DLTS measurement. Finally the measured Q-DLTS spectra and the extracted density-of-states distributions are presented in Section 4.5.

4.2 Theoretical Background of DLTS

From DLTS measurements the defect-state distribution is estimated by measuring the transient response of a Schottky diode to a voltage pulse. The trap-state distribution as a function of energy can be reconstructed from the transient, because the emission rate of electrons and holes from trap states depends strongly on the energy difference between the trap level and the conduction-band and valence-band extended states, respectively. Following the voltage pulse the depletion width changes with a rate depending on the emission of charge carriers from trap states. The changes in the depletion width are monitored via the transient in the capacitance of the device.

For *a*-Si:H the interpretation of DLTS measurements is complicated because of the continuous distribution of states within the bandgap. Cohen and Lang [74] developed a numerical model for the dynamic response of Schottky barriers with a continuous distribution of gap states. Using this model they successfully characterized the density-of-states distribution in phosphorous doped *a*-Si:H films with DLTS measurements [75].

Although for the characterization of intrinsic materials *pin* or *nip* devices have been used [77], the problem in these devices is that the changes in space charge are most pronounced in the doped layers and the DLTS spectrum therefore only partly reflects the defect-state distribution in the intrinsic layer. When instead of a *pin* device, a MIS structure is used, the changes in the space-charge region due to applied voltage pulses are located directly adjacent to the insulator. Therefore MIS structures are better suited for the characterization of intrinsic materials with DLTS than *pin* or *nip* devices. Instead of measuring the space-charge width via the capacitance, MIS structures also allow for the direct measurement of the emission of charge carriers from defect states through the (dis)charging currents because the insulator prevents DC currents from flowing through the device. This technique is referred to as current or charge DLTS (C-DLTS or Q-DLTS). As the Q-DLTS signal is obtained by the integration of the C-DLTS signal, the Q-DLTS signal is inherently less sensitive to noise. Because both procedures are otherwise equivalent we will focus on Q-DLTS.

4.2.1 Modeling of Q-DLTS

In Figures 4.1a and 4.1b the schematic steady-state band diagrams are shown for two bias conditions, V_{bias} and V_{meas} . The gray area indicates the regions where the occupation of trap levels is high. From the band diagram corresponding to an applied bias voltage of V_{bias} (Figure 4.1a), it can be seen that most trap states in the *a*-Si:H in the region adjacent to the oxide are filled. When a voltage pulse of V_{meas} is applied to the metal gate, where $V_{meas} < V_{bias}$, electrons are emitted from the hatched area indicated in Figure 4.1b. As the rate of the electron emission from trap states depends strongly on the energy level, not all traps are discharged at once. In general the shallow states, with a trap energy close to the conduction band, are discharged first followed by deeper states. In Figures 4.1c and 4.1d the bias voltage, the voltage pulse, and the resulting current are schematically shown. The Q-DLTS signal is the integrated current between t_1 and t_2 . Through the emission rate dependency on trap energy the choice in integration interval corresponds to a certain energy range in the gap. The magnitude of the Q-DLTS signal is then a measure of the number of states located in this energy range.

The rate at which a trap state is discharged during the application of the voltage pulse can be derived from Shockley-Read-Hall occupation statistics. The following differential equation for the occupation probability as a function of time can be derived from capture and emission rates (see Section 3.1)

$$\frac{\partial f(t)}{\partial t} = \frac{r_1 - r_2 + r_3 - r_4}{N_t} \\ = n(t)v_{th}\sigma_n [1 - f(t)] - e_n f(t) + p(t)v_{th}\sigma_p f(t) - e_p [1 - f(t)], \quad (4.1)$$

where *f* is the electron occupation probability, v_{th} is the thermal velocity, σ_n and σ_p are the electron and hole capture cross-sections, respectively, and e_n and e_p are the electron and hole emission coefficients, respectively. In the absence of hole injection we can neglect hole trapping. Hole injection is prevented through the chosen device structure (see Section 4.3). As during the discharging electrons are effectively being removed from trap states we ignore electron trapping and hole emission. We rewrite Eq. (4.1) to obtain

$$\frac{\partial f(t)}{\partial t} = -e_n f(t) \tag{4.2}$$

This differential equation is readily solved and gives

$$f(t) = e_n f(0) \exp(-e_n t).$$
 (4.3)



Figure 4.1: (a.) The schematic band diagram corresponding to an applied bias voltage of V_{bias} and (b.) the schematic band diagram corresponding to an applied bias voltage of V_{meas} . The gray area indicates where most trap levels are occupied by electrons, the hashed area indicates the area from where electrons are emitted when the voltage pulse is applied.(c.) The applied bias voltages during a Q-DLTS measurement and (d.) the corresponding (dis)charging current. The gray area indicates ΔQ as computed from Eq. (4.9).

The discharging is thus characterized by a rate constant of

$$k_d = e_n. \tag{4.4}$$

As discussed in section 3.1 the emission rates can be determined by applying detailed balance to the capture and emission rates. The general form of the emission rate is

$$e_n(E_t,T) = e_0 \exp\left(\frac{E_t - E_c}{kT}\right),\tag{4.5}$$

where E_t is the energy level of the trap, E_c is the conduction band mobility edge, k is the Boltzmann constant and T the temperature. It follows from Eq. (4.5) that the emission rate of electrons to the conduction band extended states increases with tem-

perature. In DLTS measurements elevated temperatures are often applied to stimulate electron emission and thereby speed up the measurements.

Note that according to Eq. (4.3) the trap state is always completely discharged for $t \rightarrow \infty$. This is the result of neglecting both hole emission and electron trapping. Nevertheless we can use Eq. (4.3) as, to a first-order approximation, we can take the Fermi-level as a demarcation energy separating filled and empty states [70]. Taking the Fermi-level as a demarcation energy leads to the situation where all states which are discharged, also discharge fully.

The strong energy dependence of the emission rate from Eq. (4.5) can be used to reconstruct the distribution of defect states as a function of energy. By applying a time-constant filter (TCF) on the discharge current, the discharging of states with one particular emission rate can be measured. The integrated charge release over a time interval $[t_1, t_2]$ of traps at certain energy level E_t equals

$$\Delta Q(E_t, t_1, t_2) = q N_t(E_t) \int_{t_1}^{t_2} f(E_t, t) dt$$

$$\approx q N_t(E_t) \Delta f^*(E_t) [\exp(-k_d(E_t)t_1) - \exp(-k_d t_2)], \quad (4.6)$$

where $\Delta f^*(E_t)$ is the change in occupation of a trap between t = 0 and $t \to \infty$, where, as we take the Fermi-level as a demarcation energy, the occupation functions are approximated by step functions. We can write for $\Delta f^*(E_t)$

$$\Delta f^*(E_t) = \begin{cases} 1 & E_f(0) > E_t > E_f(\infty) \\ 0 & E_f(0) < E_t, E_t < E_f(\infty) \end{cases}$$
(4.7)

where $E_f(0)$ and $E_f(\infty)$ are the Fermi-levels at t = 0 and for $t \to \infty$, respectively. The exponential part on the right-hand side Eq. (4.6) is the first-order TCF function

$$K(t_1, t_2) = \exp(-k_d t_1) - \exp(-k_d t_2)$$
(4.8)

The first-order TCF function is shown in Figure 4.2. This function has a maximum at a rate constant of $k_d = \ln(t_2/t_1)/(t_2 - t_1)$. We refer to this value of the rate constant as the *filter rate*. By substituting Eq. (4.4) and Eq. (4.5) in Eq. (4.8), *K* can be written as a function of t_1 , t_2 , the energy of the trap level, and the temperature. The charge release from all the single electron traps in the MIS device can then be written as

$$\Delta Q(T,t_1,t_2) = qA \int_0^d \int_{E_v}^{E_c} N_t(E_t,x) \Delta f^*(T,E_t,x) K(T,E_t,t_1,t_2) dE dx, \qquad (4.9)$$

where E_c is the conduction-band mobility edge, E_v is the valence-band mobility edge, N is the density states, A is the area of the contact, and q is the elementary charge.



Figure 4.2: The first-order TCF function as a function of the emission rate for two choices for t_1 and t_2 . The maximum is located at $e_n = \ln(t_2/t_1)/(t_2-t_1)$.

The defect density-of-states as a function of energy and position can be extracted by matching a calculated Q-DLTS signal from Eq. (4.9) to experimental results.

The Fermi-level as demarcation energy

Taking the Fermi-level as a demarcation energy is problematic for the description of amphoteric states in *a*-Si:H. It is commonly accepted that in *a*-Si:H the correlation energy of dangling bonds is positive. From the equilibrium occupation probabilities of amphoteric states (see Eqs. (3.15), (3.16), and (3.17)) it follows that there is an energy range where there is a high probability that a dangling bond is neutral and the width of this energy range is approximately equal to the correlation energy. A value of 0.2 eV is often used for the correlation energy of dangling bond defects in *a*-Si:H [50, 78]. Taking the Fermi-level as a demarcation energy is therefore not a good approximation to model the occupation on dangling bond defects in *a*-Si:H.

To allow for occupation probabilities between 0 and 1 we must allow for one or more processes charging the electronic state (i.e., electron capture or hole emission), thus allowing the charging to balance with discharging processes. We will now derive a model for Q-DLTS where we take into account electron capture. We will make the derivation for both single and amphoteric states.

For electron capture we take the trapping rate corresponding to the electron concentration for $t \to \infty$, $n(\infty)$. As the system can be treated to be in thermal equilibrium for $t \to \infty$, we can relate this capture rate to the emission rate with detailed balance

$$n(\infty)v_{th}\mathbf{\sigma}_n = \frac{e_n f(\infty)}{1 - f(\infty)},\tag{4.10}$$

where $f(\infty)$ is the occupation probability for $t \to \infty$. The trapping rate rate corresponding to $n(\infty)$ then equals $\frac{e_n f(\infty)}{1-f(\infty)} [1-f(t)]$. With this result we rewrite Eq. (4.2) as

$$\frac{\partial f(t)}{\partial t} = \frac{e_n}{1 - f(\infty)} \left[f(\infty) - f(t) \right]$$
(4.11)

This differential equation is readily solved and gives

$$f(t) = e_n \Delta f \exp\left(-\frac{e_n}{1 - f(\infty)}t\right) + f(\infty), \qquad (4.12)$$

where $\Delta f = [f(0) - f(\infty)]$ is the change in occupation probability. Now we find a rate constant of

$$k_d(e_n, f(\infty)) = \frac{e_n}{1 - f(\infty)}.$$
 (4.13)

Note that Equations (4.12) and (4.13) are the same as Equations (4.3) and (4.4), respectively, for $f(\infty) = 0$. Analogous to the derivation of Eq. (4.9) in the previous section we can now write for the Q-DLTS signal from single electron states, ΔQ_s ,

$$\Delta Q_s(T, t_1, t_2) = qA \int_0^d \int_{E_v}^{E_c} N_t(E_t, x) \Delta f(T, E_t, x) K(T, E_t, t_1, t_2) dE dx.$$
(4.14)

The differential equation for the occupation probabilities as a function of time of amphoteric states were already presented in Eq. (3.37) and Eq. (3.38). We again neglect hole trapping and emission and leave the electron capture terms

$$\frac{\partial F^+}{\partial t} = -nv_{th}\sigma_n^+ F^+ + e_n^0 F^0 \tag{4.15}$$

$$\frac{\partial F^-}{\partial t} = n v_{th} \sigma_n^0 F^0 - e_n^- F^-, \qquad (4.16)$$

where e_n^0 and e_n^- are the emission rates of neutral and negatively charged states, respectively, and F^+ , F^0 , and F^- are the probabilities that an amphoteric state is positively charged, neutral, or negatively charged, respectively. We again assume constant trapping rates during the discharging, taking the electron concentration for $t \to \infty$. From detailed balance it follows that

$$n(\infty)v_{th}\mathbf{\sigma}_{n}^{+} = e_{n}^{0} \frac{F^{0}(\infty)}{F^{+}(\infty)}$$
(4.17)

$$n(\infty)v_{th}\mathbf{\sigma}_n^0 = e_n^- \frac{F^-(\infty)}{F^0(\infty)}$$
(4.18)

We thus rewrite Eqs. (4.15) and (4.16) by substituting these capture rates

$$\frac{\partial F^+}{\partial t} = e_n^0 \left[F^0 - \frac{F^0(\infty)}{F^+(\infty)} F^+ \right]$$
(4.19)

$$\frac{\partial F^{-}}{\partial t} = e_n^{-} \left[\frac{F^{-}(\infty)}{F^0(\infty)} F^0 - F^{-} \right].$$
(4.20)

This set of differential equations can be solved analytically with the additional requirement $F^- + F^0 + F^+ = 1$. However, the analytical solution we found has too many terms[†] to be properly displayed in this document and the number of terms make the equations are difficult to work with (or simplify). For implementation in *ASA* of Eqs. 4.15 and 4.16 we have therefore chosen a numerical integration scheme. The numerical integration is carried out using a 4th order Runge-Kutta integration over the time interval $[t_1, t_2]$. When the changes in occupation probabilities over the time interval $[t_1, t_2]$, $\Delta F^-(t_1, t_2)$ and $\Delta F^+(t_1, t_2)$, are known, the Q-DLTS signal from amphoteric states, ΔQ_a can be computed as

$$\Delta Q_a(T,t_1,t_2) = qA \int_0^d \int_{E_v}^{E_c} N_t(E_t,x) \left[\Delta F^-(T,E_t,x,t_1,t_2) - \Delta F^+(T,E_t,x,t_1,t_2) \right] dE dx,$$
(4.21)

We have implemented routines in *ASA* to compute the Q-DLTS signal of an MIS structure. By solving the Poisson equation with *ASA* for a MIS structure we can obtain the steady-state occupation probabilities for the applied voltages V_{bias} and V_{meas} , which correspond to the occupation probabilities for t = 0 and $t \rightarrow \infty$, respectively, in Equations (4.14) and (4.21). Equations (4.14) and (4.21) can than be used to compute the Q-DLTS signal.

The emission rate and the Meyer-Neldel rule

It has been found in various studies that the emission rate in Eq. (4.5) is not accurate [79–81] for *a*-Si:H. The emission rate of traps in *a*-Si:H follows the "Meyer-Neldel rule". The emission rate taking into account the Meyer-Neldel rule is given by

$$e_n(E_t,T) = e_0(E_t) \exp\left(\frac{E_t - E_c}{kT}\right)$$
(4.22)

[†]Approximately 200 terms per charged state.

Although Eq. (4.22) is very similar to Eq. (4.5) the difference is in the term e_0 which follows [81]

$$e_0(E_t) = e_{00} \exp\left(\frac{E_c - E_t}{E_0}\right),$$
 (4.23)

where E_0 is a positive constant. It has been observed that the Meyer-Neldel rule influences thermally activated processes where the activation energy is much larger than the typical excitations available (phonons, in the case of the emission rate) [80, 81]. The Meyer-Neldel rule can be explained taking into account not only one-phonon excitations, but also excitations involving several phonons, either by cascade or multiphonon processes [80]. When the activation energy is large compared to the typical excitations of the system, an ensemble of many excitations is needed for the process to take place. The number of possible assembles leading to a thermally activated jump over a barrier increases with the barrier height [80]. The increase of the emission constant (e_0 in Eq. (4.22)) with the barrier height ($E_c - E_t$) is caused by the entropy associated with the number of possible ways the excitation takes place.

In our implementation of the models in the ASA program, e_00 and E_0 are defined separately for the valence-band tail states, conduction-band tail states, neutral dangling-bond states, and negatively-charged dangling-bond states.

4.3 Sample Preparation and Measurement Setup

A schematic drawing of an *a*-Si:H MIS structure is shown in Figure 4.3a. Instead of using a metal for our MIS structure we used heavily doped n-type crystalline silicon wafers with a resistivity of 0.002 Ω cm and a (100) orientation. The wafer is contacted with an aluminium layer of 750 nm thick. On the other side a 50-nm thick SiO₂ layer is grown by dry oxidation at 1150 °C. On the oxide an *a*-Si:H layer of 750 nm is grown at 450 K using PE-CVD. For contacting the *a*-Si:H layer we used a 20-nm thick layer of chromium of 4 mm by 4 mm, deposited by e-beam evaporation. One sample has several chromium contacts (typically 9 depending on the exact size of the sample). The effective area from where the Q-DLTS signal is collected may be larger as the surroundings of the contact may also be charged and discharged. This possible effect is discussed in more detail in Section 4.5.2.

Note that in the previous section we have neglected hole trapping under the assumption there is no hole injection. The chromium/*a*-Si:H Schottky barrier leads to a barrier for hole injection equal to $E_{\mu} - \phi_b$, where ϕ_b is the Schottky barrier and E_{μ} the mobility gap of the *a*-Si:H. We estimate that hole injection does not play a significant role in the discharging of traps for which $E_t - E_c < E_{\mu} - \phi_b$. The ideal Schottky barrier between chromium and *c*-Si is 0.21 eV [82]. Assuming the electron affinity of *a*-Si:H is 0.15 eV lower than the electron affinity of *c*-Si [83], we estimate the



Figure 4.3: (a) Schematic drawing of an *a*-Si:H MIS structure. (b) Schematic drawing of Q-DLTS setup

Schottky barrier between a-Si:H and chromium to be 0.36 eV. Assuming the mobility gap of a-Si:H is approximately 1.75 eV, the barrier for hole injection is 1.39 eV. This should be sufficient to characterize the dangling bond defects and perhaps even part of the valence band tail. If necessary the barrier for hole injection can be further increased by adding n-type doped layer between the a-Si:H and Cr layer.

The DLTS setup is schematically shown in Figure 4.3b. An Agilent arbitrary waveform generator, model 33250A, was used to apply voltage pulses to the sample. The current through the sample is measured over a resistor of 10 k Ω , using a model SR560 low noise amplifier from Stanford Research Systems and a Tektronics TDS2024 oscilloscope.

The sample is placed in a vacuum chamber to minimize noise in the measurement and to avoid the formation of water and ice that might short circuit the sample when measuring at low temperature. In the sample holder the sample can be cooled with liquid nitrogen and heated with a heating resistor. A proportional-integral-derivative controller (PID controller) is used to control the temperature by changing the current through the heating resistor. The temperature controller is accurate for the temperature range between room temperature and approximately 500 K. For measurements at lower temperature it is possible to use liquid nitrogen to cool the sample, however, accurately controlling the temperature of the sample by manually administering liquid nitrogen requires a considerable effort from the experimenter[‡].

