# Development of device quality a-Ge:H absorber layers by Plasma Enhanced Chemical Vapor Deposition

## Towards a new paradigm of PV technology

ву P.J. Roelandschap

in partial fulfilment of the requirements for the degree of

## Master of Science Sustainably Energy Technology

at the Delft University of Technology,

to be defended publicly on Tuesday June 1, 2021 at 13:00 AM.

Student number:	4181379	
Date:	May 24, 2021	
Supervisor:	Ir. T. de Vrijer,	TU Delft
Thesis committee:	Prof. dr. ir. A. Smets,	TU Delft
	Dr. ir. Patrizio Manganiello,	TU Delft

Dr. A. Rodrigo Mor,

TU Delft



# **Acknowledgements**

With this thesis, I conclude the Master of Science in Sustainable Energy Technology at the Delft University of Technology. I feel blessed for having had the opportunity to learn so much from so many talented teachers and students over the years. Being able to work on such a fundamental research project at the Else Kooi Laboratory makes me very proud.

First of all, I would like to express my gratitude to Thierry de Vrijer and prof. dr. Arno Smets, my supervisors, for giving me the opportunity to work on this research project. Thierry guided me as my daily supervisor with both the research fundamentals as with the organizational aspects of working in the EKL clean rooms. Arno really motivated me during our progress meetings with his enthusiasm for physics and solar energy. His ability to explain the most fundamental aspects of physics in a comprehensible and inspiring way is unique.

Second, I would like to thank Bilal Bouazzata, my predecessor at this research project. He helped us with everything we could think of. He shared his kindness and humor, but most of all his profound knowledge as an electrical engineer. Having him around the first couple of weeks was a true blessing.

Additionally, I would like to thank Julian van Dingen, my lab partner with whom I did the experiments with. It was really helpful to be able to discuss our research progress and learn all these new things together. The one person teaching us all hands-on experience in the lab was Martijn Tijssen. He gave us the instructions for all machinery and equipment we had to work with. But most of all, I'd like to thank him for his patience every time he had to come to retrieve the substrate holder from the RF chamber when I managed to let it slip again.

Last but not least, I would like to thank my family and my girlfriend Iris, for their mental support during these difficult times in the pandemic. Without their help, I would not have been able to make it this far.

Paul Roelandschap Amsterdam, May 2021

# Abstract

The next step in solar energy conversion systems is multi-junction solar cells. A multi-junction design tackles the problem of non-absorption low-energy photons and thermalization losses of high-energy photons. They utilize a broader range of the solar radiation spectrum and thereby potentially produce more power per area. Currently, multi-junction solar cells based on silicon have proven to be useful in mitigating the problem of spectral mismatching. Spectral mismatching occurs when the incident photons do not match the bandgap energy of the absorber material. If the photons have a higher energy, thermalization losses occur, while photons with lower energy than the bandgap energy don't contribute at all to the generation of charge carriers i.e., non-absorbance.

The multi-junction devices based on silicon are only able to mitigate spectral mismatching of the higher energy photons. Photons with an energy below the bandgap energy of crystalline silicon (1.12 eV) are not utilized. To be able to utilize these photons, a material with a bandgap energy below 1.12 eV is needed. Germanium is one of the most promising materials to consider for functioning as a bottom cell due to its low bandgap energy (0.67 eV) and due to the ability to be produced through low-cost processing technology; Plasma Enhanced Chemical Vapor Deposition. However, some challenges have to be overcome before device quality germanium films can be deposited through PECVD processing. These challenges are instability, a poor photo response and a low activation energy.

In this thesis, over 90 samples were deposited at different deposition conditions in CASCADE, a Radio Frequency PECVD reactor at the Else Kooi Laboratory at the TU Delft. Three approaches were used to improve the a-Ge:H films; I) Deposition condition optimization with a decreased electrode gap to increase the stability, II) Hydrogen Plasma Treatment to increase the photo response and III) Boron doping to increase the activation energy. Through approach I, we were able to produce highly dense and stable films by substantially decreasing the growth rate. Also, increasing the deposition temperature to 275°C significantly increased the material density, thereby increases the stability significantly. The hydrogen plasma treatment approach showed no significant improvement in photo response, while the boron doping experiment was not conclusive. Further research is needed to improve the photo response and increase the activation energy of PECVD processed germanium films.

# **Table of Contents**

1	Intro	duction	8
	1.1	The necessity of clean energy	8
	1.2	Potential and challenges of solar energy	9
	1.3	The necessity of energy storage	9
	1.4	Potential and challenges of germanium for PV application	10
	1.5	Research objectives and outline	10
2	Theo	retical Background	12
	2.1	Solar radiation	12
	2.2	Basic semiconductor physics	13
	2.3	PN junction	15
	2.3.1	Amorphous material structures	16
	2.3.2	Density of states	16
	2.3.3	Light Induced Degradation	18
	2.4	Processing technology	18
	2.4.1	Plasma Enhanced Chemical Vapor Deposition	18
	2.4.2	Growth chemistry of amorphous germanium films	19
3	Expe	rimental setup	21
	3.1.1	General overview of experiment	21
	3.1.2	Substrate cleaning	21
	3.1.3	Deposition	21
	3.1.4	Metal evaporation and contact annealing	22
	3.1.5	Boron doping	22
	3.2	Film Characterization techniques	22
	3.2.1	Fourier Transform Infrared Spectroscopy	22
	3.2.2	Spectroscopic Ellipsometry	23
	3.2.3	Raman Spectroscopy	24
	3.2.4	Electrical conductivity	25
4	Resu	lts	27
	4.1	Deposition Window	27
	4.2	Relationship of deposition conditions and film properties	28 4

	4.2.1	Effect of power and pressure on film properties	28
	4.2.2	Effect of varying the hydrogen plasma dilution	33
	4.2.3	Effect of Temperature on film properties	38
	4.3	Approach I: Deposition condition optimization	40
	4.4	Approach II Hydrogen Plasma Treatment	42
	4.5	Approach III: Boron Doping	45
5	Conc	lusions	47
6	Discussion and future recommendations         4		49
7	' References		50

# **List of Figures**

Figure 1
Figure 22 Decrease of total installation cost and LcoE in the last decade.
Figure 3
Figure 4
Figure 5
Figure 615 Schematic of the space charge region over the metallurgic junction.
Figure 715 Schematic representation of n- and p-type semiconductors with its corresponding band diagram.
Figure 816 Atomic structure of crystalline silicon (left) and hydrogenated amorphous silicon.
Figure 917 Defect states in the forbidden band gap.
Figure 10
Figure 11
Figure 1223 Example of fitted FTIR data with oxidation contamination present in the material.
Figure 1324 Schematic of polarization and the effect of reflection on polarization.
Figure 1429 Effect of pressure on the growth rate in nm per minute.
Figure 15
Figure 16
Figure 17
Figure 18

Figure 19
Figure 20
Figure 21
Figure 22
Figure 2335 Effect of hydrogen dilution ratio on crystal fraction.
Figure 24
Figure 25
Figure 26
Figure 27
Figure 28
Figure 29
Figure 30
Figure 3141 Relationship between the hydrogen concentration and the Activation energy.
Figure 3242 The optical bandgap $E_{04}$ plotted as a function of n@600nm.
Figure 33
Figure 3443 Effect of hydrogen plasma treatment on $\sigma_{photo}\sigma_{dark}$ .
Figure 3544 Dot plot of HPT series.
Figure 3645 Activation energy for the boron doped samples.

# **1** INTRODUCTION

This chapter will provide some information about the relevance of this thesis topic, as well as a project description. A more in-depth explanation of the physics will follow in the third chapter.

#### 1.1 THE NECESSITY OF CLEAN ENERGY

For more than ten thousand years the earth's average temperature has not changed more than one degree Celsius. This thermodynamic balance is due to Earth's atmosphere. So called greenhouse gasses in the atmosphere function as gaseous blanket, keeping the earth at a comfortable temperature of 15 degrees Celsius on average. The concentration of these greenhouse gasses, of which CO<sub>2</sub> and CH<sub>4</sub> are two of its major contributors, normally fluctuates on a scale of millennia. This time scale allowed the earth to adapt and keep the carbon cycle intact. Trees and oceans function as a carbon storage system by locking up carbon from the atmosphere and act as a buffer to maintain the global average temperature between habitable levels. However, over the past 250 years, the pace of carbon emissions increased dramatically. Since the beginning of the industrial revolution in the late 18<sup>th</sup> century, humans began to burn fossil fuels for their energy consumption. This released vast amounts of CO<sub>2</sub> that was stored in these fossil fuels during a process of millions of years. This resulted in CO<sub>2</sub> concentrations of over 400 parts per million (ppm) which has not happened before in the past 400.000 years [figure 1]. If this trend continues, the CO<sub>2</sub> concentration would reach 600ppm in the coming decades, which would result in an average global warming of 2-3 degrees Celsius. This would have detrimental effect on our stable climate and earth's habitability. To mitigate global warming, a transition towards carbon neutral energy must be made.



Figure 1: Atmospheric CO<sub>2</sub> concentrations on a timescale of hundred thousand years.