Figure 4.4 shows the applied bias to the sample during a measurement cycle as we use in our setup. Before a measurement is carried out the device is fully charged with certain bias voltage, V_{bias} . A measurement cycle starts with a *measurement pulse*, we will refer to the voltage of this pulse as V_{meas} . During the measurement pulse the

[‡]In this work several measurements were carried out below room temperature. The author thanks Kasper Zwetsloot for his considerable efforts.



Figure 4.4: The applied bias during a measurement cycle (solid black line), the end of the previous measurement cycle and the beginning of the next measurement cycle are indicated by the dashed line.

device is discharged and we measure the current. The remainder of the measurement cycle is the *charging time*, which serves to re-charge the device with a bias voltage of V_{bias} . The charging time is discussed in more detail in Section 4.4.2. During the charging time a voltage of V_{bias} is applied, however optionally the charging time starts with a charging pulse of magnitude V_{charge} . The charging pulse will be discussed in detail in Section 4.4.

The Q-DLTS signal is obtained by the integration of the measured current over a time interval $[t_1, t_2]$ during the measurement pulse. In our measurements we used a measurement pulse of 20 ms long. In case we used a charging pulse, the charging pulse was 50 ms long. Figure 4.5 shows a typical current measurement during the measurement pulse. This measurement was carried out at 443 K in response to a measurement pulse where V_{meas} was -2 V and V_{bias} was 0 V. For this measurement the amplifier was saturated during the first 2.4 ms of the measurement.

4.4 Accurate measurements of Q-DLTS spectra

4.4.1 Monitoring change in the density-of-states distribution

As discussed in Section 3.1, the defect-pool models [49, 50] state that the energy distribution of defect states in *a*-Si:H depends on the location of the Fermi-level in the bandgap through an equilibration process. This property of the distribution of defect states can be used to help calibrate the defect-pool models in our simulations.



Figure 4.5: Typical current transient from a sample at 443 K in response to a measurement pulse. In this measurement V_{bias} was 0 V and V_{meas} was -2 V.

However, during a Q-DLTS measurement the sample is exposed to both bias voltages and elevated temperatures, and therefore the defect-state distribution in the sample may change during a measurement. In this section we will discuss the equilibration process in *a*-Si:H in order to analyze the influence of measuring a Q-DLTS spectrum on the defect-state distribution.

The equilibration process is illustrated by the energy-configuration diagram in Figure 4.6. In this diagram there are two states, A and B, separated by an energy barrier, E_b . In the diagram state A can be interpreted as a strained bond in the valenceband tail, A^* as an intermediate state and B as the state in which the strained bond is broken [36]. Due to the structural disorder in a-Si:H there is in fact not one barrier to defect creation (i.e., E_b), but rather a range of such barriers exists [36, 76, 84].

The following two expressions give the defect-creation and defect-removal rates, respectively

$$r_{A-B} = N_A \cdot k_{A-B}(T, E_b) \tag{4.24}$$

$$r_{B-A} = N_B \cdot k_{B-A}(T, E_b, E_{form}),$$
 (4.25)

with

$$k_{A-B} = k_{dc} \exp\left(-\frac{E_b}{kT}\right),\tag{4.26}$$

and

$$k_{B-A} = k_{dr} \exp\left(-\frac{(E_b - E_{form})}{kT}\right),\tag{4.27}$$

where k_{dc} and k_{dr} are the attempt-of-escape frequency for the defect creation and removal process, respectively, N_A and N_B are the populations of state A and B, re-



Figure 4.6: Energy-configuration diagram

spectively, and the formation energy, E_{form} is the energy difference between state *A* and *B*. When thermal equilibrium is obtained the reaction rates from Eq. (4.24) and Eq. (4.25) are equal and the ratio between states A and B is determined by the formation energy E_{form}

$$\frac{N_A}{N_B} = \frac{k_{dr}}{k_{dc}} \exp\left(\frac{E_{form}}{kT}\right).$$
(4.28)

In non-equilibrium, the concentration of N_A is described by the differential equation

$$\frac{dN_A}{dt} = N_B \cdot k_{B-A} - N_A \cdot k_{A-B}.$$
(4.29)

If we assume that the lifetime of the intermediate state A^* is much shorter than the lifetime of states *A* and *B*, it follows that $N_B + N_A = N$ is constant. Substituting N_B with $N_B = N - N_A$ and solving this differential equation we arrive at the solution

$$N_{A}(t) = \frac{N \cdot k_{B-A}}{k_{A-B} + k_{B-A}} \left[1 - \exp\left(-(k_{A-B} + k_{B-A})t\right) \right] + N_{A}^{0} \cdot \exp\left(-(k_{A-B} + k_{B-A})t\right),$$
(4.30)

where N_A^0 is the concentration N_A at time t = 0. The excess N_A concentration, δN_A , is defined by the deviation of the concentration N_A from the equilibrium concentration of N_A and it follows from Eq. (4.30)

$$\delta N_A(t) = \delta N_A^0 \cdot \exp\left(-(k_{A-B} + k_{B-A})t\right), \qquad (4.31)$$

where $\delta N_A^0 = \frac{N \cdot k_{B-A}}{k_{A-B} + k_{B-A}} - N_A^0$ is the excess N_A concentration at t = 0.

The equilibration process described by Eq. (4.30) depends strongly on the temperature through Eq. (4.26) and Eq. (4.27). The populations of state *A* and *B* are effectively *frozen-in* for temperatures where $kT \ll E_b - E_{form}$, as the rate constant of the equilibration process, $k_{A-B} + k_{B-A}$, depends exponentially on the temperature. Therefore, the defect-state distribution in *a*-Si:H at room temperature is usually characterized by the freeze-in temperature, T^* [85,86]. The exact value of the freeze-in temperature for intrinsic *a*-Si:H is approximately 500 K for films deposited at 540 K [85]. However, since our devices are grown below 500 K, this is probably not a correct value for our material; instead we will use the deposition temperature of 453 K as the freeze-in temperature for our calculations.

When the Fermi level is shifted in *a*-Si:H by the application of a bias voltage, the defect-state distribution will re-equilibrate to the new bias condition. When a positive (negative) bias is applied an *n*-type (*p*-type) energy distribution of states can be *programmed* (see Figure 3.1. This effect has also been observed experimentally [72, 76].

Stutzmann introduced the concept of the thermalization energy [84]. The concept of the thermalization energy can be used to find a relation between the energy barrier, the temperature, and the time required to reach equilibration in the populations of *A* and *B* in a two-state system. The time required to equilibrate a two-state system is proportional to the time constant of the equilibration process, $\tau = 1/k = 1/(k_{A-B} + k_{B-A})$. Using the approximation that after time *t* the populations of state *A* and *B* have reached equilibrium for all two-state systems with $\tau \le t$ and using the approximation $k = k_0 \exp(-E_b/kT)$ (i.e., $E_{form} \ll E_b$), then all two-state systems with E_b smaller than or equal to the thermalization energy E_{th} ,

$$E_{th} = kT\ln(k_0 t), \qquad (4.32)$$

will have equilibrated populations over state *A* and *B*. Note that after a time τ , δN_A in Eq. (4.31) is reduced by a factor of e^{-1} .

When the defect-state distribution in a-Si:H is programmed at a certain temperature, the thermalization energy can be computed from the programming time using Eq. (4.32). By monitoring the change in the energy distribution of states in a-Si:H upon programming at a certain temperature, the distribution of energy barriers of the two-state systems in the a-Si:H as a function of thermalization energy can be determined from the rate of change in the distribution of states. When the distribution of energy barriers is known and we monitor the thermalization energy during a Q-DLTS measurement, we can estimate how much the Q-DLTS measurement influences the energy distribution of states.

In case the defect-state distribution re-equilibrates during a Q-DLTS measurement



Figure 4.7: Simulated density-of-states distribution in thermal equilibrium as a function of energy for three equilibration temperatures, *T*, equal to 450 K, 425 K, and 400 K. The energy is with respect to the conduction-band mobility edge. "n-type" density-of-states distribution with the Fermi-level at 0.3 eV from the conduction-band mobility edge. "i-type" density-of-states distribution with the Fermi-level at 0.85 eV from the conduction-band mobility edge."p-type" density-of-states distribution with the Fermi-level is at 0.3 eV from the valence-band mobility edge.

due to an applied bias voltage, the expression in Eq. (4.32) cannot be used directly because during the Q-DLTS measurement the temperature is varied and thereby the equilibrium distribution of defect states changes during the measurement. Therefore, to use the thermalization concept we have to make the approximation that the influence of the temperature on the equilibrium population of states A and B is small compared to the influence of the applied bias voltage, i.e. assuming E_{form} in Eq. (4.27) is small.

The influence of the temperature on the equilibrium population needs only to be considered when the time span the *a*-Si:H is kept at that temperature range is sufficient to actually change the defect-state distribution. In Figure 4.7 the simulated equilibrium density-of-states is plotted for three values for the equilibration temperature and for three positions of the Fermi level. For the simulations we used the defect-pool model from [50]. It can be seen from Figure 4.7 that the influence of the equilibration temperature is relatively small compared to the influence of the position of the Fermi level.

Under the assumption that $E_{form} \ll E_b$ we substitute $E_{form} = 0$ in Eq. (4.27) to obtain the rate constant, k as $k_{A-B} + k_{B-A} = (k_{dc} + k_{dr}) \exp(-E_b/kT)$. With Eq. (4.31) we can describe the exponential decay of the excess N_A concentration for any given time interval for which the temperature (and therefore the rate constant) is constant. By approximating the temperature as a function of time with a staircase function, we can use Eq. (4.31) to determine the thermalization energy by finding the

barrier, E_b , for which after a certain time, t, the excess N_A concentration has been reduced with a factor e^{-1}

To minimize the changes in the defect-state distribution due to the applied temperature and bias voltage it is important to make sure the equilibration reactions and the resulting changes in defect-state distribution are slow. For this reason the measurements were carried out below the deposition temperature of 453 K. As this value is well below 500 K no rapid changes in the defect-state distribution are expected [85].

4.4.2 Minimizing the change in the density-of-states distribution

In order to prevent change in the defect-state distribution during a Q-DLTS measurement, the applied V_{bias} could be taken such that the Fermi-level is not shifted with respect to the Fermi-level during the equilibration of the defect-state distribution. However, for a trap state to contribute to the Q-DLTS signal it must first be occupied during the application of V_{bias} . Figure 4.7 shows that for an "n-type" distribution the majority of the defect states are located below the Fermi-level and are therefore likely occupied by electrons. For the "p-type" distribution, however, most defect states are unoccupied by electrons. For the "i-type" distribution the deep trap states below mid-gap are charged.

In order to characterize a larger energy range within the bandgap for an "i-type" distribution we will do two measurements. With the first measurement we characterize the deep trap states located below mid-gap. For the characterization of deep trap states we can choose V_{bias} such that the defect-state distribution will not change much during the Q-DLTS measurement. With the second measurement we will characterize both the deep trap states above mid-gap and the states below mid-gap. For this we choose V_{bias} such that the Fermi-level is above mid-gap when the device is charged. The second measurement can affect the density of states distribution. However, the emission rate of the trap states above mid-gap is higher than the emission rate of the deep trap states below mid-gap, therefore we can characterize the defect states above mid-gap at a lower temperature. As the equilibration rate is strongly temperature dependent, the Q-DLTS spectrum reflecting the density of states above mid-gap is less affected by changes in the density-of-states distribution. We can use the theory from the previous section to estimate up to what temperature the second measurement is reliable.

We have observed that when V_{bias} is low (in the range of 0-3 V) and the Q-DLTS signal is measured repeatedly at temperatures above 400 K, the Q-DLTS signal depends strongly on the time V_{bias} is applied between two subsequent measurement pulses. If the time between measurement pulses is too short, the measured Q-DLTS signal decreases with each subsequent measurement. The reason for this is that the trap states are not fully charged. The problem arises only at high temperature as the



Figure 4.8: The Q-DLTS signal at 443 K as a function of the time between two subsequent measurements. Squares: a single measurement pulse is used for the measurement; Circles: The measurement pulse is followed by a charging pulse in order to recharge the sample faster

emission rate shows an exponential increase as a function of temperature (see Eq. (4.5)). For an accurate analysis of the Q-DLTS signal it is important that the trap states are fully charged to V_{bias} before a Q-DLTS measurement is carried out as in our simulations we compute $\Delta f(E,x)$ in Eq. (4.9) as the difference in occupation between the *steady-state* situations when V_{bias} and V_{meas} are applied.

In order to find correct settings for measuring Q-DLTS spectra, we measured the Q-DLTS signal where the charging time was doubled between each subsequent measurement. Further settings for this measurement were: the filter rate = 100 s^{-1} (t₁ = 7ms and t₂ = 14ms), V_{bias} = 0 V, V_{meas} = -2 V, V_{charge} = 0 V.

In Figure 4.8 the Q-DLTS signal at 443 K is shown as a function of time, t, and charging time, Δt , for this measurement (squares). We note that in the presented measurement the Q-DLTS signal corresponding to a certain charging time is not the same as the steady-state Q-DLTS, the signal one would obtain if repeated measurements were carried out with a constant charging time. In this measurement a decreasing signal means that over a measurement cycle the sample was more discharged than charged, and vice versa an increasing signal means the sample is effectively charged over a measurement cycle. The measured signal in Figure 4.8 is therefore an overestimation of the steady-state signal when the signal decreases with each subsequent measurement and an underestimation of the signal when the signal increases. Figure 4.8 shows that the time required to recharge the sample after several measurements at 443 K exceeds 2 hours.

In order to charge the sample faster we applied a charging pulse directly after the measurement pulse. The open circles in Figure 4.8 show the results for the pulse with



Figure 4.9: Q-DLTS signal as a function of the number of measurement cycles at 443 K for a charging time, Δt , of 600 s and a charging pulse of 5 V for 50 ms.

 $V_{\text{bias}} = 0V$, $V_{\text{meas}} = -2V$ for $V_{\text{charge}} = 5V$ for 50 ms. For $\Delta t > 960$ s the steadystate signal falls within 4.5 % of the signal obtained from a fully charged sample for $\Delta t = 61.3 \cdot 10^3$ s.

For the remainder of this work we chose a minimal charging time of 600 s. In Figure 4.9 the Q-DLTS signal at 443 K is shown as a function of the number of measurement cycles, the signal is normalized to the Q-DLTS signal after a charging time of 14 h. The charging time for this measurement was 600 s. The graph shows that for repeated measurements at high temperatures the error remains within 5 %.

4.5 Results

In this section we will present the results of the Q-DLTS measurements and simulations. First we will discuss the measurements. Due to the complexity of the interpretation of the measurements most of the analysis of the measurements will be carried out with the aid of simulations.

4.5.1 Experimental

For the measurements we used two different measurement cycles. Measurement cycle 1, with $V_{bias} = 0$ V, $V_{meas} = -2$ V for 20 ms, and $V_{charge} = 5$ V for 50 ms, and measurement cycle 2, with $V_{bias} = 1$ V, $V_{meas} = -2$ V for 20 ms, and $V_{charge} = 5$ V for 50 ms. In Figure 4.10 the simulated steady-state band diagram is shown for 1 V, 0 V and -2 V. Figure 4.10 shows that using a bias voltage of 0 V will not charge shallow defect states near the conduction band. Therefore, measurement cycle 1 can-



Figure 4.10: The simulated band diagrams in the MIS device for a bias voltage of 0 V,1 V and -2 V.

not be used to characterize shallow defect states. However, we will use measurement cycle 1 for characterizing un-programmed (i.e., not bias annealed) devices as with a 0-V bias it will not affect the defect-state distribution much during the measurement. Measurement cycle 2 can be used to characterize a broader range of the bandgap as the bias voltage of 1 V charges most states in the bandgap near the *a*-Si:H/oxide interface. As shallow defect states can be characterized at relatively low temperature due to their high emission rates, shallow defect states can be characterized with measurement cycle 2 without affecting the defect-state distribution much. However, at elevated temperatures measurement cycle 2 may affect the defect-state distribution in the device. When a device is measured with measurement cycle 2 it is important that a 1-V bias is applied for several hours in advance at room temperature to fully charge the device (we applied the bias overnight before a measurement resulting in 8-14 hours of charging). Unless otherwise stated all Q-DLTS signals have been obtained with a filter rate of 100 s⁻¹.

The Q-DLTS spectrum was measured with measurement cycle 1 and 2 using the same contact, contact 1, on the sample. Because measurement cycle 2 might affect the defect-state distribution, the Q-DLTS signal was measured with measurement cycle 1 first. The results are shown in Figure 4.11. Because of the possible influence of measurement cycle 2 we switched to another contact on the sample, contact 2, for our further experiments. First we verified that the Q-DLTS spectrum of contact 2 is in fact the same as the Q-DLTS spectrum of contact 1. For this we measured the Q-DLTS spectrum of contact 2 with measurement cycle 1. Figure 4.12 shows that the Q-DLTS spectra for the two contacts are in good agreement with each other.

The Q-DLTS spectrum measured with measurement cycle 2 after programming is shown in Figure 4.11. Before we started programming contact 2 at 453 K, a 1-V



Figure 4.11: The measured initial Q-DLTS signal for the two measurement cycles.



Figure 4.12: Comparison between two contacts on the same sample measured with measurement cycle 1. Apart from a temperature offset due to a variation in the surrounding temperature, the Q-DLTS spectra are a close match.

bias voltage was applied for 14 hours at room temperature. We heated the sample in approximately 600 s from room temperature to 453 K and did the first measurement directly after reaching a temperature of 453 K. The evolution of the Q-DLTS signal of contact 2 during programming with 1 V at 453 K is shown in Figure 4.13 as a function of time. Figure 4.13 shows that the density of defect states that are characterized at 453 K increases. This is expected as the defect states that are characterized at high temperature are deep-levels, located below mid-gap. In this energy range the defect-state density should increase when the defect-state distribution is programmed towards an n-type distribution.

All the measured Q-DLTS spectra in Figure 4.11 show a peak around 395 K followed by a decrease in Q-DLTS signal up to a temperature around 420 K. Above



Figure 4.13: The Q-DLTS signal at 453 K as a function time and the thermalization energy with a 1-V bias.

temperatures of 420 K the Q-DLTS signal shows a more or less linear increase. The measurement on contact 1 with measurement cycle 2 clearly shows a steeper increase in Q-DLTS signal above 420 K than the other two measurements. As the Q-DLTS signal of the programmed device is higher than the signal of the un-programmed device in this temperature region, this could indicate that the defect-state distribution is influenced during the measurement by the 1-V bias. Further Figure 4.11 shows that the Q-DLTS signal for temperatures below 360 K is lower for the programmed device than for the un-programmed device.