### 1.2 POTENTIAL AND CHALLENGES OF SOLAR ENERGY

The sun provides inexhaustible free energy to planet Earth that makes solar energy one of the most promising technologies to provide sustainable energy on large scale. The so called levelized cost of electricity (LCOE), which is a measure of total cost per kWh of electricity generated during the technology's lifetime, has decreased to record lows of 0.05-0.18 USD/kWh in 2019 [Figure 2]. This makes it cost competitive with conventional gas and coal fired power plants. In 2019, the total installed capacity for solar energy was 633.7 GWp [1] and is expected to continue its exponential growth the next coming years. The International Renewable Energy Agency (IRENA) predicts a total installed capacity of 2.840 GW in 2030, which would generate 13% of the total electricity consumption [2]. However, in 2018, solar PV only accounted for 0.6% of the total consumed energy globally [3]. This small number shows the many challenges solar energy is still facing, such as high capital investment and financing, low balance of system performances and institutional barriers such as infrastructure and a lack of skilled labor [4].



Figure 2: Decrease of total installation cost and LcoE in the last decade [5].

#### 1.3 THE NECESSITY OF ENERGY STORAGE

The main challenge of solar energy is its intermittent nature due to the rotation of the Earth. This makes it impossible to generate a constant amount of electricity throughout the day. On a daily timeframe, weather conditions play a significant role and can limit the output drastically. Also, depending on the geographic location and distance to the equator, seasonal variations form a major challenge. In the Netherlands for example, January and June differ in energy yield on average with a factor 10. As you go closer to the equator, this difference decreases.

If we want to keep consuming energy on demand, these daily and seasonal fluctuations make it necessary to store energy on an hourly, daily and monthly timeframe assuming fossil fuels are faced out in the future. On an hourly and daily timeframe, batteries have proven to be a promising technology. However, they are not yet cost effective in comparison to conventional methods. On a monthly timeframe, batteries have the problem of self-discharging which makes them not efficient for storing electricity for such a period. In addition, the scale of seasonal mismatch makes batteries too expensive. The size of the battery pack should be matched to the season that

yields the lowest amount of energy. This is, especially at higher latitudes, a size that makes it not cost-efficient. Also, lithium is too rare. According to [6], the world has about 13.5 million tons of lithium reserves. At current demand of 37.000 tons per year, this is enough for 365 years. However, if lithium batteries are used on a Terra Watt scale and for electric vehicles, demand would increase with several orders of magnitude. It is quickly visible that the current estimation of lithium reserves is not enough to challenge the problem of global energy storage. An alternative is to store energy in the form of chemical bonds e.g. fuels. Hydrogen gas is an example of such a fuel. By using electrolysis, water can be split into oxygen and hydrogen gas, and stored for long periods. The hydrogen gas can then later be used as a feedstock in fuel cells to produce electricity. However, the cycle of converting electricity into fuels and back into electricity is currently expensive and not very efficient. Current electrolyzers have an efficiency of 60 to 80% [7] and fuel cells in the range of 40-70% [8]. The complete cycle has an average efficiency of approximately 25 to 55%.

#### 1.4 POTENTIAL AND CHALLENGES OF GERMANIUM FOR PV APPLICATION

This section gives a description of the possibilities and potential challenges of germanium for PV applications. Germanium is a chemical element with the atom number 32. In the Mendeleev periodic table of elements, it is situated in the group IV elements, right below Si and above Sn. This means it has four valence electrons in its outer shell, making it possible to bind with four neighboring atoms. Germanium is, like silicon, a semiconductor material, meaning its band gap energy is in between that of a conductor and an insulator. A more in-depth description of semiconductor physics is given in section 3. While crystalline silicon, the most common PV material used in the market, has a bandgap energy of 1.12 eV, germanium in the ground state has a bandgap of 0.67 eV.

This much lower bandgap implies that it can utilize the energy of photons with a wavelength up until 1850 nm. This is the far Infrared spectrum. Due to other loss mechanisms, germanium as a standalone PV material is less efficient if compared to silicon. However, it can still be of value in addition to silicon PV technology. In multi-junction solar cells, germanium can be used as a bottom cell. A significant part of the non-absorbed photons can be utilized to create additional charge carriers. Because there are still many photons present in the infrared spectrum, the bottom cell is not current limiting. The germanium layer can function as a bottom cell and can increase the open circuit voltage ( $V_{oc}$ ).

Pure germanium is not cost efficient, which is why amorphous hydrogenated germanium (a-Ge:H) is a possible less costly alternative. This material however has still some challenges to overcome before it is able to function as a bottom cell in multi junction solar devices. These challenges involve the stability of the film, as well as the photo response and the charge carrier concentrations. This thesis aims to address these challenges. The next chapter elaborates on these research objectives.

### 1.5 RESEARCH OBJECTIVES AND OUTLINE

The aim of this thesis is to deposit device quality amorphous hydrogenated germanium (a-Ge:H) absorber layers in a Plasma Enhanced Chemical Vapor Deposition (PECVD) reactor. These absorber layers should be suitable for functioning as a bottom cell in a multi-junction solar cell device. To meet these requirements, the films must have a close to intrinsic charge carrier concentration, a low bandgap energy and a good photo response. In addition, the films should be stable and less prone to oxygen contamination. To deposit such device quality films, a thorough understanding on the relationships between the deposition conditions and the film properties must be developed. For this thesis, a deposition window is developed based on earlier research done within the Else Kooi Laboratory at the TU Delft [9]. Promising results were found in the low power/pressure regime. This is why, for this thesis, we have focused on a deposition window with

a deposition RF-power below 10W and a deposition pressure below 6.0 mbar and at with a smaller electrode separation distance of 11.5mm.

The next chapter will provide theoretical background that is necessary to comprehend the mechanisms and physics behind the performed experiments. In chapter 3, a description about the experimental setup and methods to process and characterize the germanium films. Chapter 4 presents the deposition window and the reasoning behind this. Chapter 5 presents the complete characterization results of the processed samples. In chapter 6 the conclusion is given and in chapter 7 a discussion and recommendation for future research is presented.

## **2** THEORETICAL BACKGROUND

The aim of this chapter is to provide understanding of the physics and relevant mechanisms which is necessary for the interpretation of this thesis. As a literature guide, the book 'Solar Energy' from Professor Arno Smets et al. is used [10].

#### 2.1 SOLAR RADIATION

Many forms of energy on earth comes indirectly or directly from the sun. Fossil fuels are the product of dead organisms who used to get their energy from the sun. Plants use solar energy to drive the chemical reaction of photosynthesis, where carbon dioxide and water are converted into glucose and oxygen [1].

$$6CO_2(g) + 6H_2O(l) \to C_6H_{12}O_6(s) + 6O_2(g)$$
<sup>[1]</sup>

Their energy content is solar energy stored in chemical bonds. The kinetic energy present in the moving air parcels i.e. winds are the result of temperature differences on earth due to solar radiation. The sun generates its energy through nuclear fusion. Four protons, or hydrogen atoms, fuse via a number of steps to form one helium atom. The mass of the helium atom is slightly less than that of the four hydrogen atoms, namely 0.635%. This energy difference in the form of mass is converted into radiative energy according to Einstein's famous equation:

$$E = mc^2$$
 [2]

The sun has a surface temperature of approximately 6000 Kelvin. The spectral radiance emitted due to its thermal energy can be calculated according to the blackbody spectrum as calculated by Planck's Law. We see that the sun emits electromagnetic radiation with a spectrum from the ultraviolet part to the deep infrared part or from 200 nm to 2500 nm. The sun generates a power of  $3.8 \cdot 10^{26}$  W. Because the sun is a sphere and radiates in all directions, only a fraction reaches the earth.



Figure 3: Three different solar spectra: the 6000 K blackbody radiation, the AM0 and the AM1.5 spectra.

A total of  $1.7 \cdot 10^{18}$  W reaches earth's atmosphere, or 1360 W/m<sup>2</sup>. This number is called the *solar constant*, and the spectrum is called the AM0 spectrum. The spectrum that reaches earth's surface (at sea level) after travelling through the atmosphere is called the AM1.0 spectrum. The AM1.5 spectrum is an international standard for measuring solar cells. It is the spectrum measured by a plane perpendicular to the sun and tilted 37° to the horizontal, also called the Altitude  $a_m$ . The total power density of the AM1.5 spectrum is 1000 W/m<sup>2</sup>. The spectral irradiance of the AM0 and AM1.5 spectrum is shown in Figure 3.

#### 2.2 BASIC SEMICONDUCTOR PHYSICS

This chapter describes the basic principles of a semiconductor and why its unique characteristics make it possible for photovoltaics to harvest solar energy in the form of electrical energy. A semiconductor is classified based on its conductivity which, as the name implies, lies between that of a conductor and an insulator. The conductivity of a semiconductor depends on the amount of free charge carriers present in the material. These free charge carriers are the negatively charged electrons and the positively charged holes. A hole is nothing more than the position of a missing electron in a covalent bond. This vacancy can be filled up by a neighboring electron, which in his turn leaves another vacancy. This can be viewed as the motion of a positively charged entity, the so-called hole. The movement of electrons and holes happens when thermal energy or photon energy breaks up the covalent bond. The electron is then excited from the valence band to the conduction band. These bands are continuous energy levels. The energy difference between the valence and conduction band is called the band gap, or the forbidden gap, given in equation [3].

$$E_G = E_C - E_V \tag{3}$$

Statistically, in an intrinsic defect free single crystal semiconductor, no electrons can be present in the energy levels between the valence and the conduction band. The band gap energy is therefore the minimal energy required for an electron to be excited towards the conduction band and move through the lattice. Once the electron is situated in the conduction band, it is called a free charge carrier. In semiconductor material, the electrons recombine with the holes after some time. This process happens randomly, but the average time it takes is called the free charge carrier lifetime. The distance these free charge carriers have travelled is called the diffusion length.

In a semiconductor with a perfect crystal lattice at room temperature, the number of electrons in the conduction band and number of holes in the valence band are equal. This is described by the fermi level, which lies exactly in the middle of the band gap. This is called an intrinsic semiconductor. However, in solar cells, semiconductors are *doped*. Doping in semiconductors is the manipulation of the concentration of holes and electrons. The concentration of electrons and holes is determined by the amount of impurity atoms in the lattice. This impurity atom substitutes a silicon atom (or any other atom in a semiconductor material) and is able to accept or donate a free electron. The concentration of these acceptor and donor atoms is denoted with  $N_A$  and  $N_D^+$ , respectively. Inside the semiconductor, the local charge density is given by equation [4], where n and p denote the density of electrons and holes in the conduction and valence band, respectively.

$$\rho = q(p + N_D - n + N_A) \tag{4}$$



Figure 4: A shift of the fermi level for a) intrinsic, b) n-type and c) p-type semiconductors.

The presence of the impurity atoms allows for energy levels in the bandgap. This causes a shift of the fermi level. We say a material is *n-type* when the concentration of electrons in the conduction band is higher than the concentration of holes in the valence band, and *p-type*when there are more holes in the valence than electrons in the conduction band. For an n-type material, the fermi level is then closer to the conduction band, and logically closer to the valence band when p-type. This is illustrated in Figure 4.

In n-type doping, a donor impurity atom is incorporated in the lattice. This impurity atom is usually phosphorous. Phosphorous has 5 valence electrons, which results in one extra electron that cannot take part in bonding with a neighboring atom by forming a covalent bond [5(a)]. The weakly bound valence electron is easily excited to the conduction band because its energy  $E_D$  lies close to conduction band energy level. In p-type doping, an acceptor atom is incorporated in the lattice. In a silicon lattice, this dopant is usually boron.



Figure 5: Doping illustrated with the bonding model. In a), a donor atom in the form of phosphorous donates an extra free electron. In b) an acceptor atom in the form of boron accepts neighbouring valence electrons, which creates a vacancy or hole.

Boron has only three valence electrons, which results in a vacancy in one of the neighboring silicon atom to form a covalent bond Figure 5(b). This vacancy can be described as a hole, and it can accept electrons from their neighboring atoms. As such, the hole can jump from atom to atom and can be seen as a moving positively charged particle. The energy  $E_A$  of the acceptor atom lies close to the valence band energy level.

General expressions for electrons and holes, in equilibrium and non-equilibrium state are given in equation [5] and [6] respectively, where EFn and EFp are the fermi levels with respect to the conduction band in n-type material and with respect to the conduction band in p-type material, respectively.

$$n = N_C e^{\frac{E_{Fn} - E_C}{k_B T}}$$
<sup>[5]</sup>

$$p = N_V e^{\frac{E_V - E_{Fp}}{k_B T}}$$
<sup>[6]</sup>

#### 2.3 PN JUNCTION

Now that we've covered the basics of semiconductors and doping, we can put that into practice into solar cells. This section explains how a semiconductor material can drive an electrical current by absorbing electromagnetic radiation.

As discussed earlier, a p-type semiconductor has holes as the majority carriers while an ntype semiconductor has electrons as majority carriers. This is illustrated in Figure 7. When these two materials are brought together two counteracting forces exist; a diffusion current due to the concentration difference of electrons, and a drift current due to an electric field caused by the charge difference. These two forces cancel each other out and cause a depletion region to arise over the pn junction. This is illustrated in Figure 6. The region outside the space charge region is called the quasi-neutral region. This space charge region prevents electrons or holes to move to the other side and recombine.





Figure 6: Schematic of the space charge region over the metallurgic junction when n-type and p-type are brought together.

Figure 7 Schematic representation of *n*- and *p*-type semiconductors with its corresponding band diagram. The dashed line indicates the fermi energy level.

When a semiconductor material is illuminated, photons with enough energy excite an electron from the valence band tot the conduction band. The concentration of electrons and holes in the p-type and n-type material respectively increases sharply. These minority charge carriers, the electrons in the p-type and holes in the n-type, flow across the space charge region to the other quasi neutral region.

#### 2.3.1 Amorphous material structures

An important characteristic in semiconductor material for its optoelectronic properties is the atomic structure. A perfect crystal lattice consists of atoms in a perfect structured order, where the distance between the atoms is equal as well as the bond angles. This is called diamond cubic coordination. Amorphous materials don't have this long-range structural order. The coordination of atoms and bonds is random, which results a non-uniform distribution. Group IV semiconductors, such as silicon and germanium, tend to bond to four neighboring atoms. However, in an amorphous material this is not always the case. Due to the structural disorder some are not able to form covalent bonds, and their electrons can be seen as dangling bonds. In hydrogenated amorphous materials, these dangling bonds are passivated with hydrogen. Dangling bonds can act as defect sites, which deteriorates the electrical properties of the material. This is further explained in the next section. Figure 8 displays the atomic structures of a crystal and amorphous lattice. Dangling bonds occur in various coordination structure. They can be 3-fold, 4-fold and 5-fold (floating bond). This results in less optimal material structures.



Figure 8 Atomic structure of crystalline silicon (left) and hydrogenated amorphous silicon.

#### 2.3.2 Density of states

To have a better understanding of the optical and electronic properties of amorphous semiconductors, it is necessary to understand the density of states (DOS) concept. DOS is a simple approximation that when an electron belongs to a solid structure, it can be seen as occupying a well-defined state of some discrete energy level [11]. These states have their range of energies, and the number of these available states per unit volume per unit energy is called the density of states. For semiconductors such as crystalline silicon, these states are very well defined and there are no energy levels in the bandgap that can be occupied. In less ideal materials, such as a-Si:H and a-Ge:H, these states are much more difficult to define. This is because amorphous material has a long-range structural disorder. This causes potential fluctuations inside the material, leading to an exponential distribution of so-called *tail states*. This is visualized in Figure 9, where the valence band and conduction band energy states extend into the forbidden band gap. These

extensions are called *band tails*. The width of these band tails is referred to as the Urbach energies. The tail states are described according to equations [7] and [8] [12]:

$$N_{TC} = N_{C0} e^{\frac{E_V - E}{E_{urc}}}$$
<sup>[7]</sup>

$$N_{TV} = N_{V0} e^{\frac{E - E_V}{E_{urv}}}$$
<sup>[8]</sup>

Where  $E_{urc}$  and  $E_{urv}$  are the Urbach energies of the conduction and valence band, respectively. To optimize the optoelectronic properties of amorphous material, the Urbach energies ought to be minimized [13]. High Urbach energies imply a higher structural disorder and thus more defect states. These defect states function as trap state where free charge carriers recombine and thus not contribute to a potential current. Because the defect states in amorphous material are localized, it is difficult to accurately determine the bandgap for the entire material.

Contiguous to the band tails are energy bands in the lower and upper half of the band. These energy states are considered to be related to the dangling bond of threefold coordinated germanium atoms [12]. Depending on the position of the Fermi level, the dangling bond states are referred to as positive ( $D^+$ ), negative ( $D^-$ ) or neutral ( $D^0$ ) if they are closer to the conduction band, valence band or mid gap, respectively.

It is necessary for high quality amorphous material that these defect states are minimized. Dangling bond states can be passivated by hydrogen atoms. This could lower the defect states several orders from  $1 \cdot 10^{22} \ cm^{-3}$  to  $1 \cdot 10^{18} \ cm^{-3}$  [14].

Amorphous material is characterized by its long-range structural disorder. This impedes the mobility of free electrons, mainly due to electron scattering. Figure 9 illustrates the density of states for a-Si:H, from which the electronic structure can be described [15]. The disorder causes the band edges to extend into the gap. These edges are called band tails. Electrons are frequently trapped and vice-versa from these states which further deteriorate the mobility of charge carriers.



Figure 9: Defect states in the forbidden band gap.

#### 2.3.3 Light Induced Degradation

This section briefly explains the concept of light induced degradation (LID) and what causes this effect. LID is also known as the Staebler-Wronski Effect (SWE) and causes the efficiency to drop sharply after a certain period of light exposure (Figure 10). The SWE is one of the biggest challenges for thin film solar cells and its origin is not yet fully understood. Due to recombination of the excited charge carriers by photons, metastable defects are created in the absorber layer. A metastable effect means that the effect is reversible. Annealing at temperatures above 130 Celsius reverses the degradation significantly, as can be seen in Figure 10.

The increased defect density caused by the SWE leads to a higher recombination rate in the absorber, thus inhibiting the current through the external circuit. It is generally believed that these defects are caused by dangling bonds. The dangling bond density increases due to the removal of hydrogen from a silicon atom. The required energy is provided by recombination from the excited charge carriers in the bulk of the material. It can be seen from Figure 10 that the effect is less significant for polymorphous silicon, but the effect seems irreversible. According to the authors of [16] this irreversible effect could not be explained according to the conventional paradigm based on the SWE. To understand the complete kinetics of LID more experimental research is needed. However, there is consensus that a denser material, meaning less nano-sized voids inhibits the effect of the SWE for amorphous materials [11].



Figure 10: Efficiency drop caused by LID. The annealing process reverses the effect [16].