We use the concept of thermalization energy to estimate the amount of change the 1-V bias from measurement cycle 2 induces during the recording of an entire Q-DLTS spectrum such as the spectrum shown in Figure 4.11. We determined the thermalization energy for the programming experiment in Figure 4.13. The thermalization energy is indicated by the top axis in Figure 4.13. To determine the thermalization energy we approximated the temperature during the heating of the sample by a staircase function where the temperature was constant over time intervals of 10 s. The staircase function approximated the linear function from 300 K to 453 K in 600 s. For the attempt-of-escape frequency for defect creation we used a value of 10^9 s^{-1} as determined by Flewitt *et al.* [76]. We found that after the heating of the sample the thermalization energy was 0.97 eV. As no measurements were carried during the heating of the sample this limits our analysis of the change in the defect-state distribution during bias annealing to thermalization energies above 0.97 eV.

Figure 4.14 shows the derivative of the Q-DLTS signal during the programming experiment in Figure 4.13 to the thermalization energy. As discussed in Section 4.4.1 this derivative reflects the distribution of energy barriers of two-level systems in the *a*-Si:H. Figure 4.14 shows that most energy barriers for the defect re-equilibration



Figure 4.14: The derivative of the Q-DLTS signal at 453 K to the thermalization energy. This derivative reflects the distribution of energy barriers of the two level systems in the *a*-Si:H.

process are in the range 1.0 - 1.3 eV, which is consistent with results published by Powell [36]. Note, however, that as we only monitored the change in Q-DLTS signal at 453 K and with a filter rate of 100 s⁻¹, this distribution therefore represents the barriers for the equilibration process of defect-states located in a limited energy range, namely the energy range corresponding to dangling bonds that have an emission rate around 100 s⁻¹ at a temperature of 453 K.

When we assume that the distribution of energy barriers for the defect-state equilibration process is independent of the energy level of a defect state, the programming characteristic in Figure 4.13 can be used to estimate how much the 1-V bias from measurement cycle 2 affects the defect-state distribution in the sample. In Figure 4.13 the Q-DLTS signal changes upon programming from 4.0 nC to 5.6 nC. We determined the thermalization energy for the measurement shown in Figure 4.11 on contact 1 with measurement cycle 2, and found that a thermalization energy of 1.11 eV corresponds to the measurement at a temperature of 453 K. For a thermalization energy of 1.11 eV, the Q-DLTS signal changes from about 4.0 nC to about 4.5 nC, which is 31.7 % of the total change in Figure 4.13. Similarly we find that for a thermalization energy of 1.07 eV the change in Q-DLTS signal is 18.4 % of the total change upon programming. A thermalization energy of 1.07 eV corresponds to the measurements at 435 K in Figure 4.11. At 433 K the difference between the signal of the programmed device and the un-programmed device in Figure 4.11 is $8.6 \cdot 10^{-10}$ C, both measured with measurement cycle 2. Assuming that at 433 K a thermalization energy of 1.07 eV also corresponds to 18.4 % change, we estimate that the Q-DLTS signal for the un-programmed device measured with measurement cycle 2 is $1.9 \cdot 10^{-10}$ C higher due to the 1-V bias of measurement cycle 2 and the resulting changes in defect-state distribution. This increase of $1.9 \cdot 10^{-10}$ C is 5.4 % of the actually measured signal.

4.5.2 Simulations

For the simulations we used the improved defect-pool model [50]. The simulated and measured Q-DLTS spectra are shown in Figure 4.15. The signal at high and low temperature deviates from the measured spectra. However, the simulated and measured position and height of the peak at a temperature around 390 K and the minimum at a temperature around 420 K correspond well.

The parameters for this simulation are listed in Table 4.1. In this table the parameters e_{00} and E_0 are the parameters for the emission rates from Eq. (4.5) and Eq. (4.23), respectively, where the superscript $^{+/0}$ refers to neutral defects, and $^{0/-}$ refers to negatively-charged defects. Other parameters are: E_{v0} is the valence-band tail slope, U is the correlation energy of the amphoteric defect states, σ_{dp} is the width of the defect pool, E_{μ} is the mobility gap, and E_{dp} is the position of the Gaussian defect-pool.

parameter	value
valence-band tail	
<i>e</i> ₀₀	$15 \ {\rm s}^{-1}$
E_0	0.045 eV
dangling bonds	
$e_{00}^{+/0}$	$8.0 \cdot 10^{03} \ \mathrm{s}^{-1}$
$E_0^{+/0}$	0.041 eV
$e_{00}^{0/-}$	$1.7 \cdot 10^{04} \ \mathrm{s}^{-1}$
$E_0^{0/-}$	0.041 eV
E_{μ}	1.75 eV
$\dot{E_{v0}}$	45 meV
U	0.20 eV
σ_{dp}	0.20 eV
E_{dp}	1.23 eV
T^{*}	453 K

Table 4.1: Parameter set for the Q-DLTS spectrum simulations

In the simulations the contact area was taken as $23 \cdot 10^{-6}$ m² instead of $16 \cdot 10^{-6}$ m². The larger contact area was chosen under the assumption that part of the Q-DLTS signal may originate from the periphery of the contact. Without this assumption the


Figure 4.15: The measured (symbols) and simulated (lines) Q-DLTS spectra. Open squares and dashed line: un-programmed device with measurement cycle 1, closed squares and solid line: un-programmed device with measurement cycle 2, and open circles and dashed-dotted line: device programmed with 1-V bias, measured and simulated with measurement cycle 2.

simulated Q-DLTS signal is about 30 % too low compared to the experimental Q-DLTS spectra. Note that collection from the periphery does not necessarily preserve the shape of the Q-DLTS spectrum as conductivity changes as a function of temperature my change the total area from where the Q-DLTS signal originates. Additionally the potential as a function of distance from the oxide/*a*-Si:H interface will not be the same in the surrounding of the contact as under the contact. Further away from the contact the change in occupation due to the applied bias voltages is less. As a result the changes in the position of the Fermi-level are less in the periphery than under the contact and the Q-DLTS signal from the periphery may therefore exaggerate the density of states near the Fermi-level with zero applied voltage.

The uncertainty about collection from the periphery inhibits estimating the absolute value for the density-of-states accurately from these measurements. The total density of dangling bonds in the bulk is $4.4 \cdot 10^{22}$ m³, which is in good agreement with commonly found values [50]. However, a defective interface layer has been observed adjacent to the oxide layer [75]. In our simulations we cannot discriminate between a contribution to the Q-DLTS signal of a possible defective interface layer and the contribution of the periphery of the contact. This is illustrated in Figure 4.16 which shows the simulated Q-DLTS spectrum with and without a defective interface layer adjacent to the oxide/*a*-Si:H interface. The defective interface layer was modeled by varying the valence-band tail slope of the first 10 nm of *a*-Si:H adjacent to the oxide/*a*-Si:H interface from 55 meV to 45 meV. Figure 4.16 shows the effect of such a defective layer mostly affects the magnitude of the signal and has a small influence



Figure 4.16: The simulated Q-DLTS spectrum with and without a defective interface layer adjacent to the oxide.

on the shape of the spectrum.

The extracted density-of-states for the un-programmed device are shown in Figure 4.17a as a function of energy at two positions in the device, "interface" refers the oxide/*a*-Si:H interface and "bulk" refers to the position at 350 nm distance from the oxide/*a*-Si:H interface. The density-of-states distributions for the same positions after programming are shown in Figure 4.17b. The dangling-bond concentration for the un-programmed and programmed device as a function of position is shown in Figure 4.17c. For the simulations we assumed no changes in the distribution of defect states during the measurements. We found that in our simulations we do not need to include a contribution of the conduction-band tail to explain the experimental Q-DLTS spectra. This indicates that with the rate-filter settings used the contribution of the conduction-band tail is located outside the measured temperature range.

In order to analyze the measurements from the previous section we show in Figure 4.18a the separated contributions from the emission of electrons from negative defects, $D^{0/-}$, neutral defects, $D^{+/0}$, and from the valence-band tail states. The simulation was carried out for the un-programmed device with measurement cycle 2. According to the simulations the first peak of the measurement at 390 K is due to negatively-charged defect states, the increase of the signal at temperatures above 420 K is due to the emission from neutral states and the valence-band tail. To obtain good fits we had to assume a different prefactor for the emission rate (e_{00}) for negatively-charged defect states than for neutral defect states.

For the extracted density-of-states distributions it is important to investigate where in the device the measured Q-DLTS signal comes from. In Figure 4.18b we show the cumulative contribution in percentage for various widths of a certain region adjacent to the oxide, i.e. the line for 10 nm indicates the contribution to the Q-DLTS signal



Figure 4.17: The extracted density-of-states distributions. (a) The density-of-states distribution as a function of energy for an un-programmed and programmed device. (b) The Dangling bond concentration as a function of position for the un-programmed and programmed device.

from the first 10 nm adjacent to the oxide, and the line 40 nm indicates the signal from the first 40 nm including the first 10 nm. The simulation was carried out for the un-programmed device with measurement cycle 2. It is important to realize that the spatial sensitivity is greatly influenced by the defect density-of-states near the interface. A higher defect-state distribution at the interface will result in more signal from this region and less from deeper in the device.

From the Figure 4.18b it can be seen that the signal at temperatures above 420 K is increasingly dominated by a thin region adjacent to the oxide. This can be explained by referring to the band diagram in Figure 4.10. The band diagram shows that the defect states near the valence-band mobility edge are only discharged in a thin region near the oxide interface. The temperature range from 340 K to 420 K comes from a relatively large region as in this temperature range the defects that discharge with a rate of 100 s^{-1} are located around mid-gap.

4.6 Conclusions and recommendations

The conclusions from this work on characterizing *a*-Si:H with the aid of Q-DLTS and the simulation of Q-DLTS with *ASA*, can be summarized as follows:

• We extended our device simulator *ASA* with a new model for Q-DLTS. With this model detailed simulations of Q-DLTS spectra can be carried out taking into account the spatial distribution of defect- and tail-states. The density-of-states distribution in *a*-Si:H can be extracted by fitting simulated Q-DLTS spectra to experimental Q-DLTS spectra.



Figure 4.18: a. The contributions to the Q-DLTS spectrum from negatively charged defects $D^{0/-}$, neutral defects $D^{+/0}$, and the valence-band tail. The contribution of the conduction-band tail was neglected. b.The spatial sensitivity of the simulated Q-DLTS spectra. The lines depict the cumulative contribution for of a certain region adjacent to the oxide where we varied the thickness of this region

- Due to the applied bias voltages the density-of-states distribution in *a*-Si:H can change during a Q-DLTS measurement. We have developed a model to estimate the amount of change during the Q-DLTS measurement.
- To minimize the change in defect-state distribution during a Q-DLTS measurement we developed a biasing scheme for carrying out Q-DLTS measurements. The new biasing scheme allows more freedom in choosing an appropriate bias voltage to minimize change in defect-state distribution during the measurement.
- We measured the Q-DLTS spectra for *a*-Si:H samples in un-programmed and ntype programmed state. By fitting simulated Q-DLTS spectra to experimental Q-DLTS spectra, we have extracted the density-of-states distribution in both energy and space coordinates. We were, however, not able to determine the density of states in absolute sense, as a part of the measured Q-DLTS spectrum originates from the periphery of the contact.

In order to determine accurately the influence of the 1-V bias on the defect-state distribution during a Q-DLTS measurement with measurement cycle 2, it is necessary to determine the change in Q-DLTS signal with a thermalization energy less than 0.97 eV. This could be obtained by carrying out a programming experiment at 400 K. Assuming a heating time of 600 s from 300 K to 400 K the thermalization energy after heating is about 0.88 eV. With the programming experiments presented in this chapter only the defect re-equilibration process was characterized in terms of the thermalization energy.

From the previous discussion it becomes clear that the chosen device structure has the disadvantage that it is not known if, and to what extend the measured Q-DLTS spectra originate from the periphery of the contact. The influence of the periphery on the measured Q-DLTS spectra may affect both magnitude and shape of the spectra. In order to remove the contribution of the periphery from the Q-DLTS signal the *a*-Si:H layer could be removed by etching. The chromium contact may serve as a mask. In principle the test structure could be further improved by adding a n-type doped layer between the Chromium contact end the intrinsic *a*-Si:H.

Deep Level Transient Spectroscopy

Chapter 5

Modeling of *µc***-Si:H solar cells**

5.1 Introduction

Hydrogenated micro-crystalline silicon (μ c-Si:H) is an attractive material for thinfilm silicon solar cells. In comparison to hydrogenated amorphous silicon (*a*-Si:H), μ c-Si:H is more stable to light exposure and has a lower bandgap. In particular the "micromorph" concept consisting of an *a*-Si:H top cell and a μ c-Si:H bottom cell [88] is a promising candidate for cheap and relatively stable thin-film silicon solar cells. With this type of solar cells Yamamoto *et al.* demonstrated a solar cell with an initial efficiency of 14.1 % [89]. Extensive work has been carried out on optical modeling [90–92] of μ c-Si:H solar cells, which has resulted in several light-trapping schemes in order to enhance the short-circuit current density in the cells [90]. For the optimization of the open-circuit voltage, V_{oc} , and fill factor, *FF*, the combined optical and electrical modeling can be a useful tool. It has been demonstrated that by applying several electrical and optical optimizations, in principle micromorph solar cell efficiencies of over 15 % can be reached [93].

Modeling of μc -Si:H silicon is complicated by its complex micro structural properties involving a mixed phase of crystalline and amorphous tissue, grain boundaries, inhomogeneity in the growth direction and columnar structure. The complex structural properties give rise to complex properties of electronic transport in the material, impeding a detailed analysis of its optoelectronic properties through numerical modeling.

There are two approaches to model μc -Si:H, the first approach uses separate amorphous and crystalline regions and grain boundaries [94, 95], in the second approach the various phases are replaced by a homogeneous effective medium [96]. Simu-

lations using different phases require separate input parameters for the grain boundaries, the amorphous tissue and the crystallites, adding to the complexity of the model. It is difficult to determine separate material parameters for the individual phases in the material from the macroscopic properties of the mixed phase material. Therefore the additional complexity of using separate phases to model μc -Si:H does not necessarily add to the accuracy of the model. Certainly as the feature sizes of grains and grain boundaries in μc -Si:H can be in a range where using the classical, statistical models to describe electronic processes in the material becomes imprecise [97]. In addition, accurate modeling of electronic transport in mixed phase material may require 2-D simulations, which are computation intensive and time consuming. Although including the separate phases of micro-crystalline materials in the simulations may be interesting from the physical point of view, it adds a complexity that is probably not desirable for many modeling purposes. In this work we will therefore apply the effective media approximation.

As we do not need to know the individual properties of the different phases, the effective medium approach alleviates the number of input parameters that need to be determined for μc -Si:H. Furthermore the effective medium material properties can, in principle, be determined from the macroscopic properties of the mixed phase material. However, the complex structural properties of μc -Si:H make it difficult to determine proper values for the model parameters. In particular the effective medium value of the mobility gap is controversial. Commonly a value of 1.1 eV is found, similar to the bandgap of *c*-Si [96, 98]. However, in other studies mobility gap values have been reported to be in the range of 1.48 – 1.59 eV [99, 100], depending on crystalline volume fraction.

This chapter introduces a method to determine the mobility gap of μc -Si:H using the dark current activation energy of μc -Si:H *pin* devices. The method is, in principle, valid for any *pin* device, where the recombination in the dark can be approximated with Shockley-Read-Hall (SRH) recombination, originating from mid-gap states in the intrinsic layer (e.g., *a*-Si:H *pin* devices). We derive a simple analytical model that describes the dark current activation energy and which is used to extract the mobility gap of the intrinsic layer of experimental *pin* devices.

We have determined the mobility gap on μc -Si:H material by applying our analytical model to measured dark current activation energies of μc -Si:H *pin* devices. As our analytical model is based on several approximations we compare the analytical model with detailed numerical simulations. Furthermore, using numerical simulations, we investigate the influence on the dark current activation energy of the band-tails, of an amorphous incubation layer, and of a defect-rich interface layer.

The chapter is outlined as follows: In Section 5.2 we discuss the general properties of μc -Si:H and which models are appropriate to use for modeling μc -Si:H material. The method for determining the mobility gap of μc -Si:H using the temperature characteristics of a μ *c*-Si:H solar cell is presented in 5.3. In Section 5.4 we discuss appropriate values for model parameters for the simulation of μ *c*-Si:H solar cells and compare the simulations with experimental results. Furthermore, in Section 5.4.2, we investigate the influence on the dark current activation energy of the band-tails, of an amorphous incubation layer, and of a defect-rich interface layer.

5.2 Properties and modeling of μc -Si:H

5.2.1 Growth and structural properties of μc -Si:H

In literature μc -Si:H is used as a general term for a mixed phase material consisting of varying amounts of c-Si nano-crystallites, a-Si:H, and grain boundaries. Typically a *uc*-Si:H layer shows inhomogeneity in the growth direction. Three phases can be distinguished; an *a*-Si:H incubation phase, a crystallization phase and a phase with a saturated crystalline fraction [41, 101–103]. The thickness and composition of each phase strongly depends on the deposition condition and the substrate used. During deposition nucleation of the crystallites starts after the amorphous incubation phase. During the following crystallization phase columnar agglomerates of crystallites are formed. The diameter of these columns increases with film thickness at the expense of the a-Si:H fraction, resulting in the typical conical shape of the columns during the crystallization phase. Beyond a certain thickness, a saturated crystalline fraction is reached. The diameters of the crystallites have been found to be in the order of 4-30nm [103–105]. For the columnar agglomerates of crystallites diameters in the range of 20 - 500 nm have been reported [103–105]. Figure 5.1 shows a schematic picture of typical compositions and structures found in μc -Si:H. From left to right the composition changes from amorphous to highly crystalline. The presence of crystalline grains, grain boundaries, the columnar structure, and the presence of a-Si:H tissue all influence the transport properties in μc -Si:H. We will address electronic transport in *µc*-Si:H in the next section.