#### 2.4 PROCESSING TECHNOLOGY

#### 2.4.1 Plasma Enhanced Chemical Vapor Deposition

The technology used for processing the samples for this thesis is Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF PECVD). The advantage of PECVD processing is the relatively low required temperature compared to other CVD technologies. In the case of PECVD, not thermal energy delivers the activation energy for the growth reaction but the energy present in the plasma delivers the energy to dissociate the molecules. Plasma is often seen as the fourth

fundamental state of matter after solids, liquids and gasses. A plasma consists of electrons, ionized molecules, neutral and ionized fragments of molecules and free radicals. The plasma is excited by the energy gained by an electric field. This electric field is created between the two electrodes by a fluctuating potential. The electric field breaks down the covalent bonds between the gas molecules by exciting the electrons from its valence shell to higher energy states. This leaves high energy electrons and neutral broken up fragments of the molecule or free radicals. The free radicals are extremely reactive and are able to attach themselves to the substrate. This generally happens at a constant rate throughout the process.



Figure 11: A simple schematic of a PECVD reactor.

#### 2.4.2 Growth chemistry of amorphous germanium films

One of the most important aspects of PECVD processing is the growth chemistry. For the stability and optoelectronic properties of the films, it is necessary to have a somewhat homogeneous insertion reaction of  $GeH_X$  radicals towards the substrate. The insertion reaction is a lateral diffusion reaction, where a germanium radical bonds to a vacant site on the surface.

To achieve this, the reactions inside the plasma need to be forced in one direction. Multiple different germane radicals are produced in the plasma, which lead to different kind of insertion reactions. The main chemical reactions inside the plasma, with  $H_2$  and  $GeH_4$  as precursor gasses, are the following [17]:

$$e + GeH_4 \leftrightarrow GeH_3 + H^+$$
  
 $e + GeH_3 \leftrightarrow GeH_2 + H^+$   
 $H^+ + GeH_4 \leftrightarrow GeH_3 + H_2$ 

According to [17], the *GeH*<sub>3</sub> radical (germyl) is the most important one. An excess of Hydrogen dilution in the plasma force the production of germyl and could lead to a somewhat homogenenous insertion reaction. Another advantage of hydrogen dilution is that excess hydrogen ions prevent the interactions of radicals with eachother. This would lead to higher polymers and to a prolonged structural disorder in the material. However, a high hydrogen incorporation in the bulk of the material leads to an increase of the optical bandgap [18]. Whilst one of the objectives of this thesis is to process a material with a low bandgap, excess hydrogen plays an ambiguous role. It is proposed by [13] to use controlled ion bombardment to force the generation of germyl radicals. Inert ions such as helium or argon can etch the hydrogen off the surface. This etching is also necessary since the bond breaking strength of Ge-Ge is 1.9 eV and that of Ge-H is 2.99 eV. This means that is unfavorable for a Ge atom to replace an H atom bonded to Ge. The removal of hydrogen from the surface is thus necessary to grow the Ge:H films.

# **3 EXPERIMENTAL SETUP**

This section describes the experimental setup as well as the method of processing and characterizing the germanium films. At first, a general overview is given. Later all single steps in the process are described in more detail

### 3.1.1 General overview of experiment

All samples are processed in the Else Kooi Laboratory at the Delft University of Technology using Cascaded Arc Solar Cell Apparatus Delft Eindhoven, or CASCADE, an RF PECVD reactor. The films are processed on two different substrates. These substrates are crystalline silicon (c-Si) wafers and glass. The silicon wafers are circular with diameter of 10 cm and a thickness of 500 µm and crystal orientation (100). The films are processed on these two substrates simultaneously. Before the substrates are loaded into the RF chamber of CASCADE, the substrates are cleaned. The glass substrates are cleaned in an isopropanol and acetone ultrasonic bath to remove dust particles and other contaminants. The c-Si wafers are Marangoni dried in an HF solution to remove the surface oxides. The films are then processed onto the substrates with a thickness of 80-140 nm. After processing, aluminum contacts are deposited onto the film through metal evaporation and a subsequent annealing step. After this step, the samples are finished, and they are stored into a vacuum box located in the cleanroom.

#### 3.1.2 Substrate cleaning

As mentioned above, the substrates are cleaned and treated prior to deposition. The glass substrates are from Corning Inc. and are cut into slices of 10 cm x 2.5 cm. The glass substrates are placed into an acetone and isopropanol (IPA) ultrasonic bath for 10 minutes. Acetone is first used due to its characteristics that it dissolves almost all organic matter. Second, IPA is used because it displaces water very well in contrast to acetone, which leaves a residue. Finally, the glass substrates are blow-dried with nitrogen gas. Now the glass substrates are ready for deposition.

The c-Si wafers are treated in a hydrofluoric acid (HF) bath and dried with so called IPA drying, also known as Marangoni drying. The HF solution has a molar concentration of 0.5% HF. HF is a very strong acid and is used to remove or etch the silicon oxide layer. This etching is done for 4 minutes. IPA drying makes use of the Marangoni effect, which relies on the low surface tension of IPA compared to demi water [19]. A surface tension gradient is formed between the water and IPA present on the wafer surface. The gradient makes the water flow away from the wafers. If done in a slow and careful process, the wafers come out clean and dry. After letting them rest for 30 seconds, the wafers are ready for deposition.

### 3.1.3 Deposition

After cleaning and drying, the substrates are placed on a substrate holder. The substrate holder is brought inside the load lock which is then pumped down to near vacuum pressures (3E-4 mbar). The valve between the load lock and RF reaction chamber is then opened and the substrate holder brought into the RF chamber. The substrate holder is then locked in the RF chamber with the substrates facing down. The substrate is placed between the electrodes, with a diameter of 10 cm and spacing of 11.5 mm.

The internal parameters that can be varied are temperature, pressure and RF power. The temperature is controlled via conductive heating. The pressure is kept constant by a turbo pump and butterfly valve. The pressure range for the processed samples is 1 to 6 mbar. The power supply is an RF generator with a power range of 1 to 60 W. A matchbox is installed to match the impedance

of the power supply and the plasma, to ensure a maximal power transfer and minimize reflective power.

The gas inlet system regulates and controls the flow of the precursor gasses. There are 5 available inlet pipes, but only the  $H_2$  and  $GeH_4$  precursor gasses are used during this research. The  $H_2$  flow is kept constant during all depositions at 200 sccm, while the GeH<sub>4</sub> gas is varied from 0.5 to 2.0 sccm in steps of 0.5 sccm. After the films have reached approximately 100 nm, the RF power supply is turned off and reaction chamber is emptied by opening the butterfly valve 100%. The substrate holder is brought back to the load lock where the samples are passively cooled for 30 minutes in vacuum. The RF-chamber is then purged with argon gas for 2 minutes to flush away the remaining GeH<sub>4</sub> and H<sub>2</sub>.

### 3.1.4 Metal evaporation and contact annealing

After the samples are processed the metal contacts have to be fabricated to be able to conduct electrical measurements. This is done in PROVAC 500 through metal evaporation. A target metal, in this case aluminum, is bombarded with a high intensity electron beam in a vacuum environment. Atoms from the target metal evaporate due to this beam and find any solid to form a coating on. The samples are placed on a mask, enabling the gaseous metal to form a structured shape on the substrate. The contacts are processed to be 500 nm thick. Finally, the samples are annealed in an oven at 130 C for 30 mins to ensure high quality contacts and strong cohesion between the contacts and the film. After this final step, the samples are ready for measurements.

### 3.1.5 Boron doping

Finally, three samples were selected based on their promising properties to be processed once more with a boron diluted plasma. The other internal processing parameters were kept constant. Two different methods were used for this doping experiment. First, on a substrate of corning glass a thin layer of boron atoms was deposited using PECVD. To ultimately incorporate the boron atoms into the germanium lattice, the glass substrates with the boron deposition were placed on the substrate holder together with the new substrates to be processed inside CASCADE. The reasoning behind this method is that the hydrogen etching due to hydrogen diluted plasma creates a mixture of germanium radicals and boron radicals. This should lead to a uniform layer of germanium and boron dopants.

### 3.2 FILM CHARACTERIZATION TECHNIQUES

### 3.2.1 Fourier Transform Infrared Spectroscopy

After processing and cooling, the wafer sample is put immediately into the Fourier Transform Infrared Spectroscopy apparatus (FTIR). FTIR is a method for vibrational analysis. With FTIR the absorption of the sample for different wavenumbers in the infrared region (400-4000 cm<sup>1</sup>) can be measured. The infrared light is absorbed by a chemical bond in the material if the vibrating frequency of the bond is equal to the frequency of the infrared light. When absorption takes place, a peak is shown in the absorption data plot. Through these peaks, the different chemical bonds in the material can be analyzed. It should be noted that only the chemical bonds that create a dipole moment when vibrating are detected with the FTIR measurement.

The hydrogenated germanium films were analyzed by measuring two wafer samples: one with germanium deposition (sample) and one without (background). By subtracting the sample with the background, the Ge:H film is isolated and can be analyzed without interference of the c-Si absorption. The data is fitted using the Fityk software, where multiple Gaussians decompose the absorbance peaks, and a baseline is manually subtracted from the absorbance data.

The chemical bonds that are of main interest for the characterization of the Ge:H films are the Ge-O bonds. This is because oxidation of the film results in an increase of the bandgap energy and thus impedes the development of a low bandgap material [20]. Also, oxidation indicates instability of the material. One of the main criteria for a cell quality film is that it should be stable and thus poor of oxides. It is suspected that large volumetric voids facilitate post-oxidation reactions. An example of the fitted Gaussians corresponding with oxides are presented in Figure 12, the peak at 846 cm<sup>-1</sup> is the dominant peak when a sample is oxidized. When fitting these Gaussians, it is important to consider carefully to attribute a peak to the 846 wavenumber or the 830 wavenumbers because they represent bonds with different chemical elements. It is still disputed what bond belongs to the peak at the 830 frequency, which is why it is labelled GeX. A further examination of the chemical bonds is given in the results section.



Figure 12: Example of fitted FTIR data with oxidation contamination present in the material [20].

#### 3.2.2 Spectroscopic Ellipsometry

With spectroscopic ellipsometry (SE), the optical characteristics such as refractive index, extinction coefficient and absorption coefficients were determined. For measurements the J.A. Woollam variable angle M-2000D Ellipsometric was used. The working principle of SE is based upon the polarization state of light. As light is an electromagnetic wave, it has an oscillating electric field and magnetic field. The electric field determines the polarized state of the light. Light can be s-polarized and p-polarized, or perpendicular and parallel respectively. This is illustrated in Figure 13. If the p-wave and s-wave are in phase and have the same amplitude, the light is linearly polarized. When two polarization waves have different amplitudes or arbitrary phases, the polarization state is elliptical. When light is reflected from a material structure, the s-polarized and p-polarized are reflected differently. This results in a change of the complex reflectivity ratio, which is measured in ellipsometry. Equation [9] displays this reflective ratio, where  $\Psi$  denotes the amplitude ratio,  $\Delta$  the phase difference and  $R_p$  and  $R_s$  the reflectivity of the p- and s-polarized light [21].

$$\frac{R_p}{R_s} = \tan\left(\Psi\right)e^{i\Delta}$$
<sup>[9]</sup>



Figure 13: Schematic of polarization and the effect of reflection on polarization. The p- and s-component of the electric field reflect differently, thus changing the ratio.

The optical characteristics are determined by means of a fit, performed within the CompleteEASE software from J.A. Woollam. The measurements were fitted using the Cody-Lorentz oscillator. The software has many built in functions that can be used for different material structures. The accuracy of the fit is quantitatively represented by the mean square error (MSE). In general, a model fit with a MSE below 10 was assumed to be accurate. The fit automatically tabulates the film thickness, Tauc bandgap energy and the optical constants n and k over a wavelength range of 100 - 1650 nm. For comparison of the samples, we used the refractive index in the visible light region (600 nm).

#### 3.2.3 Raman Spectroscopy

Raman spectroscopy is a non-destructive measurement technique to do qualitative and quantitative analysis upon the chemical and crystal structure of the material. The technique is based on the Raman Effect, which is a scattering mechanism that occurs when light interacts with a material. When a monochromatic light beam such as a laser, interacts with a sample, a part of the light is transmitted, and a part is scattered. About 99% of the intensity of the scattered light has the same frequency as the incident light. This is called Rayleigh scattering. When the emitted light has a different frequency than the incident light, it is called Raman scattering. To look more closely into this effect, we have to visualize the vibrational energy states of electrons. If an electron with energy state E absorbs a photon, it is excited to a virtual energy state corresponding to its initial energy plus the energy of the incident photon, or  $hv_i$ . Once it relaxes again, it falls down in energy level corresponding to the scattering photon, or  $hv_s$ . When  $hv_s = hv_h$  logically the electron falls back to its original energy level E. When  $hv_s \neq hv_i$ , the energy falls back to a different level. When this level is higher than the original state, the electron has absorbed energy meaning  $hv_s < hv_i$ . This is called stokes lines. When the electron releases energy, the electron falls back to a lower vibrational energy level. This is called anti stokes lines. The intensity of the peaks holds information about the density of the observed structures (qualitative analysis) and the center frequency of the peaks about the respective bonds and phonon modes (qualitative analysis).

For this research, the Renishaw inVia Raman Microscope with an Argon laser with a wavelength of 514 nm. Through earlier research, the Ge-Ge bonds and phonon modes could be attributed to the centre frequencies of the peaks. These are tabulated in Table 1.

Centre Frequency [cm <sup>-1</sup> ]	Chemical bond	Phonon Mode	
80	a-Ge	TA [transverse acoustic]	
177	a-Ge	LA [longitudinal acoustic]	
230	a-Ge	LO [transverse optic]	
278	a-Ge	TO [transverse optic]	
297-300	nc-Ge	Localized optical phonons in Ge nanocrystals	
295	c-Ge	Single crystal Ge, non-symmetric	
300.7	c-Ge	Single crystal Ge	

Table 1: Ge-Ge bonds with its corresponding raman center frequencies and phonon modes [22, 23, 24, 25, 26].

The crystallinity of the germanium films is calculated according to [10].

$$X_C = \frac{I_{300} + I_{295}}{I_{300} + I_{295} + \gamma I_{278}}$$
[10]

Where  $X_c$  is the crystal fraction in % and  $I_X$  the area of the Gaussian fit of the Raman spectra with its respective centre frequencies at x. The  $\gamma$  is a correction factor, which is chosen to be equal to 0.85. Reasoning behind this is that commonly a correction factor of 0.8 is chosen for a-Si:H and a correction factor of 1 for a-Ge:H. This factor of 0.85 is chosen by [9]. For good comparison the same  $\gamma$  is chosen for this research.

#### 3.2.4 Electrical conductivity

One of the most critical factors for high quality PV material are the electronic properties and its photoresponse. To quantify these properties photoconductivity and dark conductivity measurements are performed. In a semiconductor, the conductivity depends on the concentration and mobility of the free charge carriers (p- and n-type). This relationship is given in equation [11].

$$\sigma = e(\mu_e n + \mu_h p) \tag{11}$$

Where  $\sigma$  is the conductivity in S/cm, *e* is the elementary charge,  $\mu_e/\mu_h$  the electron/hole mobility and *n/p* the electron/hole concentration. The general expressions for *n* and *p* are given in equation [5] and [6].

The photoconductivity is measured with the AAA class Wacom WXSS156S-L2 solar simulator. For these measurements the standard test conditions are applied, which correspond to the irradiance of the AM1.5 spectrum and a temperature of 25.0 °C. The AM1.5 spectrum is simulated with a combination of a Halogen lamp and a Xenon lamp. The probes are connected to the contact of the sample and apply a potential of 10V.

$$\sigma_{ph} = \frac{I}{V} (bd)^{-1}$$
<sup>[12]</sup>

The current that flows between the contacts is measured and the conductivity is calculated

according to equation [12], where b is the ratio of the length of the aluminum contacts and the spacing between them and d is the film thickness in centimeters. For this research, a b value of 40 is used.

The dark conductivity,  $\sigma_d$ , is calculated according to equation [12] as well. However, to calculate the conductivity as a function of temperature, equation [13], also known as the Arrhenius equation, is used,

$$\sigma_d(T) = \sigma_0 e^{\frac{-E_A}{kT}}$$
<sup>[13]</sup>

where  $E_A$  is the activation energy, *k* the Boltzmann constant in electron volts, T the temperature in Kelvin and  $\sigma_0$  the temperature independent conductivity. The activation energy is calculated with the slope of the linear regression line of the ln(1/kT) as a function of  $ln(1/\sigma)$ . 14The dark conductivity as a function of temperature is measured with the Keithley 617 multimeter. This is done by applying a constant potential of 10V at a temperature range of 60 °C to 130 °C in steps of 5 °C and measuring the current.

# **4 RESULTS**

This section provides an overview and understanding of the experimental results. The research objective of the experiments was to produce a device quality absorber layer that can be used as a bottom cell in multi-junction PV technology. Because we are focusing on a bottom cell material, germanium was chosen based on its relative low bandgap energy of 0.67 eV (ground state at 300 K). For a device-quality germanium absorber layer, the material should be stable, intrinsic and have a good photo response. To improve the stability and electrical properties of the films, three approaches were used:

- 1. Deposition condition optimization at small electrode separation to increase the film material density.
- 2. Post deposition Hydrogen Plasma Treatment (HPT) to decrease the defect density by passivating dangling bonds.
- 3. Counter doping with boron to make the material less n-type. The dominant defect type in a-Ge:H layers brings the Fermi level closer to the conduction band which makes it n-type. By adding a p-type dopant such as boron, we aim to make the material more intrinsic and thereby decreasing the dark conductivity.

To achieve to above mentioned objectives, a thorough understanding of the relationship between the deposition conditions and the material properties must be developed first. These relationships are treated in 4.2. The deposition condition optimization is presented in 4.3. The post deposition HPT experiment is treated in 4.4, while the counter doping experiment is treated in 4.5.

### 4.1 **DEPOSITION WINDOW**

Deposition Parameter	Range	Unit
Hydrogen Dilution [H <sub>2</sub> /GeH <sub>4</sub> ]	100-400	[-]
Chamber pressure	1-6	mbar
RF Power	2.5-10	Watt
Substrate Temperature	200-275	Celsius
Electrode gap	11.5	mm

Table 2: Range of deposition condition settings used in this thesis.