5.2.2 Modeling of electronic transport in μc -Si:H

Much work has been carried out to investigate the electrical transport properties of μc -Si:H [94, 95, 102, 105–112]. In this section we will give a short review of the transport properties of μc -Si:H and how these properties can be taken into account in our numerical simulations. As our aim is to model solar cells we will only consider current flow along the growth direction of the film and we will therefore not discuss the anisotropic properties of μc -Si:H. As the lateral dimensions of solar cells are far greater than the size of the features influencing the anisotropic transport prop-



Figure 5.1: Schematic presentation of the structural properties of μc -Si:H. From left to right the composition changes from amorphous to highly crystalline (after Collins *et al.* [41]).

erties (i.e. columnar growth [110]) it is sufficient to describe the average transport properties for currents along the growth direction of the film.

The Arrhenius plot of the dark conductivity of μc -Si:H is usually non-linear and drift mobility measurements show that electronic transport in μc -Si:H is highly dispersive [107, 108, 111]. To account for these effects several transport mechanisms have been proposed.

Barrier limited transport The barrier limited transport model was originally developed by Seto [113] to model transport in polycrystalline silicon. In the barrier limited transport model electrons trapped at grain boundaries give rise to potential barriers. The mobility of the charge carriers is then limited by the potential barriers as the charge carriers need to overcome these barriers by thermionic emission. Recently, the barrier limited transport models were extended to include tunneling effects in order to describe the Hall mobility in n-type μc -Si:H [112]. However, there are indications that the grain boundaries between the crystallites in μ c-Si:H do not form potential barriers. Ruff et al. [111] studied the transport properties of μc -Si:H by analyzing the temperature dependent dark conductivity. He argues that for their *intrinsic* µc-Si:H samples it is not possible that the grain boundaries between the crystallites form potential barriers as this would require such a large number of trapped electrons this would require the Fermi-level to be close to the conduction band. However, it is still possible that the boundaries between the *columns* act as potential barriers. We therefore conclude that barrier limited transport may play a role when the Fermi-level is close to the conduction band and in coplanar transport in μc -Si:H films.

Multiple-trapping in band tails Several studies indicate that the multiple trapping

model can be used to explain Time-of-Flight measurements and the drift mobilities in μc -Si:H [107, 108, 114]. In a multiple trapping model charge carriers have a fixed mobility in extended states and are immobile when they are trapped in localized states. The temperature dependency of the drift mobility and the dispersive transport properties of μc -Si:H are then explained by the dynamics of trapping of charge carriers on localized states and the thermal emission of charge carriers from localized states.

Potential fluctuations Ruff *et al.* [111] suggests that the activation energy of the dark conductivity may also be explained by a model developed by Overhof *et al.* [115] that attributes the temperature activated behavior to potential fluctuations caused by inhomogeneously distributed charged centers.

The discovery that dispersive transport and temperature dependence of drift mobilities can be explained using a multiple trapping model is important as it implies that we can treat electronic transport the same way it has been treated for *a*-Si:H, and that the basic assumptions of the multiple trapping model can be used [47]:

- There is a mobility edge, separating states with a finite mobility and states with zero mobility.
- The mobility edge is sharp with respect to the localized tail-state distribution.
- The localized tail-states are distributed exponentially in energy.
- The localized states have energy independent capture cross-sections.

As the multiple trapping model can already account for the non-linear Arrhenius plot of the dark conductivity of μc -Si:H, we will not, in addition, assume the grain boundaries act like potential barriers, regardless of the position of the Fermi-level.

It was suggested by Overhof *et al.* [106] that conduction through μc -Si:H takes place through a percolation path. Percolation theory describes the behavior of connected clusters in a random graph. Overhof applied percolation theory to electronic transport in μc -Si:H where he assumed that the electronic transport to take place predominately through clusters of crystallites. For the transport to be dominated by transport through clusters of crystallites the crystalline volume fraction must be high enough for the material to contain clusters that make long range connections, i.e. the crystalline volume fraction must be higher than the percolation threshold. As in this work the effective medium approach is used we do not take into account separate crystallites or clusters of crystallites. However, whether transport takes place through a long range clusters of crystallites, or "percolation-path", can be of influence on the relation between effective media material properties and the observed macroscopic properties of the material. When conduction takes place through percolation-paths, the properties of the crystallites and the barriers in-between the crystallites determine the transport properties where the amorphous phase has little influence on electronic transport. Thus, in describing electronic transport the properties of the crystallites are more influential than the properties of the amorphous phase, requiring the characterization of the individual phase of the crystallites, for example in terms of the mobility gap and the density of localized defect states. In this work we follow the percolation theory of electronic transport in μc -Si:H. In Section 5.4.1 we will discuss in detail the parameter values we use for our simulations of μc -Si:H solar cells and how these parameters are determined. However, we will first investigate the value of the mobility gap in Section 5.3 as the correct value of the mobility gap is not only essential for accurate modeling of μc -Si:H solar cells, its value is also highly controversial.

5.3 Determination of the mobility gap in μc-Si:H solar cells

As mentioned in the introduction the mobility gap of μc -Si:H is controversial. On the one hand several authors have reported values near 1.1 eV [96,98], on the other hand values have been reported in the range of 1.48 - 1.59 eV [99,100]. This section introduces a method to determine the mobility gap of μc -Si:H using the dark current activation energy of μc -Si:H *pin* devices. The method is, in principle, valid for any *pin* device, where the recombination in the dark can be approximated with Shockley-Read-Hall (SRH) recombination, originating from mid-gap states in the intrinsic layer (e.g., *a*-Si:H *pin* devices). We derive a simple analytical model that describes the dark current activation energy and which is used to extract the mobility gap of the intrinsic layer of experimental *pin* devices.

The dark current is written as the integral of the recombination through the device including surface recombination at the contacts. Recombination in *a*-Si:H and μc -Si:H materials is dominated by recombination via dangling-bond and tail-states. These recombination processes are limited by the minority carrier concentration. As in the doped layers and at the contacts the minority carrier concentrations are low, the recombination in *a*-Si:H and μc -Si:H pin devices is dominated by recombination in the intrinsic layer. We therefore approximate the dark current through this type of *pin* device by the integral of the recombination rate in the intrinsic layer

$$J = q \int_0^W R(x) \mathrm{d}x,\tag{5.1}$$

where W is the width of the intrinsic layer, q is the elementary charge, and R(x) is

the recombination as a function of the position, x. In the next two sections we will derive an expression for the thermal activation energy of Eq. (5.1). In our derivation we approximate the recombination via the amphoteric dangling-bond states with SRH recombination (i.e., the decoupled approach). The derivation presented here is similar to the derivation of the dark J-V characteristics of a-Si:H pin devices from Berkel et al. [116]. However, in order to understand under which circumstances the determined expressions for the dark current activation energy are valid, it is useful to explicitly derive the activation energy of SRH recombination processes as a function of position and trap energy in a pin device. We therefore first derive general expressions for the thermal activation energy of SRH recombination as a function of trap energy in Section 5.3.1. In Section 5.3.2 we will apply the results of Section 5.3.1 to a pin device and determine the dark current activation energy.

5.3.1 Activation energy of SRH recombination

In deriving the activation energy of SRH recombination processes we will, for simplicity, use the following approximations:

- We take the capture cross-sections for electrons and holes equal ($\sigma_n = \sigma_p = \sigma$)
- We take the effective density of states in the valence and conduction band equal $(N_c = N_v = N)$ and thus:

$$n = N \exp\left(\frac{E_{fn} - E_c}{kT}\right) \tag{5.2}$$

$$p = N \exp\left(\frac{E_v - E_{fp}}{kT}\right) \tag{5.3}$$

According to the Taylor and Simmons approximation (see Section 3.1) the recombination efficiency of a trap depends on the energy level of the trap with respect to the quasi-Fermi levels for trapped charge. Taking the listed approximations into account we rewrite Eq. (3.32) for the recombination efficiency:

$$\eta_R(E_t) = \begin{cases} v_{th} \sigma_{n+p}^{np} \left[1 + \exp\left(\frac{E_t - E_{fn_t}}{kT}\right) \right]^{-1} & E_t > E_{\mu}/2 \\ v_{th} \sigma_{n+p}^{np} \left[1 + \exp\left(\frac{E_{fp_t} - E_t}{kT}\right) \right]^{-1} & E_t < E_{\mu}/2 \end{cases},$$
(5.4)

where v_{th} is the thermal velocity, E_{fn_t} and E_{fp_t} are the quasi-Fermi levels for trapped electrons and holes, respectively, E_t is the energy of the trap level, and E_{μ} is the mobility gap. Using the same approximations the quasi-Fermi levels for trapped charge

(Eq. (3.28) Eq. (3.31)) become:

$$E_{fn_t} = E_c + kT \ln\left(\frac{n+p}{N}\right) \tag{5.5}$$

$$E_{fp_l} = E_v - kT \ln\left(\frac{n+p}{N}\right).$$
(5.6)

Under the listed assumptions the quasi-Fermi-levels for trapped charge are located symmetrically around mid-gap, i.e. the distance between the quasi-Fermi level for trapped electrons and the conduction band edge is equal to the distance between the quasi-Fermi level for trapped holes and the valence band edge. Furthermore, the quasi-Fermi level for the majority carriers is approximately equal to the quasi-Fermi level for trapped majority carriers $|E_{fn_t,p_t} - E_{fn,p}| \le kT \ln(2)$, where E_{fn_t,p_t} and $E_{fn,p}$ refer to the quasi-Fermi levels for the *majority* carriers). In the following derivation of the activation energy of SRH recombination processes, we make use of the symmetry around mid-gap by first considering only traps in the upper half of the bandgap ($E_t > E_{\mu}/2$), and then determine the activation energy of traps located in the lower half from the symmetry around mid-gap.

We approximate Eq. (5.4) by substituting the expression between brackets on the right with 1, when $E_t \leq E_{fn_t}$, and $\exp\left(\frac{E_{fn_t}-E_t}{kT}\right)$, for $E_t > E_{fn_t}$, as illustrated in Figure 5.2. Eq. (5.4) then becomes:

$$\eta_R(E_t) = \begin{cases} v_{th} \sigma_{n+p}^{np} & E_t \le E_{fn_t} \\ v_{th} \sigma_{n+p}^{np} \cdot \exp\left(\frac{E_{fn_t} - E_t}{kT}\right) & E_t > E_{fn_t} \end{cases}$$
(5.7)

Note that this approximation is not particulary good around the quasi-Fermi levels for trapped charge, as can be seen from Figure 5.2. For an energy difference of more than 3kT between trap energy and a quasi-Fermi level for trapped charge, the error introduced by this approximation is less than 5 %.

At this point it is important to note that several of the used parameters are temperature dependent. It will not come as a surprise that the thermal velocity is temperature dependent. The thermal velocity follows the following temperature dependent relation [117]:

$$v_{th} = \sqrt{\frac{3kT}{m_e^*}},\tag{5.8}$$



Figure 5.2: Illstration of the approximation we make in Eq. (5.7) to simplify the recombination efficiency according to the Taylor and Simmons approximation in Eq. (5.4). The difference between the recombination efficiency according to the Taylor and Simmons approximation (solid line) and according to our approximation in Eq. (5.7) (dashed line) is indicated by the gray area. The error is largest around the quasi-Fermi levels for trapped charge.

where m_e^* is the effective electron mass. Also the effective density of states is temperature dependent and can be written as [117]:

$$N = N_{T_0} \left(\frac{T}{T_0}\right)^{\frac{3}{2}},$$
(5.9)

where N_{T_0} is the effective density of states at temperature T_0 . Substitution of Eq. (5.8) and Eq. (5.9) in Eq. (5.7) and rearranging terms gives:

$$\eta_R(E_t) = \begin{cases} \sqrt{\frac{3k}{m_e^* T_0^3}} \sigma T^2 \frac{\tilde{n}\tilde{p}}{\tilde{n}+\tilde{p}} & E \le E_{fn_t} \\ \sqrt{\frac{3k}{m_e^* T_0^3}} \sigma T^2 \frac{\tilde{n}\tilde{p}}{\tilde{n}+\tilde{p}} \cdot \exp\left(\frac{E_{fn_t}-E_t}{kT}\right) & E_t > E_{fn_t} \end{cases},$$
(5.10)

where \tilde{n} and \tilde{p} are the electron and hole concentrations, respectively, where we take temperature independent effective density of states (i.e., we substitute the temperature dependent *N* with the temperature independent N_{T_0} in Eqs. (5.2) and (5.3)).

We define the thermal activation energy of a quantity *X* as

$$E_a = -\frac{\partial \left[\ln \left(X \left(\left[(kT)^{-1} \right] \right) \right) \right]}{\partial \left[(kT)^{-1} \right]}.$$
(5.11)

The term $\frac{np}{n+p}$ in the expressions for the recombination efficiency is approximately equal to the minority carrier concentration when $n \gg p$ and when $p \gg n$. Therefore, this term reflects that the recombination efficiency is limited by the least available carrier and thus its activation energy equals the activation energy of the minority carrier concentration, E_a^m . The activation energy of the minority carrier concentration is equal to the maximum energy distance of either quasi-Fermi level with its respective band. We write:

$$E_a^m \equiv \begin{cases} E_{fp} - E_v & n \ge p \\ E_c - E_{fn} & n
(5.12)$$

When there is no minority carrier (i.e. $n \approx p$), $\frac{np}{n+p}$ reduces to approximately half of either carrier concentration. Note that also in this case Eq. (5.12) holds as in then the activation energies of both electrons and holes are approximately equal.

Applying Eq. (5.11) to the remaining terms of Eq. (5.10) we obtain for the activation energy of the recombination efficiency:

$$E_{a}^{R}(E_{t}) = \begin{cases} E_{a}^{m} + 2kT & E_{t} \leq E_{fn_{t}} \\ E_{a}^{m} + 2kT - E_{fn_{t}} + E_{t} & E_{t} > E_{fn_{t}} \end{cases},$$
(5.13)

where the term 2kT reflects the temperature dependencies of the thermal velocity and the effective density of states.

Finally, we use the symmetry argument to derive the activation energy of the recombination efficiency of traps located in the lower half of the bandgap and obtain:

$$E_a^R(E_t) = \begin{cases} E_a^m + E_{fp_t} - E_t + 2kT & E_t < E_{fp_t} \\ E_a^m + 2kT & E_{fp_t} \le E_t \le E_{fn_t} \\ E_a^m - E_{fn_t} + E_t + 2kT & E_t > E_{fn_t} \end{cases}$$
(5.14)

We recall that the quasi-Fermi-levels for trapped charge are located symmetrically around mid-gap and the quasi-Fermi level for the majority carriers is approximately equal to the quasi-Fermi level for trapped majority carriers. Using this result we approximate Eq. (5.14) as:

$$E_{a}^{R}(E_{t}) \approx \begin{cases} -\Delta E_{fnp} + E_{c} - E_{t} + 2kT & E_{t} < E_{fp_{t}} \\ E_{a}^{m} + 2kT & E_{fp_{t}} \leq E_{t} \leq E_{fn_{t}} \\ E_{\mu} - \Delta E_{fnp} + E_{t} - E_{c} + 2kT & E_{t} > E_{fn_{t}} \end{cases}$$
(5.15)

where ΔE_{fnp} is the separation between quasi-Fermi levels $(E_{fn} - E_{fp})$. The relation in Eq. (5.15) is illustrated in Figure 5.3. Between the quasi-Fermi levels for trapped charge the activation energy of the recombination efficiency is equal to $E_a^m + 2kT$. Outside the energy range between the quasi-Fermi-levels for trapped charge, the ac-



Figure 5.3: Activation energy of recombination processes as a function of trap energy

tivation energy increases linearly towards the band edges and the activation energy at the band edges is equal to $E_{\mu} - \Delta E_{fnp} + 2kT$.

5.3.2 Activation energy of a *pin* device

For the derivation of an analytical expression of the activation energy of a *pin* device we make the additional approximations that the separation between the quasi-Fermi levels is equal to the applied voltage, V, and the quasi-Fermi levels are constant in the device with respect to the potentials at the contacts. Furthermore, we assume that the electric field in the device is uniform. With these assumptions, we can draw a schematic band diagram, as is shown in Figure 5.4a. As the electric field and the quasi-Fermi levels are constant, the separations between the quasi-Fermi levels and their respective bands become linear functions of position. We therefore write for the carrier concentrations in the intrinsic layer:

$$n = n_0 \exp\left(-\frac{E_0(x-x_0)}{kT}\right) \tag{5.16}$$

$$p = p_0 \exp\left(\frac{E_0(x-x_0)}{kT}\right), \qquad (5.17)$$

where E_0 is the uniform electric field in the intrinsic layer, n_0 and p_0 are the electron and hole concentration, respectively, at position x_0 in the intrinsic layer. For convenience we define x_0 such that $n_0 = p_0$. From Eq. (5.4) it follows that the recombination efficiency scales with the term $\frac{np}{n+p}$. In Figure 5.4b the term $\frac{np}{n+p}$ is schematically shown as a function of position in the *pin* device. Using Eq. (5.16) and Eq. (5.17)



Figure 5.4: Schematic band-diagram with corresponding term $\frac{np}{n+p}$ as a function of position. (a) Schematic band diagram of a *pin* device. Indicated are the voltage *V* and the quasi-Fermi levels for electrons and holes (E_{fn} and E_{fp} , respectively), and the quasi-Fermi levels for trapped electrons and holes (E_{fn_t} and E_{fp_t} , respectively). The gray area depicts the energy range between the quasi-Fermi levels for trapped electrons and holes. (b) Schematic figure of the term $\frac{np}{n+p}$ as a function of position in the device.

and substituting $n_0 = p_0$, we write:

$$\frac{np}{n+p} = \frac{n_0}{\exp\left(\frac{E_0(x-x_0)}{kT}\right) + \exp\left(\frac{-E_0(x-x_0)}{kT}\right)},$$
(5.18)

Eq. (5.18) peaks at x_0 , where the carrier concentrations are equal, and decays exponentially in either direction away from x_0 .