The electrode gap is brought to 11.5 mm, the lowest setting possible for our reactor. Bouazatta and Ravichandran [20] have investigated a deposition window with a higher electrode gap (20 mm) and a higher power density regime. Research has shown that for silicon processing with RF PECVD a smaller electrode spacing leads to a larger volumetric crystal fraction and less defects in the material [27]. In the past, research has been conducted on the effect of smaller electrode separation on the material properties of a-Ge:H processed with PECVD [27]. These results showed that by increasing the electrode gap from 10 mm to 32 mm the material became more heterogeneous, and the electrical properties deteriorated. These results strengthen the hypothesis that a smaller electrode gap results in a more dense and homogeneous film. At smaller electrode spacing a

stronger electric field is present according to equation [15], where V is the applied RF voltage and d the electrode spacing. In this case, the voltage is proportionally related to the applied RF power.

$$|\vec{E}| = \frac{V}{d}$$
[15]

Compared to the deposition window investigated in [20], more focus is placed on a low deposition rate. To achieve this, a low power/pressure regime has been selected. Over 80 samples with an RF power range between 2.5–10W and a pressure range of 1-6 mbar are processed. Earlier germanium processing research had less focus in this deposition window, with a wider electrode gap and a power range of 10-100 W in increments of 10-20 W [28] [11] [29] [30]. These experiments showed better results regarding electrical properties for the low power density depositions, which confirms our approach. However, the relationship is not linear and therefore it is not possible to simply interpolate the optimal processing power. This is why in this research the deposition window is narrowed down and the increments are smaller.

### 4.2 RELATIONSHIP OF DEPOSITION CONDITIONS AND FILM PROPERTIES

#### 4.2.1 Effect of power and pressure on film properties

In order to investigate the effect of the deposition power and pressure on film properties, a series with 5 different pressures values and 3 different power values are deposited. This is performed for two different dilution regimes. The complete list of deposition conditions is tabulated in the table below.

Table 3: Deposition condition settings for the power/pressure series. 15 combinations of power and pressurewere used for two different hydrogen dilution settings.

Parameter	Value/Range	Unit
RF Power	2.5 – 5 – 10	W
Pressure	2 - 3 - 4 - 5 - 6	mbar
Deposition Temperature	200	°C
Electrode Spacing	11.5	mm
Film Thickness	90-110	nm
F(H2)/F(GeH4)	200 – 400	-

As earlier research already found, the increasing deposition power and pressure results in an increase of the growth rate [9]. This is in line with our results. With increasing power/pressure combinations, the growth rate increases too. Only for the  $10W - 200C - 400 [F(H_2)/F(GEH_4)]$  series the growth rate doesn't show this relationship. This could be explained by the fact that these samples show an increasing crystal fraction up to 60%, whereas the others only reach crystal fractions up to 5%.



Figure 14: Effect of pressure on the growth rate in nm per minute. Temperature and hydrogen dilution ratio were constant at 200 °C and 400, respectively.



Figure 16: Effect of deposition power on the growth rate. Temperature and hydrogen dilution ratio were constant at 200 °C and 400.



Figure 15: Effect of deposition power on growth rate. Temperature and hydrogen dilution ratio were constant at 200 °C and 200, respectively.

According to [31], the formation of nanocrystals is a more time-consuming process and therefore results in a lower growth rate. Also, the growth rate is determined by simply taking the ratio of the film thickness over the deposition time. As crystal structures are more dense than amorphous structures, a smaller film thickness is measured for more crystal film, hence a lower growth rate. The crystal formation in the 10W-200°C-400[ $F(H_2)/F(GEH_4)$ ] is stimulated by higher pressure, as can be seen in Figure 24. The expected higher growth rate for higher pressure depositions could therefore be counteracted by the formation of nanocrystals in these samples. Figure 16 and Figure 15 show the effect of deposition power on the growth rate. From these figures it is clear that the growth rate increases with increasing power. The observed deviation from the trend at the 6 mbar series in Figure 15 and Figure 16 can be explained by the same logic as described above. The 6mbar samples show increasing crystal fractions with increasing deposition power. As mentioned above, formation of nanocrystals result in a lower growth rate.



Figure 17: Effect of pressure on the growth rate in nm per minute. Temperature and hydrogen dilution ratio were constant at 200 °C and 200, respectively.

Figure 19 and Figure 20 show the influence of the power and pressure combination on the films' optical and electrical properties. Figure 19 introduces the metric [W\*bar] and Figure 20 introduces [W/bar]. These two metrics should be analyzed together. The logic behind this is that both power and pressure have the same effect on growth rate, namely both positive. By comparing the trends of [W\*bar] and [W/bar], it can be concluded which of the two has a dominant effect (assuming both have the same effect). As discussed earlier, depositions with a high growth rate result in films with higher porosity. This effect is somewhat visible when looking at the refractive index in Figure 19, where a declining trend can be observed both the blue and orange samples. When comparing the plot of the refractive index in Figure 19 and Figure 20, it can be concluded that the deposition pressure has a more dominant effect on the porosity than the deposition power. The refractive index is rising for higher power/pressure ratios, while the product [W\*bar] shows a negative correlation with the refractive index. These relationships suggest that lowering the pressure has a stronger effect than lowering the power conditions of the depositions.

The Tauc bandgap energy,  $E_{tauc}$ , of the films processed at a dilution ratio of 200 and 400 show a different relationship with the product of power and pressure. The films processed at  $F(GeH_4)/F(H_2) = 400$  show a clear downtrend with increasing power\*pressure, whereas the films processed at  $F(GeH_4)/F(H_2) = 200$  don't seem to have any significant correlation between the tauc

bandgap and power\*pressure deposition conditions. This could possibly be explained by the higher hydrogen concentration inside the plasma. Increasing the power and pressure results in stronger hydrogen etching, which could offset the effect of the increase in the growth flux.

It should be noted from Figure 20 that there is a clear relationship between the dark conductivity and the power/pressure ratio. The aim was to lower the dark conductivity by optimizing power and pressure combinations. This relationship obtained from Figure 20 suggests that the optimal power/pressure combination is to minimize the RF power and to maximize the deposition pressure. The sample that measured the lowest dark conductivity was processed at 2.5W and 6 mbar, which is the lowest RF power setting and highest chamber pressure. This strengthens the suggestion that the optimal power pressure regime for processing films with a low dark conductivity is that of low power and high pressure. This is backed up by Figure 18, where the dark conductivity declines for increasing pressure and increases with increasing power.



Figure 18: The dark conductivity (log-scale) vs the deposition pressure. The size and colour of the markers denote the deposition power.



Figure 19: Scatterplot of the influence of the product of the deposition power and pressure on the TAUC bandgap, refractive index, dark conductivity and the activation energy.



Figure 20: Scatterplot of the influence of the ratio of the deposition power over pressure on the TAUC bandgap, refractive index, dark conductivity and the activation energy.

The photo response of the films, which is denoted by the ratio of the photoconductivity over the dark conductivity, seems to increase for higher power and pressure combinations [Figure 21]. This could be attributed to the fact that films that have a higher porosity show a higher oxygen contamination in the material structure. These defect types have energy levels close to the conduction band, which increases the photoconductivity stronger than it increases the dark conductivity [20].



Figure 21: The photo response as a function of the deposition power and pressure ratio and product.

#### 4.2.2 Effect of varying the hydrogen plasma dilution

This section treats the results of the hydrogen dilution experiment and describes the effects on the growth chemistry. Hydrogen dilution is expressed as the flowrate ratio of the inlet gasses, which are molecular hydrogen ( $H_2$ ) and germane (GeH<sub>4</sub>). Altering this ratio greatly affects the growth mechanism and thereby the material properties. A higher hydrogen plasma dilution could stimulate hydrogen etching and ion bombardment, which eliminates the heterostructure in a-Ge:H [27]. A more homogeneous structure is possibly more dense and less rich of defects. According to this logic it could be expected that increasing the hydrogen dilution ratio may have a positive effect on the photo response and the stability of the film.

To examine the effect of the hydrogen dilution ratio a series of four different samples is recreated with four different hydrogen dilution ratios. The deposition conditions are tabulated in Table 4.

Table 4: Deposition parameters of dilution and temperature series.	. A total of 16 samples were processed in these
series.	

Parameter	Value	Unit
RF Power	2.5 – 10	W
Pressure	4 – 5	mbar
Deposition Temperature	200 – 275	°C
Electrode Spacing	11.5	mm
Film Thickness	90-110	nm
F(H <sub>2</sub> )/F(GeH <sub>4</sub> )	100 - 200 - 300 - 400	-

It is clear from Figure 22 that a higher Hydrogen plasma dilution results in a lowering of the deposition rate. The green markers, which are processed at a high-pressure power combination of 5mbar and 10W, respectively, have a strong dependence on the dilution ratio. The series indicated with the blue markers, which are processed at a lower pressure power combination of 4mbar and 2.5W, respectively, show a similar trend. This effect could be explained by the fact that there simply is less germane gas present in the plasma which automatically leads to a decrease in growth material. Also, excess hydrogen etching reduces the growth rate. While the deposition rate behaves according to the same trend for the series 5mbar-10W-200/275°C, only the 275 °C series show significant crystallinity. According to [29] and [32], plasma with excess hydrogen could enhance the formation of crystal structures. This effect can be seen in the 5mbar-10W-275°C series [Figure 23], where the crystal fraction rises sharply with higher dilution rates. Since this is not clearly the case for the lower temperature series, crystal growth might also be influenced by temperature. The influence of temperature on crystal growth is treated in section 4.2.3.

According to [33], the structural disorder in a-Ge:H is strongly reduced when the germane is diluted at 1% in H<sub>2</sub>. They attribute this result to a better surface passivation by the hydrogen atoms during the growth of the material. This could lead to a lower defect density. The excess hydrogen in the plasma can force the creation of GeH<sub>3</sub>, the most important radical for material growth in the plasma [17]. This should lead to a somewhat homogeneous insertion reaction. According to [27], ion bombardment and etching is necessary to obtain a more homogenous structure. The presence of excess hydrogen in the plasma could prevent the reaction between the germanium radicals and therefore the formation of higher polymers [17]. High polymers as growth material may result in a higher structural disorder. Also, the passivation of dangling bonds is key to decrease recombination losses. Hydrogen can potentially passivate these dangling bonds.