To a first order approximation we assume the recombination takes place between the quasi-Fermi levels for trapped charge (the Taylor and Simmons 0 K approximation [58]). Furthermore we assume that the recombination rate profile in the device follows $\frac{np}{n+p}$, i.e., the spatial variation in trap state density is small compared to the spatial variation in the term $\frac{np}{n+p}$. In case the spatial variation in trap state density is small we can leave out the trap state density and integrate the recombination efficiency over the width of the intrinsic layer. Although this integral does not give us the current as we do not take into account the density of states, this does provide us the temperature dependency of the recombination, provided the density of states is temperature independent. The integral of Eq. (5.18) over the intrinsic layer:

$$\int_{0}^{W} \frac{np}{n+p} dx = \int_{0}^{W} \frac{n_{0}}{\exp\left(\frac{E_{0}(x-x_{0})}{kT}\right) + \exp\left(\frac{-E_{0}(x-x_{0})}{kT}\right)} dx$$
$$= \frac{n_{0}kT}{E_{0}} \left[\arctan\left(\exp\left[\frac{E_{0}(x-x_{0})}{kT}\right]\right)\right]_{x=0}^{x=W}$$
$$\approx \frac{n_{0}kT}{E_{0}}\pi.$$
(5.19)

We first determine the activation energy of the term n_0 . At x_0 the quasi-Fermi levels are located symmetrically around mid-gap. As the separation of the quasi-Fermi levels is equal to *V*, it follows that $E_a^m = \frac{E_\mu - V}{2}$. Thus, using Eq. (5.15), the activation energy of n_0 is equal to:

$$E_a^R = E_a^m + 2kT = \frac{E_\mu - V}{2} + 2kT.$$
 (5.20)

Using Eq. (5.11) the activation energy of the expression obtained in Eq. (5.19) then becomes

$$E_a^{pin} = \frac{E_\mu - V}{2} + 3kT.$$
 (5.21)

Our assumption that the electric field is uniform in the device is not very realistic. In practice band bending at the p-i and the i-n interface results in a reduction of the electric field in the middle of the device. However, the recombination is highest where $n \approx p$, which naturally leads to a space charge close to zero. Therefore the electric field actually is fairly uniform in the most relevant part of the integral in Eq. (5.19). The integral of the recombination over the entire intrinsic layer can thus be approximated by changing the integration interval to x = [a, b] in Eq. (5.19), such that the integration interval excludes the regions with strong band bending at the p-i and i-n interfaces. The electric field should, in this case, represent the electric field at x_0 . The dark current activation energy is therefore not sensitive to the exact electric field distribution in the device.

By applying the inverse of Eq. (5.11) to Eq. (5.21) we find that the current as a function of voltage and temperature is proportional to:

$$J \propto T^3 \exp\left(\frac{V - E_{\mu}}{2kT}\right),$$
 (5.22)

which corresponds to the diode equation with an ideality factor of 2. It is well known that the ideality factor of *a*-Si:H and μc -Si:H devices is, in general, smaller than 2.

There are several explanations of this effect. According to Berkel *et al.* [116], the energy distribution of traps influences the ideality factor when the number of traps between the quasi-Fermi levels for trapped charge varies strongly with the applied voltage. He attributes ideality factors less than 2 in *a*-Si:H *pin* diodes to this voltage dependency of the number active recombination centers. However, this effect on the ideality factor is independent of temperature and therefore will not affect the slope of dark current activation energy versus the voltage. We therefore define the "thermalideality factor" as the denominator in Eq. (5.21). We ascribe differences between the thermal-ideality factor and the ideality factor determined from J-V characteristics to a voltage dependency of the number of active recombination centers.

Also spatial effects may lead to an ideality factor less than 2. The activation energy of recombination processes in a pin device depend on the activation energy of the minority carrier concentration. This activation energy is not constant through the device. As a consequence the dark current activation energy, and thus also the ideality factor, depends on the spatial distribution of the recombination rate [118, 119]. The effect of the spatial variation of the activation energy of the minority carrier concentration is taken into account in the integral of Eq. (5.19), leading to a difference of kT between Eq. (5.20) and Eq. (5.21). However, as the integral in Eq. (5.19) is over the recombination *efficiency*, this result is only valid as long as the spatial variation in defect density is small compared to the spatial variation in recombination efficiency. In case of a highly inhomogeneous defect state distribution, a significant part of the recombination could take place in a region where $n \not\approx p$, and hence $E_a^m > \frac{E_\mu - V}{2}$. For the extreme case we evaluate the activation energy for recombination at an interface with a doped layer, where the quasi-Fermi level of the majority carriers is pinned. Due to this pinning of the quasi-Fermi level for majority carriers, E_a^m varies linearly with the applied voltage and therefore the slope of the activation energy versus the voltage is -1 for these recombination processes, hence the thermal-ideality factor for these recombination processes is 1. Similarly, recombination via traps outside the energy range confined by the quasi-Fermi levels for trapped charge, leads to changes in the thermal-ideality factor. From Eq. (5.15) it follows that the thermal-ideality factor for these recombination processes is 1 ($\Delta E_{fnp} = V$). Note that due to the steep band tails in μc -Si:H a significant portion of the tail-state recombination may take place outside the energy range between the quasi-Fermi levels for trapped charge.

The analytical model that was presented in this section is based on many approximations, such as a uniform field, the Taylor and Simmons approximation, the decoupled approach for amphoteric states, etc.. Furthermore, both the effect of a inhomogeneous spatial distribution of defect states and recombination via traps outside the energy range confined by the quasi-Fermi levels for trapped charge may play a role in the dark current activation energy μc -Si:H *pin* devices. In Section 5.4 we



Figure 5.5: Schematic presentation of the etching of the μ *c*-Si:H solar cells. (a) A solar cell after deposition of the back contact. (b) A solar cell after etching of the ZnO in a HCl solution. (c) A solar cell after removal of the silicon layer stack with reactive ion etching.

therefore compare the analytical model with a detailed numerical model to verify the approximations and in Section 5.4 we analyze the influence of tail-state recombination or the presence of a defect-rich or amorphous interface layer on the dark current activation energy. However, before we discuss numerical simulations we present in the next section experimental results for μ c-Si:H solar cells of which we determine the mobility gap using the dark current activation energy.

5.3.3 Experimental

In order to measure the current through a μ c-Si:H solar cell accurately at low bias voltages, it is important to prevent current spreading (see Section 2.4). This is achieved by removing the silicon in the surroundings of the contacts, leaving patterned solar cells. The μ c-Si:H solar cells consisted of a glass substrate covered with ZnO, a 15 – 20 nm μ c-Si:H p-layer, a 1.15 μ m μ c-Si:H intrinsic layer, and a 15 – 20 nm *a*-Si:H n-layer. The back contact and reflector consists of a ZnO(80 nm)/Al(300 nm)/Cr(50 nm) stack. After deposition of the cells the surroundings of the contacts were etched away in two steps, as illustrated in Figure 5.5. First the ZnO of the back contact layer stack was etched around the metal contacts in a HCl solution; during this step the Cr layer prevented etching of the underlying Al and ZnO. Subsequently the silicon layer stack was removed using reactive ion etching. The solar cell parameters for the etched solar cell are: an efficiency of 7.2 %, a short-circuit current density of 20.8 mAcm⁻², an open-circuit voltage of 0.49 V, and a fill factor of 72 %.

We measured the dark current of the cells at 289 K, 298 K, 308 K, and 323 K. In Figure 5.6a and Figure 5.6b typical dark J-V characteristics at different temperatures are shown of two patterned cells, Cell 1 (Figure 5.6a) and Cell 2 (Figure 5.6b). Cell 2 still shows a shunt resistance for bias voltages below 0.25 V at a temperature of 289 K. The origin of this shunt resistance is not clear, however, the effect of the

shunt resistance on the J-V characteristics becomes less pronounced at higher temperatures. Thus, we conclude that the thermal activation energy of this shunt is lower than the activation energy of the exponential current voltage relation that dominates the current at bias voltages above 0.25 V. Figure 5.6c shows the dark current activation energy for the two cells. The low activation energy of the shunt resistance of Cell 2 has a large effect on the activation energy at voltages below 0.25 V. The dark current activation energy of the cells without shunt resistance follows the predicted linear voltage dependency for low forward bias voltages (between 0 V to 0.3 V). Using Eq. (5.21) the mobility gap was determined as 1.19 eV from the dark current activation energy, which is the average mobility gap determined on the interval from 0 V to 0.3 V. In Figure 5.6c the expression from Eq. (5.21) is plotted for the extracted mobility gap of 1.19 eV, which also shows that the slope of the activation energy versus voltage is -0.5 from 0 V to 0.3 V, and thus the thermal-ideality factor is 2. In comparison, the ideality factor of the J-V characteristics in the same voltage range is 1.6, which shows that the ideality factor indeed is affected by the number of active recombination centers. Furthermore, the thermal-ideality factor of 2 in this voltage range suggests that Eq. (5.21) is valid as for these forward bias voltages there is no indication of a significant influence of tail-state recombination or the presence of a defect-rich or amorphous interface layer on the dark current activation energy. In Figure 5.6.d the Arrhenius plot of the dark current at several bias voltages is shown. It can be seen that the Arrhenius plots are quite linear over the measured temperature range and voltage range, as indicated by the error bars in Figure 5.6.c. The linearity of the Arrhenius plots shows that over the measured temperature range the band mobility and mobility gap do not change significantly.

5.3.4 Discussion

From the dark current activation energy of μc -Si:H *pin* devices, we determined the mobility gap of the intrinsic layer as 1.19 eV. Xu *et al.* [99] carried out internal photo-emission measurements to determine band offsets between p-type μc -Si:H and *a*-Si:H and found a mobility gap for μc -Si:H of 1.59 eV for a crystalline volume fraction of 80 %. Hamma *et al.* [100] determined the mobility gap of μc -Si:H using *in situ* contact potential measurements combined with dark conductivity activation energy measurements and found mobility gaps of 1.48 eV and 1.55 eV, for material with a crystalline fraction of 70 % and 30 %, respectively. Xu *et al.* [99] explain the difference between the mobility gap of μc -Si:H and the bandgap of crystalline silicon with quantum-size effects. However, Carius *et al.* [98] report that the optical bandgap of crystallites in μc -Si:H does not show a large influence of quantum-size effects and is close to the bandgap of crystalline silicon.

If the mobility gap of the material would be significantly higher than the bandgap



Figure 5.6: The characteristics of the prepared isolated solar cells. (a) The dark J-V characteristics of Cell 1, a cell without shunting effects, at 289 K, 298 K, 308 K, and 323 K. (b) The dark J-V characteristics of Cell 2, a cell with shunting effects, at 290 K, 298 K, 309 K, and 323 K. (c) The activation energy of Cell 1 and Cell 2 as a function of bias voltage. The analytical model from Eq. (5.21) is plotted for a mobility gap of 1.19 eV. (d) Arrhenius plots of Cell 1 at various bias voltages and the linear least squares fits to the Arrhenius plots to determine the activation energy. The Arrhenius plots are linear in the measured temperature range.

of the crystallites, many band states in the crystallites would be localized, or at least confined to the crystallites and electronic transport would not take place through these states. Such localization of band-states in the crystallites would effectively turn these band-states into trap-states. Even for low crystalline volume fractions such large concentration of trap-states would render the material poorly conductive and difficult to dope. As μc -Si:H solar cells with relatively high efficiencies have been be obtained, we conclude that for the material in these devices the band-states of the crystallites are not acting as trap-states and therefore the mobility gap of the mixed phase material is close to the bandgap of the crystallites. In light of the percolation theory of electronic transport in μc -Si:H we therefore expevt that for material with a crystalline volume

fraction below the percolation threshold, the mobility gap is determined by the amorphous phase as the crystalline phase does not provide long range connections. For crystalline volume fraction above the percolation threshold, we expect that the mobility gap of the material assumes a value close to the bandgap of the crystallites, as conduction primarily takes place through the crystalline phase.

The determined value for the mobility gap of μc -Si:H of 1.19 eV is much closer to the bandgap of c-Si (1.1 eV) than to the mobility gap of a-Si:H and thus, as expected from the percolation theory of conduction in μc -Si:H, the mobility gap of μc -Si:H is primarily determined by the crystalline phase rather than by the amorphous phase. The difference of 70 meV between the determined mobility gap and the bandgap of c-Si may be caused by quantum confinement, however, it may also be related to the assumption of abrupt mobility edges. In case the mobility edges are not abrupt, it is expected that the measured mobility gap increases with temperature [26]. In the limited temperature range of our experiments we have not observed a strong temperature dependency of the mobility gap (i.e. the Arrhenius-plots are linear over the measured temperature range, as indicated by the small error-bars in Figure 5.6c over the relevant voltage range).

5.4 Simulation results

5.4.1 Model parameters for μc -Si:H

In order to study the dark current activation energy of μc -Si:H *pin* devices in more detail, we carried out numerical simulations using the ASA program. For the simulations we use the effective medium approximation. For experimental reference results we use the same solar cells as in Section 5.3. Apart from the mobility gap, which we already determined, we determine input parameters for our simulations from literature, through physical arguments, or by fitting the simulation results to experimental results.

- **Mobility gap** The mobility gap μc -Si:H was determined as 1.19 eV from the dark current activation energy of a μc -Si:H solar cell (see Section 5.3).
- Effective density of states As discussed in Section 5.2 we assume that electronic transport predominantly takes place through clusters of crystallites. We therefore expect the transport properties of μc -Si:H to be mainly determined by the properties of the crystallites. In addition it means that as the current flows through only a fraction of the volume (i.e. the long range clusters of crystallites), only the transport states of this fraction of the material are relevant for the description of electronic transport. The effective density of states should

therefore scale with the number and size of the clusters of crystallites making long range connections. For simplicity we will assume the effective density of states scales linearly with the crystalline volume fraction. Due to the similarities in mobility gap of μc -Si:H and bandgap of c-Si we assume that the band structure of the crystallites is similar to the band structure in c-Si and therefore we assume the effective density of states in the crystallites is equal to the effective density of states of c-Si ($N_c = 2.8 \cdot 10^{25} \text{m}^{-3}$, and $N_v = 1.0 \cdot 10^{25} \text{m}^{-3}$ at 300 K).

- **Band offsets** By assuming conduction takes place through clusters of crystallites and assuming that the band structure of the crystallites similar to *c*-Si, the band offsets between μc -Si:H and *a*-Si:H should be approximately equal to the band offsets between *c*-Si and *a*-Si:H. Matsuura *et al.* [83] used C-V and J-V measurements to determine the band offset in the conduction band as 0.15 eV, where the electron affinity of *a*-Si:H was determined as 3.98 eV and of *c*-Si was assumed to be 4.13 eV. Similarly, Smidt *et al.* [120] found a conduction band offset of 0.14 eV at a μc -Si:H/*a*-Si:H heterojunction.
- **Band Mobility** Recently, measurements on μc -Si:H thin-film transistors have shown conduction band mobilities of $50 \cdot 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ [121]. In general the hole mobility is found to be about 3 times lower and therefore we assume a hole mobility of $15 \cdot 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$.
- Band tails As discussed in Section 5.2 we assume exponential tails. TOF measurements on μc -Si:H revealed a width of 31 meV for the valence-band tail [108, 122]. From transient photocurrent in μc -Si:H devices a width of 33 meV has been inferred for the conduction-band [123]. Furthermore simulation of photoluminescence of *µc*-Si:H, assuming the same slope for the valence and conduction-band, yield a characteristic energy of 31 meV [124]. In all these results the slope of the band tails is assumed to be constant in temperature, which is not the case for a-Si:H [125, 126]. In a-Si:H the band tails seem to exhibit a freeze-in temperature, above which the tail slope becomes temperature dependent [126]. Furthermore, at room temperature both band tail distributions in a-Si:H are temperature dependent. It therefore is important to consider the temperatures used for the measurements. Dylla et al. [108, 122] carried out transient photocharge measurements in a temperature range of 100 - 300K and derived the tail slope from fitting the multiple trapping model to the measurements at various temperatures. Reynolds et al. [123] carried out transient photoconductivity measurements at temperatures between 150 K and 350 K. However, only the part of this temperature range between 150 K to 250 K is used for the characterization of the exponential part of the conduction-band

tail [127]. Finally the tail slope determined from the photoluminescence measurements carried out by Merdzhanovata *et al.* [124] was determined at 60 K and was confirmed up to 150 K[†]. The results obtained by Dylla *et al.* [108] indicate that there is no large temperature effect on the valence-band tail up to 300 K. In our work we will, by lack or experimental evidence, assume temperature independent band tails up to a temperature of 323 K, the maximum temperature used in our experiments.

- **Mid-gap states** From electron spin resonance (ESR) spectroscopy it has been found that there are two dangling bond distributions with different paramagnetic properties in μ c-Si:H [128], presumably these two dangling bond distributions are separated spatially where one distribution is located within the crystallites and the other in the *a*-Si:H tissue at the columnar boundaries [103]. The total defect density was found to be in the range $5 \cdot 10^{21} 1 \cdot 10^{22}$ m⁻³. As we are interested in parameter values for the effective media approximation and we assume transport predominantly to take place through the crystalline part of the material, the effective density of defect states could be lower than the total defect state density. We therefore assume that the effective defect state density is in the range $1 \cdot 10^{21} 1 \cdot 10^{22}$ -m⁻³ and derive a value for the effective defect state density obtained properties. The total dangling-bond distribution can be considered broad [103, 128] and therefore we assumed a Gaussian distribution with a standard deviation of 150 meV.
- **Capture cross-sections** The capture cross-sections of neutral dangling bond and tail states will be used as a fitting parameter. It is expected that charged states have a larger capture cross-section than neutral states due to coulomb attraction between a charged trap and charge carriers with an opposite charge [129]. We used a fixed ratio of 10 for the ratio of charged to neutral capture cross-sections. The factor of 10 has previously been used to model defects in both *a*-Si:H and μc -Si:H material [96].
- **Contacts** At the ZnO/semiconductor contacts we assume an excess charge carrier density of zero, i.e. infinite surface recombination velocity.

Optical simulations were carried out using the semi-coherent model *GENPRO3*, taking into account both coherent and incoherent light propagation. For scattering at rough interfaces we used semi-empirical relations for the haze as described in Section 3.2. In our simulations we used an RMS roughness of 100 nm for the TCO-p

[†]The photoluminescence was also measured at higher temperatures, however, due to limitations of the photodetector no tail slope could be determined at temperatures above 150 K [124].

interface and for the ZnO/Al interface. Scattering at other interfaces is neglected in our simulations. The optical properties of μc -Si:H are estimated using the effective medium approximation [130]. In this approach the refractive index is computed from the refractive indices of the two phases, *a*-Si:H and μc -Si:H, and the crystalline volume fraction. Although this method may not be the most accurate for determining the refractive index of the materials used in the solar cell, the method has the advantage that it allows for a flexible variation of the crystalline volume fraction in simulations. In our simulations we used a crystalline volume fraction of 60 %.

We fitted simulated solar cell characteristics to experimental results by varying the following parameters:

- The capture cross-sections of neutral dangling-bond and neutral band-tail states
- The density of states at the mobility edges
- The density of defect states
- The activation energy of the p-layer
- The series resistance

In order to make this procedure as reliable as possible we fitted the simulations to experimental results simultaneously for the dark and illuminated J-V characteristics, the external quantum efficiency, and the dark current activation energy of the solar cell as a function of bias voltage. The dark current activation energy was determined the same way as in Section 5.3, using the same temperatures (289 K, 298 K, 308 K, and 323 K). The EQE was measured and simulated at 0 V.

In Figure 5.7 experimental results and simulation results are compared for several solar cell characteristics. The parameters used for this simulation are listed in Table 5.1 and the complete ASA input file for the simulation can be found in Appendix A. To obtain the results in Figure 5.7 we set the capture cross-sections for neutral dangling-bond states to 3.0×10^{-20} m², and for neutral tail-states to 5.0×10^{-20} m². Other fitted parameters were: the density of states at the valence and conduction band mobility edges were set to 1.04×10^{26} m⁻³ eV⁻¹ and 2.8×10^{26} m⁻³ eV⁻¹, respectively, the density of dangling bonds was set to 5.0×10^{-10} m² to fit the current density at voltages above 0.5 V. The dark and illuminated J-V characteristics (Figure 5.7a and Figure 5.7b) both show a close match between measurements and simulations. The simulated short-circuit current density in Figure 5.7b is slightly too high. In Figure 5.7c the simulated and measured external quantum efficiency is shown. The simulated EQE is overall slightly higher than the measured EQE, which corresponds to the too large simulated short-circuit current density. In Figure 5.7d the



Figure 5.7: Measured (symbols) and simulated (lines) solar cell characteristics: (a) the dark J-V characteristics, (b) the illuminated J-V characteristics, (c) the spectral response, and (d) the dark current activation energy.

simulated and experimental dark current activation energy are shown. It can be seen from Figure 5.7d that we obtained a good match between simulation and experiment for the dark current activation energy. In Section 5.3 we determined the mobility gap using Eq. (5.21) and the dark current activation energy obtained from experiments. Applying the same procedures on the simulated dark current activation energy we obtain a value for the mobility gap, which should be approximately the same as the mobility gap used in the simulations. We found a mobility gap of 1.17 eV using Eq. (5.21), compared to 1.19 eV for the mobility gap taken in the simulations. Comparing the analytical approximation of the dark current activation energy with the simulated dark current activation energy we find the analytical approximation is quite accurate, despite the many approximations made in Section 5.3.

5.4.2 Numerical analysis of the dark current activation energy

In this section we analyze the dark current activation energy through numerical modeling. We first verify through numerical simulations the validity of the approxima-

		DIRECTOR	L	
	p-layer	i-layer	n-layer	unit
d	$30 \cdot 10^{-9}$	$1.15 \cdot 10^{-6}$	$30 \cdot 10^{-9}$	m
	Transport, d	OPING AND E	XTENDED ST	TATES
	p-layer	i-layer	n-layer	unit
E_{μ}	1.18	1.18	1.75	eV
ϵ_r	11.9	11.9	11.9	_
χ	4.05	4.05	3.9	eV
N_{v}	$5.2 \cdot 10^{24}$	$5.2 \cdot 10^{24}$	$4.0 \cdot 10^{26}$	m^{-3}
N_c	$1.4 \cdot 10^{25}$	$1.4 \cdot 10^{25}$	$4.0 \cdot 10^{26}$	m ⁻³
μ_n	$5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$m^2 V^{-1} s^{-1}$
μ_p	$1.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	$\mathrm{m}^{2}\mathrm{V}^{-1}\mathrm{s}^{-1}$
$\dot{E_a}$	0.16	(-)	0.3	eV

Table 5.1: Values of parameters used for the simulation of the μ *c*-Si:H solar cell. STRUCTURE

VALENCE BAND TAIL STATES

	p-layer	i-layer	n-layer	unit
E_{v0}	31	31	80	meV
N_{v0}/N_v	20	20	10	eV^{-1}
σ_p^0	$5.0 \cdot 10^{-20}$	$5.0 \cdot 10^{-20}$	$5.0 \cdot 10^{-20}$	m ²
σ_n^+	$50\cdot 10^{-20}$	$50\cdot 10^{-20}$	$50\cdot 10^{-20}$	m ²

CONDUCTION BAND TAIL STATES				
	p-layer	i-layer	n-layer	unit
E_{c0}	31	31	70	meV
N_{c0}/N_{c}	20	20	10	eV^{-1}
σ_n^0	$5.0\cdot10^{-20}$	$5.0 \cdot 10^{-20}$	$5.0 \cdot 10^{-20}$	m ²
σ_p^-	$50 \cdot 10^{-20}$	$50\cdot10^{-20}$	$50 \cdot 10^{-20}$	m ²

DANGLING BOND STATES

	p-layer	i-layer	n-layer	unit
U	0.2	0.2	0.2	m ⁻³
N_{db}	$1.0\cdot10^{22}$	$6.0 \cdot 10^{21}$	$1.6 \cdot 10^{24}$	m ⁻³
σ_p^0	$3.0 \cdot 10^{-20}$	$3.0 \cdot 10^{-20}$	$3.0\cdot10^{-20}$	m^2
σ_n^0	$3.0 \cdot 10^{-20}$	$3.0 \cdot 10^{-20}$	$3.0\cdot10^{-20}$	m^2
σ_p^-	$30 \cdot 10^{-20}$	$30 \cdot 10^{-20}$	$30\cdot10^{-20}$	m^2
σ_n^r	$30 \cdot 10^{-20}$	$30\cdot 10^{-20}$	$30 \cdot 10^{-20}$	m ²

FRONT CONTACT

		unit
R _{series}	$4.5 \cdot 10^{-5}$	Ωm^2



Figure 5.8: (a) The simulated band diagram at 0.2 V for the μc -Si:H solar cell. (b) The recombination rate profile in the μc -Si:H solar cell at 0.2 V (solid line), the estimated activation energy (dashed line), and the minimal activation energy ($(E_{\mu} - V)/2 + 2kT$) of recombination processes in the device (dotted line). (c) For three positions in the device are shown: the recombination as a function of energy (solid line), the activation energy of recombination on dangling bonds (dashed line), and $E_a^m + 2kT$, the approximated activation energy for recombination between the quasi-Fermi levels for trapped charge (dotted line). The three positions are, p-i: at 20 nm from the p-i interface, bulk: in the middle of the intrinsic layer, and i-n: at 20 nm from the i-n interface.

tions made to arrive at the analytical expressions in Section 5.3. In order to do that we show the simulated band diagram at 0.2 V of the μ c-Si:H solar cell in Figure 5.8.a. In Figure 5.8.b we show the simulated recombination rate profile and in Figure 5.8.c we show the recombination rate and the activation energy of recombination on dangling bonds as a function of energy at three positions in the device for an applied voltage of 0.2 V.

The band diagram in Figure 5.8.a shows that the field distribution in the device is, as expected, far from uniform, with high fields near the p-i interface and i-n interface and a relatively low electric field in a large part of the intrinsic layer. The recombination rate in the device is shown in Figure 5.8.b. By comparing Figure 5.8.a and Figure

5.8.b we observe that the area with high recombination coincides with the part of the intrinsic layer with a low and fairly uniform field. In Eq. (5.14) we derived that the activation energy of recombination processes on mid-gap states is equal to $E_a^m + 2kT$, where E_a^m is the activation energy of the minority carrier concentration. As most recombination events involve mid-gap states, we plot the value of $E_a^m + 2kT$ in Figure 5.8.b, where we determined E_a^m from the band diagram shown in Figure 5.8.a. Furthermore, according to Eq. (5.21) the activation energy of the total recombination is $(E_\mu - V)/2 + 3kT$, which is also indicated in Figure 5.8.b with the dotted line. In the region with a high recombination rate the activation energy of the recombination processes varies around the value of $(E_\mu - V)/2 + 3kT$.

In Figure 5.8.c we show the recombination on dangling bond states for three positions in the device: at 20 nm from the p-i interface, in the middle of the intrinsic layer, and at 20 nm from the i-n interface. For these three positions we also show the computed thermal activation energy of recombination as a function of energy of the trap level. Furthermore we indicate in Figure 5.8.c the value of $E_a^m + 2kT$ for these three positions. The value of $E_a^m + 2kT$ is a good approximation for the activation energy of recombination on mid-gap states. Furthermore the thermal activation energy as a function of trap energy roughly follows the shape in Figure 5.3. The differences between Figure 5.3 and the computed thermal activation energy as a function of trap energy originate from the difference in capture cross-sections for electrons and holes, the difference in capture cross-sections for charged and neutral defects, and the application of recombination statistics for amphoteric states (see Section 3.1) while Eq. (5.14) was derived for single electron states.

In order to assess the limitations of the procedure to determine the mobility gap we will study the several influences on the thermal activation energy of μc -Si:H *pin* devices:

- Recombination on band-tail states. Recombination on tail states is expected to lead to an increase in activation energy. In these simulations we will evaluate to what extend the measurements are influenced by the recombination on tail states.
- Influence of a defect rich interface layer. As the activation energy of recombination is generally higher near the p-i interface and near the i-n interface, we will study the influence of a highly inhomogeneous spatial defect-state distribution in the device. In particular in light of the inhomogeneous growth of μc -Si:H it is interesting to investigate the influence of a high defect-state density near the p-i interface.
- Influence of an a-Si:H interface layer. The inhomogeneous growth of µc-Si:H may lead to an a-Si:H incubation layer, which could lead to a change in the

dark current activation energy due to the higher mobility gap of a-Si:H.

Influence of band tails on the dark current activation energy

In Section 5.3 we derived an expression of the current density through a *pin* device by integrating the recombination rate through the device according to Eq. (5.1). In order to study the influence of recombination through tail states, we will distinguish between current due to tail states and the current due to defect-states. The current density due to recombination through tail states, the tail-recombination current density, is determined by integrating the recombination analogous to the integral Eq. (5.1), where the total recombination is replaced with the recombination on tail states only. Likewise the current density due to recombination current density, is determined by integrating the recombination through dangling-bond defect-states, the dangling-bond-recombination current density, is determined by integrating the recombination through dangling bonds in the device.

In Figure 5.9a we show the tail-recombination current density and the danglingbond recombination current density for a temperature of 298 K. For reference the total simulated current density is also shown. For voltages below 0.3 V the total current density approximately equals the dangling-bond-recombination current density. For higher voltages the tail-recombination current density becomes increasingly important, while at the same time the effects of series resistance and space charge limited current start to play a role. In Figure 5.9b we show the thermal activation energy of the dangling-bond-recombination current density and the tail-recombination current density. For reference the simulated activation energy of the total current density is also shown in Figure 5.9b. Up to a voltage of 0.3 V the activation energy of the total current density is primarely determined by the activation energy of the dangling-bond-recombination current density. Above 0.3 V the activation energy is partly determined by recombination via tail-states and the activation energy does not follow Eq. (5.21).

Influence of a defective or amorphous p-i interface on the dark current activation energy

In Figure 5.10 we show the influence on the dark current density (Figure 5.10.a) and the dark current activation energy (Figure 5.10.b) when the defect density in a 10-nm thick layer adjacent to the p-i interface is varied. A defect density of $5 \cdot 10^{21} \text{ m}^{-3}$ is equal to the defect density in the rest of the intrinsic layer. For a defect density varying over several orders of magnitude, the influence on the dark current density and the activation energy is marginal. Figure 5.10.a shows that, for a defect density of $5 \cdot 10^{24} \text{ m}^{-3}$ the dark current density is considerably higher than for a defect density of $5 \cdot 10^{23} \text{ m}^{-3}$ and lower. However, even for a defect density of $5 \cdot 10^{24} \text{ m}^{-3}$ the dark current



Figure 5.9: (a) The tail-recombination current density and the dangling-bond-recombination current density at 298 K. (b) The thermal activation energy of the tail-recombination current density and the dangling-bond-recombination current.

activation energy is only marginally affected. The mobility gap determined from the simulated dark current activation energy was 1.17 eV for all simulations with a defect density less than $5 \cdot 10^{24} \text{ m}^{-3}$, and 1.14 eV for a defect density of $5 \cdot 10^{24} \text{ m}^{-3}$. The simulations suggest that the value for the mobility gap determined by the dark current activation energy is not sensitive to the spatial distribution of dangling-bond defects.

In order to explain that the dark current activation energy is hardly affected by a defect-rich interface we show the band diagrams at 0.2 V of a cell without defect-rich interface (Figure 5.11.a), and of a cell with a defect density of $5 \cdot 10^{24}$ m⁻³ in the 10-nm thick layer adjacent to the p-i interface (Figure 5.11.b). In Figure 5.11 only the first 300 nm is shown in order to see clearly the influence of the thin defect-rich layer close to the p-i interface. Note that Figure 5.11.a corresponds to the first 300 nm of Figure 5.8.a. The band diagrams in Figure 5.11.a and Figure 5.11.b show that the introduction of a 10-nm thick defect-rich interface layer leads to significant bandbending in this region. The recombination rate profiles corresponding to the band diagrams in Figure 5.11.a and Figure 5.11.b are shown in Figure 5.11.c and Figure 5.11.d, respectively. The recombination rate profiles show that the defect-rich interface induces a recombination peak within the defect-rich layer and increases recombination in the first 200 nm of the intrinsic layer next to the p-i interface. The total recombination current density is significantly increased as is shown Figure 5.10.a. However, despite the significant increase in recombination near the p-i interface, the activation energy is not increased nor do we see a significant change in thermal ideality factor, as shown in Figure 5.10.b. The band diagram in Figure 5.11.b shows that the band bending induced by the defect-rich interface layer leads to fairly symmetrical quasi-Fermi levels around mid-gap close to the p-i interface, even within the defect-rich interface layer. As a result the additional recombination induced by



Figure 5.10: (a) The dark current density of the μc -Si:H solar cell for various defect densities in a 10-nm thick layer is adjacent to the p-i interface. The defect density in the bulk is $5 \cdot 10^{21}$ m⁻³. (b) The dark current activation energy for the various defect densities in the defect rich interface.

the defect-rich layer does not cause significant changes in the dark current activation energy compared to the case without defect-rich layer.

In Figure 5.12.a the dark current density is shown of a μc -Si:H solar cell with and without a 10-nm thick *a*-Si:H layer between the p-layer and the μc -Si:H intrinsic layer. The current density is the same up to 0.15 V for the solar cells with and without *a*-Si:H interface layer. Above 0.15 V the current density through the cell with an amorphous interface layer is considerably lower than without. Similar to the previous section we integrated the recombination in the device according Eq. (5.1). However, this time we integrated the total recombination rate in the device, excluding surface recombination (which is not computed explicitly in *ASA*). The thus obtained device-recombination current density is shown in Figure 5.12.a. For voltages above 0.35 V there is an increasing difference between the device-recombination current density and the total simulated current density, showing there is a large contribution of the surface recombination to the total current. The surface recombination current density is computed as the difference between the total current density and the device-recombination current density and is also shown in Figure 5.12.a.

The influence of the amorphous interface layer between the p-layer and the μc -Si:H intrinsic layer is explained as follows: The valence band offset between *a*-Si:H and μc -Si:H is rather large (0.41 eV) and inhibits the injection of holes from the p-layer into the intrinsic layer. For a 10-nm thick *a*-Si:H incubation layer the limitations on the injection of holes becomes prominent above 0.15 V. As a result the hole concentration (not shown) and thus the recombination rate in the intrinsic layer are reduced, resulting in a relatively larger contribution of surface recombination.

Figure 5.12.b shows the dark current activation energy of the solar cells with and



Figure 5.11: (a) Band diagram of the μc -Si:H solar cell without defective interface at 0.2 V. (b) Band diagram at 0.2 V of the μc -Si:H solar cell with a defect density of $5 \cdot 10^{24}$ m⁻³ in the 10-nm thick layer is adjacent to the p-i interface. (c) Recombination rate profile belonging to the μc -Si:H solar cell without defective interface at 0.2 V. (d) Recombination rate profile belonging to the band diagram in (b).

without *a*-Si:H interface layer and the activation energy of the device-recombination current density and of the surface recombination current density. Eq. (5.21) is not valid as the slope of the voltage-dependent dark current density activation energy is only -0.5 in the voltage range 0 - 0.15 V. The simulations suggest that an incubation layer of 10 nm prevents a straightforward determination of the mobility gap. It should be noted that, for thin *a*-Si:H incubation layers, tunneling of holes through the incubation layer may reduce the influence of the amorphous layer on the dark current.

5.5 Conclusions

We presented a method to determine the mobility gap from the dark current activation energy of μc -Si:H *pin* solar cells. The method is, in principle, also valid for *a*-Si:H and other semiconductors where the dark current is predominantly a SRH recombination current originating from midgap states in the intrinsic layer. Using this method we found a mobility gap of 1.19 eV. This is in line with the findings of Brammer [96] *et al.* but considerably lower than the reported values of 1.59 and 1.48 eV for crystalline



Figure 5.12: (a) The dark current density of the μ c-Si:H solar cell with and without a 10-nm thick *a*-Si:H layer adjacent to the p-i interface. For the solar cell with an *a*-Si:H layer the current density computed as the integral of the recombination over the device (without surface recombination) is also shown. The difference between the recombination current density and the total current density is the current density arising from surface recombination. (b) The dark current activation energy for a solar cell with and without a 10-nm thick *a*-Si:H layer adjacent to the p-i interface. For the solar cell with an *a*-Si:H layer the dark current activation energy of the recombination in the device, and the activation energy of the surface recombination current density are also shown.

fractions of 30 % and 70 %, respectively [100]. The determined mobility gap suggests that the transport properties of μc -Si:H are primarily determined by the crystallites, which is in line with the percolation theory of electronic transport in μc -Si:H.

We derived a parameter set for the effective media approach to μc -Si:H. We discussed the influence of the percolation theory of electronic transport on the choices of effective parameters for the mixed phase material. We argue that according to the percolation theory of electronic transport in μc -Si:H the effective density of states depends on the crystalline volume fraction. We obtained a good correspondence between simulations and experimental results for the dark and illuminated J-V characteristics, the spectral response, and the dark current activation energy.