Figure 22: This figure shows the film's growth rate as a function of  $F(H_2)/F(GeH_4)$ . The series shown in green are plotted on the right y-axis, while the series shown in blue are plotted on the left y-axis.



Figure 23: Effect of hydrogen dilution ratio on crystal fraction. The series shown in green is plotted at the right yaxis at the left. Note that right y-axis differs an order of magnitude with te right y-axis.



Figure 24: Effect of pressure on crystal fraction. Both series are processed at 10W - 200C. The yellow and blue series at a dilution ratio of 400 and 200, respectively.

One of the other research objectives is to create a low bandgap material. The effect of hydrogen dilution on the optical bandgap  $_{E04}$  is not conclusive when looking at Figure 26. Earlier research by [18] stated that excess hydrogen etching of a-SiGe:H leads to an increase in the defect density and thereby a widening of the bandgap. When looking at Figure 26, a decrease in the  $E_{04}$  can be observed for the samples processed at 10W, 5mbar and 275°C, while the samples processed at 200°C show no correlation with H dilution. This may suggest that increasing H dilution at higher temperature increases the defect density, while it slightly decreases the defect density at lower temperatures. This suggestion is backed by the dark conductivity plot in Figure 26. As a relatively high dark conductivity for the samples processed at respectively 275°C and 200°C, indicate that the effect of H dilution on the defect density might be temperature dependent.

The activation energy of the samples processed at 275°C decreases slightly with increasing H dilution ratio, while the activation energy of the samples processed at 200°C slightly increases (Figure 26). One possibility is that H incorporation is more effective at higher processing 35

temperature, meaning a higher H dilution rate causes more H to form bonds inside the lattice. Hydrogen might activate neutral defects inside the lattice into donor type defects [34]. This results in a more n-type material, so in this case decreases the activation energy. There is a somewhat negative correlation between the hydrogen concentration and the activation energy of our processed filmsFigure 31. This relationship is conforming the theory presented by [34]. However, the hydrogen concentration of the samples decreases with increasing hydrogen dilution, as can be seen in Figure 25. De Vrijer et al. found a strong relationship between the oxygen contamination of the films and their activation energy [20]. They developed a metric to quantify the level of oxidation within the film, the  $\alpha_{GeOx}$ . Oxygen defects have energy levels closer to the conduction band and therefore result in a decreased activation energy [35]. By means of the FTIR data, we calculated the  $\alpha_{GeOx}$  for our samples accordingly. The  $\alpha_{GeOx}$  as a function of the hydrogen dilution ratio is plotted in Figure 27. It can be concluded from this figure that solely increasing the hydrogen dilution ratio does not decrease the level of oxidation in the sample, and therefore does not increase the stability of the films. The  $\alpha_{GeOX}$  of the samples processed at 10W and 5mbar, which is the high end of our deposition window with regard to power/pressure, increases with increasing hydrogen dilution ratio from 100 to 300, but decreases sharply at 400. The  $\alpha_{GeOx}$  of the samples processed at 2.5W-4mbar show no clear trend with increasing hydrogen dilution ratio.

One more possibility is the fact that due to a strong decrease in growth rate, the deposition time was much higher for the samples processed in highly diluted plasma. As can be seen in Figure 22, the growth rate decreases a factor 4 with the dilution ratio increasing from 100 to 400. Because we aimed all films to be 100nm thickness, this strong effect on the growth rate resulted in a prolonged deposition time. This increased deposition time at high temperatures, and thereby a greater annealing effect, could cause changes in material structure. Also, annealing a-Ge:H layers at temperatures above 200°C could cause hydrogen out diffusion [36] from the bulk towards the surface and thereby possibly changing the bulk structure and chemistry.



Figure 25: Hydrogen concentration as a function of the plasma hydrogen dilution ratio.



Figure 26: The effect of hydrogen dilution on the dark conductivity, Activation energy, optical bandgap and refractive index at 600nm.



Figure 27: Oxidation coefficient as a function of the hydrogen dilution ratio.

#### 4.2.3 Effect of Temperature on film properties

In this research, no extensive experiments are performed regarding temperature effects on the growth chemistry of a-Ge:H. These experiments were performed prior to this thesis at the TU Delft by [9]. All samples in this thesis are processed at deposition temperatures of either 200 °C or 275 °C. As can be seen from Figure 22, there is no significant difference in growth rate between the series processed at 200 °C or 275 °C. However, temperature does seem to influence crystal growth and refractive indices. As can be seen Figure 28, there is a strong difference in refractive index between the 200 °C and 275°C processed samples, which indicates a more dense material growth at deposition temperature of 275°C. Temperature and pressure were kept constant at 10W and 5mbar for all samples. This could be attributed to a higher diffusion of GeH<sub>3</sub> radicals across the growth surface for higher probability of a more homogenous material growth. However, higher temperature also results in so-called H abstraction reactions [37]. This phenomenon decreases the H coverage of the growth surface, which limits the diffusion length of the radical. Therefore, a certain optimal temperature has to be found for the growth of Ge:H films in PECVD.



Figure 28: Crystal fraction of Ge:H samples versus its's refractive index at 600 nm. All samples are processed at 10W - 5mbar. Yellow dots are processed at 200 Celsius, red dots at 275 Celsius.

In addition, the crystallinity of the material seems to be enhanced by the temperature difference, as can be seen in Figure 28. Research has shown that the heating of nanoparticles encourages the formation of strong Ge-Ge bonds [29], while lower temperature depositions result in high H incorporation in the structure. This can also be seen in Figure 30, where the 200°C depositions clearly have an overall higher hydrogen content compared to the 275°C samples. According to [34], there is significant hydrogen out diffusion at 200°C, and at 250°C on or near the surface of the germanium sample. The formation of dihydrides at the surface is a significant source of surface recombination. This could explain the decrease in photoconductivity for the samples processed at 275 °C. While the samples processed at 275 °C show a higher refractive index and a more crystalline structure, the electrical properties seem to be deteriorated for the samples processed at high temperatures. This is contradictory to the results presented by [31], where a more crystalline and dense film shows stronger electrical properties. From Figure 29, it can be



observed that there is clear separation in photoconductivity between the samples that are processed at 200°C and samples that are processed at 275°C.

Figure 29: Dark conductivity and the photo response as a function of the photoconductivity. Colour of the markers denote the deposition temperature, while the size of the markers represents the hydrogen concentration.



Figure 30: Hydrogen concentration as a function of the refractive index at 600nm. All samples are processed at 10W and 5mbar and a dilution ratio of 300. Colour of markers denotes deposition temperature.

One explanation for this observation could be the difference in hydrogen concentration between the low and high temperature samples. Sixteen samples were processed at 10W, 5mbar and 200°C with an average hydrogen content of 6.55%. Another 16 samples were processed at the same 10W and 5mbar, but at 275°C and average a hydrogen concentration of 4.85%. So, increasing the temperature from 200°C to 275°C results in a 26% decrease in hydrogen content.

#### 4.3 APPROACH I: DEPOSITION CONDITION OPTIMIZATION

This section describes the deposition conditions of the optimal samples with respect to stability and electrical properties. The refractive index is used to assess the film's stability. This is because a higher refractive index indicates a film with a higher density. A dense film leaves less room for volumetric defects, which is detrimental for the film's stability. To assess the electrical properties of the film, the ratio of the photoconductivity,  $\sigma_{photo}$ , and the dark conductivity,  $\sigma_{dark}$ , is a valuable parameter. We want to achieve samples with activation energy levels close to half of the bandgap energy width (~500 meV).

One observed trend that is already mentioned in section 4.2.3 is the increased refractive index for samples processed at 275°C with respect to samples processed at 200°C. For all experiments, solely increasing the substrate temperature from 200°C to 275°C leads to a significant increase in refractive index. The higher refractive index for the higher substrate temperature could be explained by in-situ annealing of the films [38]. During this process, weakly bonded hydrogen atoms defuse from the lattice. This gives the lattice the possibility to restructure and form stronger Ge-Ge bonds. The optical bandgap  $E_{04}$  decreases at a deposition temperature of 275°C with respect to a deposition temperature of 200°C. This is in line with the theory that an increase in defect density (e.g., decrease of the refractive indices) in the lattice increases the bandgap energy.

The activation energy decreases when the substrate temperature is elevated form 200°C to 275°C. Only the samples processed at a dilution ratio of 400 and a power-pressure combination of 10W-5mbar don't show this trend. It is also noticed that for the samples processed at 275°C, the activation energy decreases with increasing dilution ratio, while the activation energy of the samples processed at 200°C slightly increase with increasing dilution ratio. However, the film with the highest activation energy is still very well below the half of the bandgap, which was the aim of this thesis. Apparently, the defects still present in the lattice have energy states closer to the conduction band, which makes the film n-type. Another explanation for the fermi level being close to the conduction band edge could be found in the role of hydrogen. Studies found that when hydrogen bonds to a neutral defect in the germanium bulk, it binds with an extra electron and acts like a negative ion [36]. In this way, hydrogen acts as an n-type defect. As amorphous germanium is rich of neutral defects [36], this process of activating neutral defects into negative ions could significantly lower the activation energy and make the material n-type. This effect can be seen in Figure 31, where the red markers denote samples that were treated with a post deposition hydrogen plasma treated. We see a trend for both the red and yellow markers that indicates a negative correlation between the hydrogen concentration and the activation energy. This is in line with the suggestion that hydrogen inside germanium bulk activates defects into donor dopants and makes the films more n-type.