Using numerical simulations we analyzed the dark current activation energy of μc -Si:H *pin* devices and possible disturbances of the presented procedure to determine the mobility gap from the dark current activation energy. We found the dark current activation energy is fairly insensitive to a defect rich interface layer. An amorphous incubation layer, however, can have a large influence on the dark current activation energy. An *a*-Si:H incubation layer may lead to a non-neglectable contribution of surface recombination to the dark current density, making a straight-forward interpretation of the dark current activation energy difficult.
Chapter 6

Conclusions

The density-of-states distribution in intrinsic *a*-Si:H is of central importance for the understanding and modeling of *a*-Si:H devices. In Chapter 4 we therefore developed a tool to extract the density-of-states distribution in *a*-Si:H. Charge Deep-Level Transient Spectroscopy (Q-DLTS), is a technique that can be used to characterize deep-levels in intrinsic *a*-Si:H. Usually Q-DLTS is measured on Metal-Insulator-Semiconductor (MIS) structures. For the interpretation of such measurements usually a simple, small signal model was used based on the depletion approximation. For large-signals and for *intrinsic a*-Si:H we developed a physical model which we implemented in *ASA*.

When the Fermi level is shifted in *a*-Si:H by the application of a bias voltage, the defect-state distribution will re-equilibrate to the new bias condition. In order to prevent that the applied bias voltage during a Q-DLTS measurement affects the defect-state distribution during the measurement we developed a biasing scheme to minimize the change in defect-state distribution. Furthermore we developed a method to estimate the amount of change in the defect-state distribution during a Q-DLTS measurement. Using this biasing scheme we measured the Q-DLTS spectra for *a*-Si:H samples in un-programmed and n-type programmed state. By fitting the experimental Q-DLTS spectra by simulations we have extracted the density-of-states distribution in both energy and space coordinates. We were, however, not able to determine the density-of-states in absolute sense, as a part of the measured Q-DLTS spectrum originates from the periphery of the contact. Because of this uncertainty in the effective area it is not possible to determine whether there is a defective interface region adjacent to the oxide/*a*-Si:H interface. In order to remove the contribution of the periphery from the Q-DLTS signal the *a*-Si:H layer could be removed by etching.

We have used ASA for the characterization of a-Si:H and μ c-Si:H materials by

self consistently modeling various experiments. In case of μc -Si:H and μc -Si:H solar cells we have focussed on the mobility gap as the mobility gap is both a key parameter and, in case of μc -Si:H, its value is controversial. We developed a method to determine the mobility gap of μc -Si:H using the dark current activation energy of μc -Si:H *pin* devices. The method is, in principle, valid for any *pin* device, where the recombination in the dark can be approximated with Shockley-Read-Hall (SRH) recombination, originating from mid-gap states in the intrinsic layer (e.g., *a*-Si:H *pin* devices). We derived a simple analytical model that describes the dark current activation energy and which is used to extract the mobility gap of the intrinsic layer of experimental *pin* devices. The mobility gap of the μc -Si:H material in the solar cells we investigated was 1.19 eV.

As our analytical model is based on several approximations we compared the analytical model with detailed numerical simulations. For the simulations we used the effective medium approximation. We determined a calibrated parameter set for the simulation of μc -Si:H. Apart from the mobility gap, which we already determined, we determined all parameters in this parameter set from literature, through physical arguments, or by fitting the simulation results to experimental results. With the numerical simulations we verified our analytical model.

Appendix A

Example ASA input file

The following is a verbatim ASA input file for the simulation of a μ c-Si:H solar cell as was used in Section 5.4.1 of Chapter 5:

```
# variables
                              #;
# effective density of states;
variable Nceff=0.6*2.08e+25;
variable Nveff=0.6*1.04e+25;
# mobility gap;
variable Bgeff=1.18;
# mobilities;
variable emob=0.005;
variable hmob=0.0015;
# temperature independent tail width;
variable Wt=0.031;
# doping;
variable Eactp=0.15;
variable Eactn=0.3;
# capture rates;
variable cap_neut=30e-16;
variable cap_char=10*cap_neut;
```

```
variable cap char t=10*cap neut t;
variable Rseries=0.045e-3;
# calculated values, do not edit #;
variable nvemob=20*Nveff;
variable ncemob=20*Nceff;
variable Ndef=5e21;
# The Rest
                         #:
options
             suppress.warnings ignore.bounds;
layers
             front=2 electrical=3 back=2;
# Structure definition;
            d=1.5e-3;
grid[f.1]
grid[f.2]
             d=900e-09;
grid[1]
            d=20.0e-9 spaces=30;
             d=1.15e-6 spaces=400;
grid[2]
             d=20.0e-9 spaces=20;
grid[3]
             d=20e-9;
grid[b.1]
             d=300e-9;
grid[b.2]
# Refractive index data;
optical[f.1] ref.index=1.5 ext.coeff=0 incoherent;
optical[f.2] lnk.file="zno.lnk";
optical[1] lnk.file="muc 05.lnk";
optical[2]
             lnk.file="muc_05.lnk";
optical[3] lnk.file="tud_n.lnk";
optical[b.1] lnk.file="zno.lnk";
optical[b.2] lnk.file="tud_al.lnk";
# Scattering at rough interfaces;
interface[i.3] adf.s.rf=cossg adf.s.rb=cossg adf.s.tf=cossg adf.s.tb=cossg;
interface[i.3] adf.h.rf=cossq adf.h.rb=cossq adf.h.tf=cossq adf.h.tb=cossq;
interface[i.3] adf.h.file=sct_tco-p_muc.dat;
interface[i.4] adf.s.rf=cossg adf.s.rb=cossg adf.s.tf=cossg adf.s.tb=cossg;
```

variable cap_neut_t=50e-16;

```
interface[i.4] adf.h.rf=cossg adf.h.rb=cossg adf.h.tf=cossg adf.h.tb=cossg;
interface[i.5] adf.s.rf=cossg adf.s.rb=cossg adf.s.tf=cossg adf.s.tb=cossg;
interface[i.5] adf.h.rf=cossg adf.h.rb=cossg adf.h.tf=cossg adf.h.tb=cossg;
interface[i.6] adf.s.rf=cossg adf.s.rb=cossg adf.s.tf=cossg adf.s.tb=cossg;
interface[i.6] adf.h.rf=cossg adf.h.rb=cossg adf.h.tf=cossg adf.h.tb=cossg;
interface[i.7] adf.s.rf=cossg adf.s.rb=cossg adf.s.tf=cossg adf.s.tb=cossg;
interface[i.7] adf.h.rf=cossq adf.h.rb=cossq adf.h.tf=cossq adf.h.tb=cossq;
interface[i.7] adf.h.file=sct zno al muc.dat;
bands[1]
               e.mob=Bgeff chi=4.05 nc=Nceff nv=Nveff epsilon=11.9;
bands[2]
               e.mob=Bgeff chi=4.05 nc=Nceff nv=Nveff epsilon=11.9;
bands[3]
               e.mob=1.75 chi=3.9 nc=4.0E+26 nv=4.0E+26 epsilon=11.9;
doping[1]
               e.act.acc=Eactp;
doping[3]
               e.act.don=Eactn;
               mu.e=emob mu.h=hmob;
mobility[1]
               mu.e=emob mu.h=hmob;
mobility[2]
mobility[3]
               mu.e=20e-4 mu.h=5e-4;
cbtail[1]
               n.emob=ncemob c.neut=cap_neut_t c.neg=cap_char_t e.range=0.9;
cbtail[1]
               levels=30;
cbtail[2]
               n.emob=ncemob c.neut=cap_neut_t c.neg=cap_char_t e.range=0.9;
cbtail[2]
               levels=30;
cbtail[3]
               e.char=0.070 n.emob=7.0e27 c.neut=0.7e-15 c.neg=7e-15;
cbtail[3]
               e.range=0.9 levels=30;
```

```
vbtail[1]
               n.emob=nvemob c.neut=cap_neut_t c.pos=cap_char_t e.range=0.9;
vbtail[1]
               levels=30:
vbtail[2]
               n.emob=nvemob c.neut=cap_neut_t c.pos=cap_char_t e.range=0.9;
vbtail[2]
               levels=30:
vbtail[3]
               e.char=0.080 n.emob=5.0e27 c.neut=0.7e-15 c.pos=7e-15;
vbtail[3]
               e.range=0.9 levels=30;
dbond[1]
               e.corr=0.2 ce.neut=cap_neut ce.pos=cap_char ch.neut=cap_neut;
dbond[1]
               ch.neg=cap_char d.e=0.15 e.range=5.0;
```

```
dbond[1] levels=40 n=1e22 e.rel.mg=0.0;
```

dbond[2] e.corr=0.2 ce.neut=cap_neut ce.pos=cap_char ch.neut=cap_neut;

```
dbond[2] ch.neg=cap_char d.e=0.15 e.range=5.0;
```

```
dbond[2] levels=40 n=Ndef e.rel.mg=0.0;
```

dbond[3] ep.def.pool=1.22;

```
dbond[3] e.corr=0.2 ce.neut=0.7e-15 ce.pos=7.0e-15 ch.neut=0.7e-15;
```

```
dbond[3] ch.neg=7e-15 d.e=0.15 e.range=5.0;
```

```
# Include tails and dangling bonds in simulation, use defect pool model to;
# determine dangling-bonds in n-layer;
             vbtail cbtail dbond;
model[1]
             vbtail cbtail dbond;
model[2]
model[3]
             vbtail cbtail dbond powell.deane.1996.mod;
model
             external;
# Some settings for the simulation:
           max.iter=25 damp=3 gummel.starts=2;
settings
             t.freeze.in=500 newton;
settings
settings
             Rs=Rseries Rp=1e30 D0=1e-30 ;
# Compute optical generation rate;
             spectrum=am15 300 1200.dat gp3;
opticgen
print
             opticgen file=MucSim_gen.dat gnuplot;
# Solve at 289 K;
# ASA assumes temperature dependent tails according to [Stutzmann]:
                                                                    #;
\# Ech(T) = (Ech(0)^2 + (kT)^2)^(1/2)
                                                                    #;
# Note that ASA assumes this for both valence- and conduction-band tails. #;
                                                                    #;
# For micro-crystalline we do not want any of that, so we feed ASA
                                                               #;
# a value for the tails at 300 K that results in the correct value at the #;
# desired temperature (0.031 eV).
                                                                    #;
                                                                    #;
# M. Stutzmann, "A comment on thermal defect creation in hydrogenated
                                                                    #;
# amorphous silicon", Phil. Mag. Lett., vol. 66, no. 3, p. 147, 1992.
                                                                    #;
                                                                    #;
# This code sets the temperature and the tails right:
                                                                    #;
variable
             Ech0=sqrt(Wt^2-(k*289/q)^2);
variable
             Ech=sqrt(Ech0^2 + (k*300/q)^2);
vbtail[1-2]
             e.char=Ech;
cbtail[1-2]
             e.char=Ech;
             temp=289;
settings
solve
             equil;
             v.start=-0.2 v.step=0.01 v.end=1 jv;
solve
              jv file=MucSim_Temp289.dat gnuplot;
print
# Solve at 298 K;
```

```
variable
               Ech0=sqrt(Wt^2-(k*298/q)^2);
variable
               Ech=sqrt(Ech0^{2} + (k*300/q)^{2});
vbtail[1-2]
               e.char=Ech;
cbtail[1-2]
               e.char=Ech;
               temp=298;
settings
solve
               equil;
solve
               v.start=-0.2 v.step=0.01 v.end=1 jv;
print
               jv file=MucSim_Temp298.dat gnuplot;
# At 298 K we also solve illuminated JV and SR;
               v.start=0 v.step=0.02 v.end=0.6 jv illum;
solve
print
               jv file=MucSim_liv.dat gnuplot;
               sr v.bias=-0.0 dark;
solve
print
               sr file=MucSim_sr.dat qnuplot headers=0;
# Solve at 308 K;
variable
               Ech0=sqrt(Wt^2-(k*308/q)^2);
variable
               Ech=sqrt(Ech0^2 + (k*300/q)^2);
vbtail[1-2]
               e.char=Ech;
cbtail[1-2]
               e.char=Ech;
settings
               temp=308;
solve
               equil;
solve
               v.start=-0.2 v.step=0.01 v.end=1 jv;
               jv file=MucSim_Temp308.dat gnuplot;
print
# Solve at 323 K;
variable
               Ech0=sqrt(Wt^2-(k*323/q)^2);
               Ech=sqrt(Ech0^{2} + (k*300/q)^{2});
variable
vbtail[1-2]
               e.char=Ech;
cbtail[1-2]
               e.char=Ech;
settings
               temp=323;
solve
               equil;
solve
               v.start=-0.2 v.step=0.01 v.end=1 jv;
print
               jv file=MucSim_Temp323.dat gnuplot;
```

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List of symbols

Symbol	Description	Unit
Α	Contact area	m ²
d	Thickness	m
$E^{+/0}$	+/0 transition level of a dangling-bond	eV
$E^{0/-}$	0/- transition level of a dangling-bond	eV
E_0	Intrinsic trap-level	eV
E_0	Characteristic energy of the Meyer-Neldel relation	eV
E_{04}	Iso-absorption optical bandgap	eV
E_a	Activation energy	eV
E_a^m	Activation energy of the minority carrier concentration	eV
E_b	Energy barrier	eV
E_c	Conduction band mobility edge	eV
E_{c0}	Characteristic energy of the conduction-band tail	eV
$E_{db0}^{+/0}$	Center of the Gaussian distribution of +/0 transition lev-	eV
ubo	els	
$E_{db0}^{0/-}$	Center of the Gaussian distribution of 0/- transition levels	eV
$E_{dn}^{\mu\nu\sigma}$	Center of the Gaussian defect-pool	eV
$E_f^{\mu_P}$	Fermi-level	eV
$\vec{E_{fn}}$	Quasi-Fermi level for trapped electrons	eV
E_{form}	Formation energy	eV
E_{fp_t}	Quasi-Fermi level for trapped holes	eV
E_{μ}	Mobility gap	eV
\vec{E}	Electric field	Vm^{-1}
E_{ph}	Photon energy	eV
$\dot{E_t}$	Trap energy level	eV
Etauc	Tauc optical bandgap	eV
E_{th}	Thermalisation energy	eV
E_{v}	Valence band mobility edge	eV
E_{v0}	Characteristic energy of the valence-band tail	eV
E_{vac}	Vacuum energy level	eV

Symbol	Description	Unit
e ₀₀	Prefactor of the Meyer-Neldel relation	s^{-1}
e_n	Electron emission coefficient	s^{-1}
$e_{n}^{0/-}$	Emission rate of 0/- transition levels	s^{-1}
$e_{n}^{+/0}$	Emission rate of +/0 transition levels	s^{-1}
e_n	Hole emission coefficient	s^{-1}
F^{P}	Occupation function for negatively charged dangling- bond states	_
F^+	Occupation function for positively charged dangling- bond states	_
F^0	Occupation function for neutral dangling-bond states	_
F_{eq}^0	Equilibrium occupation function for neutral dangling-	_
F_{eq}^{-}	Equilibrium occupation function for negatively charged dangling-bond states	_
F_{eq}^+	Equilibrium occupation function for positively charged dangling-bond states	_
FF	Fill factor	_
f	Electron occupation probability	_
f_{P}^{in}	Dependence of scattering on incident angle for reflection	_
f_T^{in}	Dependence of scattering on incident angle for transmit-	_
fout	Angular distribution of the scattered reflected light	_
$\int_{T}^{T} R$	Angular distribution of the scattered transmitted light	_
G	Generation rate	$m^{-3}s^{-1}$
H	Hydrogen concentration	m ⁻³
H	Haze	_
H_R	Haze for reflection	_
H_T	Haze fro transmission	_
J	Current density	Am^{-2}
J_0	Reverse bias saturation current density	Am^{-2}
J_{mpp}	Current at the maximum power point	Am^{-2}
\vec{J}_n	Electron current density	Am^{-2}
\vec{J}_p	Hole current density	Am^{-2}
J_{ph}	Photo-current density	Am^{-2}
$\dot{J_{sc}}$	Short circuit current density	Am^{-2}
Κ	Time-constant filter	_
k	Boltzmann's constant	eVK^{-1}
m_e^*	Effective electron mass	Kg
Ν	Effective density of states in valence- or conduction-band	m^{-3}
Ν	Density of states	m^{-3}
N_c	Conduction band effective density of states	m^{-3}

Symbol	Description	Unit
N _{c0}	Density of conduction-band tail states at E_c	$eV^{-1}m^{-3}$
N _{cbt}	Density of conduction-band tail states	$eV^{-1}m^{-3}$
N _{db}	Total dangling bond concentration	m ⁻³
$N_{db}^{+/0}$	Distribution of energy levels arising from the $E^{+/0}$ tran- sition level	m^{-3}
$N_{db}^{0/-}$	Distribution of energy levels arising from the $E^{0/-}$ tran- sition level	m^{-3}
N^0	Neutral amphoteric-state concentration	$eV^{-1}m^{-3}$
N_{ii}	Negatively-charged amphoteric-state concentration	$eV^{-1}m^{-3}$
Nasa.	Concentration of Electrons in Si-Si bonding states	m ⁻³
N _m	Effective density of states at temperature T_{0}	m^{-3}
N	Concentration of trap states	$v^{-1}m^{-3}$
IN _t	Volence hand effective density of states	$ev m^{-3}$
IN _V	Density of unless hand tail states at E	111 - 32 - 32 - 32 - 32 - 32 - 32 - 32 -
N_{v0}	Density of valence-band tail states at E_v	$eV^{-1}m^{-3}$
N _{vbt}	Density of valence-band tail states	ev m s
п	Index of refraction	3
п	Electron concentration	m
n ~	Diode ideality factor	_
n	Complex index of refraction	- 2
n_{eq}	Equilibrium electron concentration	m ⁻³
n _i	Intrinsic carrier concentration	m ⁻⁵
n_{ph}	number of photons	
Р	Defect-pool function	$eV^{-1}m^{-3}$
P_{max}	Maximum power	W
р	Hole concentration	m ⁻³
p_{eq}	Equilibrium hole concentration	m ⁻³
q	Electronic charge	С
Q	Charge	С
R	Recombination rate	$m^{-3}s^{-1}$
R _{scatt}	Scattered reflected light	_
Rseries	Series resistance	Ωm^2
R _{tot}	Total reflected light	_
Т	Temperature	К
T^*	Freeze-in temperature	K
Tscatt	Scattered transmitted light	_
T_{tot}	Total transmitted light	_
t	Time	S
U	Correlation energy	eV
V	Applied voltage	V
V_{dc}	Attempt-of-escape frequency for defect creation	s^{-1}
v_{dr}	Attempt-of-escape frequency for defect removal	s^{-1}

Symbol	Description	Unit
V _{mpp}	Voltage at the maximum power point	V
V_{oc}	Open circuit voltage	V
v_{th}	Thermal velocity	ms^{-1}
W	Thickness of the intrinsic layer	m
x	Position	m
α	Absorption coefficient	m^{-1}
δ_{rms}	Root-mean-square roughness of an interface	m
ε	Dielectric constant	Fm^{-1}
ϵ_0	Dielectric constant of vacuum	Fm^{-1}
ε _r	Relative dielectric constant	_
η_{eqe}	External quantum efficiency	_
η_R	Recombination efficiency	_
θ^{in}	Angle of incidence	0
θ^{out}	Angle of outbound light	0
κ	Extinction coefficient	_
λ	Wavelength	m
μ_n	Free electron mobility	$m^2 V^{-1} s^{-1}$
μ_p	Free hole mobility	$m^2 V^{-1} s^{-1}$
ρ	Space charge density	Cm^{-3}
σ	Conductivity	Sm^{-1}
σ	Capture crossection for electrons or holes	m ²
σ_0	Prefactor of the dark conductivity	Sm^{-1}
σ_n^0	Electron capture cross-section neutral states	m ²
σ_p^0	Hole capture cross-section of neutral states	m ²
σ_d	Dark conductivity	Sm^{-1}
σ_{db}	Standard deviation of the Gaussian distribution of +/0 transition levels	eV
σ_{dn}	Standard deviation of the Gaussian defect-pool	eV
σ_n^+	Electron capture cross-section positively charged states	m ²
σ_n	Electron capture cross-section	m ²
σ_n^-	Hole capture cross-section of negatively charged states	m ²
σ_{p}^{ν}	Hole capture cross-section	m ²
τ	Time constant	S
ϕ_{nh}	Photon flux	s^{-1}
χ	Electron affinity	v
Ψ_{vac}	Vacuum potential	V

Summary

Our economic systems are closely linked to the ecosystems on earth as the ecosystems provide resources and recycle waste in ecocycles. Before the industrial revolution, economic systems drew almost all their resources, food, materials and energy sources, directly from local ecosystems. Therefore, the productivity of ecosystems (photosynthesis) posed effective (and rather narrow) boundaries to economic development. Generally, the physical and biological impact of economic systems on ecosystems was small. The industrial revolution, however, added large quantities of useful energy from fossil sources to the economic systems. This led to much higher levels of productivity, pushing the limits of producing food, materials and final products far beyond previous (natural) levels. This in turn causes serious disruptions of natural cycles such as pollution, deforestation, loss of biodiversity, climate change, etc. as the ecosystems cannot recycle the large amounts of waste fast enough nor regenerate the resources (e.g., fossil fuels and metals) at the rate they are used. To reduce the amount of material resources used in our economic systems we can make use of solar cells to meet (part of) of our need for available energy.

At present most commercially available solar cells are made of crystalline silicon (c-Si). The disadvantage of crystalline silicon solar cells are the high material cost and energy consumption during production. A cheaper alternative can be found in thin-film silicon solar cells. The thin-film silicon used in this type of solar cells is in a different phase than c-Si and usually alloyed with hydrogen. The most common thin-film silicon phases are hydrogenated amorphous silicon (a-Si:H) and hydrogenated micro-crystalline silicon (µc-Si:H). These materials are usually deposited from the gas phase onto a substrate, such as glass. Thin-film silicon solar cells can be made very thin resulting in less material consumption. Furthermore, the production of thin-film silicon solar cells consumes less energy than crystalline silicon solar cell technologies. Thin-film solar cells are usually deposited at low temperatures (typically 150 - 300 °C), which allows for the use of low cost substrates like glass and even some plastics. Furthermore, as the solar cells are very thin, flexible solar cells can be made by depositing the solar cell on a flexible substrate, such as a metal film or plastic foil. The deposition techniques allow for large area deposition of solar cells. A drawback to the thin-film silicon technologies are the relatively low efficiency and the light induced degradation of a-Si:H (µc-Si:H is generally stable). The light induced degradation leads to an initial efficiency decrease of a-Si:H solar cells, after which the efficiency stabilizes. Thin-film silicon modules are a good candidate for those

photovoltaic applications where low cost is more important than high efficiency. In particular building integration, where a sufficient surface area is available without extra cost.

a-Si:H and μ *c*-Si:H are disordered semiconductors. Typical for disordered materials is that the material properties of these materials may vary over a broad, continuous range. These variations in material properties do not only occur from sample to sample, also samples are generally found to be inhomogeneous. Furthermore, also the electronic characteristics of the materials are complex, requiring complex physical models to describe these properties. The complex models combined with the variations in material properties hamper the interpretation of measurements and thus the characterization of the materials and devices made from these materials. A device simulator based on physical models is a useful tool for the characterization of semiconductor materials and the operation of semiconductor devices. Using a device simulator one can, through the detailed and *consistent* modeling of several different experiments on a device or devices, obtain a more accurate estimate of the used model parameter values. We have used the device simulator Advanced Semiconductor Analysis (*ASA*) for the characterization of *a*-Si:H and μ *c*-Si:H materials by self consistently modeling various experiments.

Thin-film silicon materials have, just like *c*-Si, a band structure of electronic states. However, the disorder in the thin-film materials lead, in addition to the valence- and conductionband, to so called "band tails". These band tails are localized states at the extremities of both energy bands. Furthermore, the disorder in thin-film silicon materials lead to the situation where for some atoms the bonding requirements are not met, leading to "dangling bonds". These dangling bonds form electronic states between the valence- and conduction-band and are, just like the band tail states, localized. Charge carriers in localized states contribute very little to electronic transport in the material because the mobility of charge carriers in localized states is very low. The thin-film silicon equivalent of the bandgap in crystalline materials is therefore the "mobility gap". The recombination in doped p- and n-type thin-film silicon layers is relatively high because doped thin-film silicon layers usually have higher concentration dangling bonds that intrinsic layers. For this reason thin-film silicon solar cells usually consist of *pin* devices (with an intrinsic *i*-layer between the p- and n-layers).

The density-of-states distribution in intrinsic *a*-Si:H is of central importance for the understanding and modeling of *a*-Si:H devices. In Chapter 4 we therefore developed a tool to extract the density-of-states distribution in *a*-Si:H. Charge Deep-Level Transient Spectroscopy (Q-DLTS), is a technique that can be used to characterize deep-levels in intrinsic *a*-Si:H. Often Q-DLTS is measured on Metal-Insulator-Semiconductor (MIS) structures. For the interpretation of such measurements usually a simple, small signal model was used based on the depletion approximation. For large-signals and for *intrinsic a*-Si:H we developed a physical model which we implemented in *ASA*.

When the Fermi level is shifted in *a*-Si:H by the application of a bias voltage, the defectstate distribution will re-equilibrate to the new bias condition. In order to prevent that the applied bias voltage during a Q-DLTS measurement affects the defect-state distribution during the measurement we developed a biasing scheme to minimize the change in defect-state distribution. Using this biasing scheme we measured the Q-DLTS spectra for *a*-Si:H samples in un-programmed and n-type programmed state. By fitting simulated Q-DLTS spectra to experimental results we have extracted the density-of-states distribution. In Chapter 5 we discussed the modeling and characterization of μc -Si:H material. A key parameter for modeling *a*-Si:H material is the mobility gap. The value of the mobility gap, however, is controversial. We developed a method to determine the mobility gap of μc -Si:H using the dark current activation energy of μc -Si:H *pin* devices. The method is, in principle, valid for any *pin* device, where the recombination can be approximated with Shockley-Read-Hall (SRH) recombination, originating from mid-gap states in the intrinsic layer (e.g., *a*-Si:H *pin* devices). We derived a simple analytical model that describes the dark current activation energy and which is used to extract the mobility gap of the intrinsic layer of experimental *pin* devices. The mobility gap of the μc -Si:H material in the solar cells we investigated was 1.19 eV. As our analytical model is based on several approximations we verified the analytical model with detailed numerical simulations.

Samenvatting

Onze economie is nauw verbonden met de ecosystemen op aarde. De ecosystemen leveren vele grondstoffen en recyclen veel van onze afvalstoffen. Voor de industriële revolutie betrokken economiën bijna alle grondstoffen, voedsel, materialen en energie, direct uit de locale ecosystemen. De productiviteit van de ecosystemen (fotosynthese) legde effectieve (en tamelijk smalle) grenzen op aan de economische ontwikkeling. Over het algemeen waren de fysieke en biologische invloeden van de economiën op de ecosystemen klein. Echter, sinds de industriële revolutie maken we grootschalig gebruik van beschikbare energie uit fossiele brandstoffen. Hierdoor konden de economiën een veel hogere productiviteit bereiken, ver boven de productiviteits limieten die de ecosystemen voorheen oplegden. De keerzijde hiervan is dat natuurlijke cycli in de ecosystemen verstoord worden door vervuiling, ontbossing, verlies van biodiversiteit, klimaat verandering, etc., omdat de ecosystemen de grote hoeveelheden afval die de economiën produceren niet snel genoeg kan verwerken en ook de gebruikte grondstoffen niet snel genoeg kan regenereren. Om het grondstoffenverbruik te reduceren kunnen we gebruik maken van zonnecellen om (deels) in onze energie behoefte te voorzien.

Op dit moment zijn de meeste commercieel verkrijgbare zonnecellen gemaakt van kristallijn silicium (c-Si). Dit type zonnecellen heeft als nadeel dat de materiaal kosten en het energie verbruik tijdens de productie, tamelijk hoog zijn. Dunne-film silicium zonnecellen kunnen een goedkoper alternatief bieden. Het dunne-film silicium wat in dit type zonnecellen wordt gebruikt is in een andere fase dan c-Si en wordt meestal gelegeerd met waterstof. De meest gebruikte fases van dunne-film silicium zijn gehydrogeneerd amorf silicium (a-Si:H) en gehydrogeneerd micro-kristallijn silicium (μc -Si:H). Deze materialen worden uit de gasfase gedeponeerd op een substraat zoals bijvoorbeeld glas. Dunne-film silicium zonnecellen kunnen heel dun gemaakt worden wat resulteert in minder materiaal gebruik. Daarbij kost de productie van dunne-film silicium zonnecellen minder energie dan de productie van c-Si zonnecellen. Dunne-film silicium zonnecellen worden meestal bij lage temperatuur deponeert (typisch 150-300 °C), wat het mogelijk maakt om goedkope substraten te gebruiken zoals glas en zelfs bepaalde soorten plastic. Omdat de zonnecellen dun zijn kunnen de zonnecellen ook flexibel gemaakt worden door de zonnecel op een flexibel substraat te deponeren, zoals metaal- of plastic-folie. De depositie technieken bieden de mogelijkheid om op groot oppervlak te deponeren. Een nadeel van dunne-film zonnecellen is dat de zonnecellen een relatief lage efficiëntie hebben en dat a-Si:H onder invloed van licht degradeert (μc -Si:H is redelijk stabiel). De licht geïnduceerde degradatie leidt tot een initiële vermindering van efficiëntie tijdens gebruik, waarna de efficiëntie stabiliseert. Dunne-film zonnecellen zijn een goede kandidaat zoor zonnecel toepassingen waar lage kosten belangrijker zijn dan een hoge efficiëntie. In het bijzonder integratie van zonnepanelen in gebouwen is zeer aantrekkelijk omdat daar relatief veel oppervlak beschikbaar is zonder extra kosten.

a-Si:H en μc -Si:H zijn wanordelijke halfgeleiders. Typisch voor wanordelijke materialen is dat de eigenschappen van deze materialen variëren over een breed en continu bereik. Deze variaties in materiaal eigenschappen vinden niet alleen plaats tussen verschillende stalen maar ook stalen zelf zijn over het algemeen inhomogeen. Ook de elektronische eigenschappen van deze materialen zijn complex en vereisen complexe modellen. De complexe modellen en de variaties in materiaaleigenschappen maken de interpretatie van metingen en dus de karakterisatie van materialen en elektronische componenten gemaakt van deze materialen moeilijk. Een simulatieprogramma voor halfgeleider componenten, die gebaseerd is op fysische modellen, is een nuttig hulpmiddel voor de karakterisatie van halfgeleider materialen en de werking van halfgeleider componenten. Met behulp van een simulatieprogramma voor componenten kan men, door het gedetailleerd en consistent modelleren van verschillende experimenten aan een component, meer accurate schattingen maken van model parameters in de gebruikte modellen. Wij hebben met behulp van het simulatieprogramma Advanced Semiconductor Analysis (*ASA*) verschillende materiaaleigenschappen van *a*-Si:H en μc -Si:H op deze wijze gekarakteriseerd.

Dunne-film silicium materialen hebben, net als kristallijn silicium, een bandenstructuur van elektronische toestanden. Echter, de wanorde in dunne-film silicium materialen leidt ertoe dat er naast een conductie en valentie band ook zogenaamde "band tails" zijn. Deze band tails zijn gelokaliseerde elektronische toestanden aan de extremen van de conductieen valentie-band. Daarbij leidt de wanorde in dunne-film silicium materialen ertoe dat niet ieder atoom in het materiaal het optimale aantal covalente bindingen heeft. Dit leid tot zogenaamde "dangling bonds". Deze dangling bonds vormen elektronische toestanden tussen de valentie- en conductie-band en zijn net als de band tails gelokaliseerd. Omdat de mobiliteit van ladingsdragers in gelokaliseerde toestanden zeer gering is leveren ladingsdragers in deze toestanden nauwelijks een bijdrage aan elektronisch transport in het materiaal. Het dunne-film silicium equivalent van de bandafstand in kristallijne materialen wordt daarom de mobiliteitsbandafstand genoemd. De vele gelokaliseerde toestanden in het materiaal leiden tot relatief veel recombinatie van ladingsdragers. Omdat gedoteerde dunne-film silicium p- en n-type lagen over het algemeen veel hogere dichtheden van dangling bonds hebben dan intrinsiek materiaal, is de recombinatie in gedoteerde lagen relatief hoog. Dunne-film silicium zonnecellen worden daardoor meestal als pin diodes opgebouwd (met in intrinsieke i-laag tussen de gedoteerde p- en n-lagen).

De toestandsdichtheid distributie in intrinsiek *a*-Si:H is een belangrijke parameter voor het begrijpen en modelleren van *a*-Si:H componenten. In Hoofdstuk 4 hebben we daarom een hulpmiddel ontwikkeld om de toestandsdichtheid distributie in *a*-Si:H te bepalen. Charge Deep-Level Transient Spectroscopy (Q-DLTS), is een techniek waarmee elektronische toestanden tussen de conductie- en valentie-band kunnen worden gekarakteriseerd. Vaak wordt Q-DLTS op Metaal-Isolator-Halfgeleider structuren gemeten. Voor de interpretatie wordt gewoonlijk een eenvoudig klein-signaal model gebruikt wat gebaseerd is op de depletie benadering. Wij hebben een groot-signaal model ontwikkeld en in ASA geïmplementeert voor intrinsiek a-Si:H.

Wanneer het Fermi-niveau in a-Si:H verschoven wordt door een aangelegde spanning zal de defect-toestand distributie re-equilibreren tot een evenwicht met de aangelegde spanning is bereikt. Op deze wijze kan een a-Si:H component worden "geprogrammeerd". Om te voorkomen dat de aangelegde spanning tijdens een O-DLTS meting de defect-toestand distributie beïnvloed hebben we een methode ontwikkeld om Q-DLTS te meten waarbij de aangelegde spanning zo is aangepast dat de verandering in defect-toestand distributie tijdens de meting wordt geminimaliseerd. Met deze methode hebben we ongeprogrammeerde and ntype geprogrammeerde componenten gemeten. Door simulaties van O-DLTS spectra aan deze metingen te fitten hebben we de toestandsdichtheid distributie bepaald. n hoofdstuk 5 hebben we het modelleren en karakteriseren van μc -Si:H materiaal besproken. Een belangrijke parameter voor de beschrijving van μc -Si:H is de mobiliteit-bandafstand. De waarde van deze mobiliteits-bandafstand is echter, in het geval van μc -Si:H, controversieel. Wij hebben een methode geïntroduceert om de mobiliteits-bandafstand van μc -Si:H te bepalen uit de aktiveringsenergie van de donkerstroom door μc -Si:H pin diodes. De methode is in principe bruikbaar voor elke pin diode waar de recombinatie benadert kan worden met Shockley-Read-Hall (SRH) recombinatie op elektronische toestanden in het midden tussen de valentie- en conductie-band in de intrinsieke laag (bijvoorbeeld a-Si:H pin diodes). We hebben een eenvoudig analytisch model afgeleid dat de donkerstroom activeringsenergie beschrijft. Met behulp van dit analytisch model kan de mobiliteits-bandafstand worden bepaald van experimentele *pin* diodes. De door ons onderzochte *µc*-Si:H *pin* diodes hadden een mobiliteits-bandafstand van 1.19 eV. Omdat in de afleiding van ons analytische model een aantal benaderingen zijn toegepast hebben we het model geverifieerd met gedetailleerde numerieke simulaties.

Curriculum Vitae

Bart Elger Pieters was born on March 30th, 1976 in Leiderdorp, the Netherlands. He attended the Agnes College (presently Bonaventuracollege) in Leiden in 1989 and obtained his VWO diploma in 1995. Subsequently he studied electronics at the Delft University of Technology. His degree work introduced him in the field of thin film silicon solar cells and the Electronic Components, Technology and Materials Laboratory (ECTM). In December 2002 he obtained his master degree. After his degree he continued his work in the thin-film silicon research field in the same group. He has been working on various aspects of modeling (thin-film) solar cells. Main focus of his research revolved around the device simulator Advanced Semiconductor Analysis, which he extended with various models for modeling of (multi-)crystalline silicon solar cells, optical models for thin-film solar cells, and a model for Charge Deep-Level Spectroscopy. Part of this work is described in this thesis.

List of Publications

Publications related to this thesis

B. E. Pieters, H. Stiebig, M. Zeman, and R. A. C. M. M. van Swaaij, "Determination of the mobility gap of intrinsic μc -Si:H in pin solar cells." to be published in J. Appl. Phys.

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