Figure 31: Relationship between the hydrogen concentration and the Activation energy. Red markers denote samples that underwent a post deposition HPT. The size of the red markers represents the HPT power (1,2.5,5,10,20 W).

The  $\sigma_{dark}$  shows an increasing trend with increasing power/pressure ratios, as illustrated in Figure 20. These samples also have the highest  $\sigma_{photo}/\sigma_{dark}$ . The  $\sigma_{dark}$  also decreases at the higher deposition temperature of 275°C. This indicates a decrease in defect density. This effect is not immediately visible when looking at the  $\sigma_{photo}/\sigma_{dark}$  because the  $\sigma_{photo}$  also decreases significantly at 275°C. There is also a strong decrease in photoconductivity for the samples processed at 275°C with respect to 200°C. It is suggested that this is the result of the outdiffusion of hydrogen from the bulk towards the surface, where they form dihydrides and act as recombination centers and strongly enhance the surface recombination velocity [34]. However, surface recombination is less significant for our samples due to their very high bulk defect density. Nonetheless, with this theory in mind, temperature may have an ambiguous effect on the desired film properties. Increasing the temperature results in more dense films and thereby increases its stability while it also causes hydrogen to leave the bulk and form dihydrides on or near the surface. More research is needed to find the optimal deposition temperature for germanium PECVD processing with an electrode separation of 11.5mm.

Post deposition oxidation is the root cause for films being unstable. For germanium films, trying to prevent this process is extra relevant because germanium is hygroscopic [39], meaning it reacts with water molecules in its surroundings. The oxygen in the water molecules bond with the germanium and acts as a defect and thereby increases the width of the bandgap. As mentioned earlier, more porous films are more prone to post-deposition oxidation than denser films [20]. This relationship can be seen in Figure 32, where a negative correlation can be observed between the  $E_{04}$  and the refractive index.  $\alpha_{tot}$  is a developed parameter to quantify the level of oxidation and carbon contamination in the film. It can be observed that the more porous films (low refractive index) have a higher oxygen and carbon contamination signature. This is in line with the theory presented by [20] and [40] that more dense films have a lattice constant diameter that is too small for water molecules to be able to diffuse into the lattice.



Figure 32: The optical bandgap  $E_{04}$  plotted as a function of n@600nm.  $\alpha_{tot}$  is denoted by the colour and size of the markers. The makers inside the red oval are all processed at 10W, 5mbar, 200°C and 300 dilution ratio  $F(H_2)/F(GeH_4)$ .

All samples with a refractive index below 4.6 were deposited at 10W, 5mbar and 200 °C, illustrated within the red oval in Figure 32. As mentioned earlier in section 4.2.3, by increasing the temperature to 275°C this can be counteracted.

The deposition conditions were optimized to increase the film's stability and its activation energy and to decrease the bandgap energy and the defect density. The most promising results were obtained at the higher deposition temperature. It strongly increased the material density and thereby prevents post deposition oxidation i.e., instability. It is also found that the dark conductivity, which is a measure of defect density, decreases by lowering the deposition power to a minimum of 2.5W and increasing the pressure in the reaction chamber up to 6mbar.

#### 4.4 APPROACH II HYDROGEN PLASMA TREATMENT

Hydrogen Plasma Treatment (HPT) is a process of post deposition annealing and hydrogen etching of the samples. The idea behind this technique is that the surface dangling bonds will be passivated by the hydrogen atoms in the plasma and that hydrogen etching results in reformation of structural voids. This could make the films less prone to post deposition oxidation and thereby increase their stability and also decrease the defect density. Therefore, in this thesis, HPT is used as an approach to improve the photo response and increase the stability of the Ge:H films. Two samples from our data set were selected based on their oxygenation signature and photo response. The samples were processed again and treated with hydrogen plasma for three different timeframes and five different RF power values. The complete parameters of this series are tabulated in Table 5.

Parameter	Value	Unit
Temperature	200 – 275	°C
RF Power	10	W
Pressure	5	mbar
HPT Power	1.5 - 3 - 5 - 10 - 20	W
HPT Duration	2 - 5 - 10	Minutes

Table 5: Deposition parameters for the HPT experiment.



Figure 33: Effect of hydrogen plasma treatment on  $\sigma_{photo/}\sigma_{dark}$ . The sample - which was processed at 200C, 5mbar, 10W- was given a hydrogen plasma treatment of 2, 5 and 10 minutes at 1, 3, 5, and 10W.



Figure 34: Effect of hydrogen plasma treatment on  $\sigma_{photor}\sigma_{dark}$ . The sample - which was processed at 275C, 5mbar, 10W- was given a treatment of 2, 5 and 10 minutes at 1, 3, 5, and 10 W.

The hypothesis that the samples treated with a post deposition hydrogen plasma would be less prone to post deposition oxygen contamination could not be confirmed with our experiment. As can be seen in Figure 35, there is no strong correlation in either the duration of the HPT nor the RF Power of the HPT and the oxidation coefficient  $\alpha_{Ox}$ . Also, no strong effect is seen in the photo response of the germanium films as can be seen in figures 31 and 32.



Figure 35: Dot plot of HPT series. The time on the y-axis indicates the duration of the HPT in minutes, while the power on the x-axis represents the RF-power of the HPT. The colour and size of the markers represent the level of oxidation. All samples are processed at 10W and 5 mbar and a  $F(H_2)/F(GeH_4)$  of 300. Upper graph represents 200°C series, lower graph 275°C series.

One explanation for the small effect of HPT for germanium films is the relative low solubility of H in Ge [34]. Hydrogen in the gas phase does not easily permeate into the already solid structure of the samples. Thereby, the already existing voids inside the structure could not reached by the H atoms and the dangling bonds may not passivated. Therefore, despite using a systematic approach, we were not able to meet the research objective of increasing the photo response by decreasing the film's defect density.

#### 4.5 APPROACH III: BORON DOPING

An important parameter for device quality material is the activation energy of the semiconductor material. The activation energy equals the difference between the Fermi level and the conduction band for n-type material or between Fermi level and the valence band for p-type material. We have concluded that a-Ge:H behaves like n-type material, based on the type of defects and their influence on the activation energy. Samples rich of defects such as oxygen contamination tend to have a low activation energy, and oxygen defects have energy levels close to the conduction band [20]. To serve as a thin film PV device, the a-Ge:H layer must be preferably intrinsic. The activation energy must therefore be increased to that of half the bandgap energy, or 500-600 meV.



Figure 36 A) samples are processed without boron doping, B) Boron covered glass substrates are placed alongside glass substrates during deposition, C) Same configuration as for experiment B, but hydrogen plasma is activated 5 minutes before germanium deposition.

A presumed method to do this is by using boron as a doping atom. Boron acts as a p-type dopant in the lattice that can accept an electron from a neighboring atom. Boron doping should therefore make the n-type material more intrinsic and bring the Fermi level closer to half the bandgap energy. Two different methods were used for this doping experiment. First, on a substrate of corning glass a thin layer of boron atoms was deposited using PECVD. To ultimately incorporate the boron atoms into the germanium lattice, the glass substrates with the boron deposition were placed on the substrate holder together with the new substrates to be processed inside CASCADE. The reasoning behind this method is that the hydrogen etching due to hydrogen diluted plasma creates a mixture of germanium radicals and boron radicals. We used two methods on identically processed samples. For the first method, deposition is started immediately, while the second method first ignites a hydrogen plasma for 5 minutes with the aim to etch the boron atoms from the glass substrate and mix the boron radicals in the plasma.

For this experiment, two different samples were chosen for boron doping. A sample with a high crystal fraction of 61% and moderate  $E_{act}$  of 132 meV and sample with no crystal fraction and

relatively high  $E_{act}$  of 226 meV were doped according to two different methods. Figure 36 shows the effect of the two different methods on the  $E_{act}$ . The results are for the two different samples are contradicting with regard to the effect on the  $E_{act}$ . While the  $E_{act}$  of the crystalline sample slightly decreases, the  $E_{act}$  of the amorphous sample slightly increases for the samples processed with boron diluted plasma. It is difficult to be conclusive on these results. The level of successful boron incorporation in the germanium lattice is not determined. The methods used to mix the B with the H<sub>2</sub> and GeH<sub>4</sub> is not a proven method. Further work is needed to be able to conclude on the boron doping experiment.

# **5 CONCLUSIONS**

The research objectives of this thesis were to find the optimal deposition conditions for the PECVD processing of device quality Ge:H thin films. Prior research examined a broad deposition window with respect to power, pressure and hydrogen dilution and a fixed electrode separation distance of 20mm. This research had more focus on the low power pressure regime and a relative highly diluted hydrogen plasma. Also, the electrode separation distance was brought to a minimum of 11.5mm to be able to lower the growth flux. The aim of this thesis was to deposit a highly dense material with strong electronic and optical properties, meaning being intrinsic, low bandgap and having a strong photo response.

93 samples were deposited in CASCADE at the Else Kooi Laboratory at the TU Delft. The deposition window was designed to deposit films at a small growth rate. We processed at the lowest power and pressure conditions possible at an electrode gap of 11.5mm. Lower power and pressure conditions did not sustain a stable plasma. These low power and pressure conditions lowered the deposition rate substantially, which enabled a denser material growth.

We found that the activation energy increases and the optical bandgap  $E_{04}$  decreases for less porous films (high refractive index). We found that by increasing the deposition temperature up to 275°C the refractive index was significantly increased, indicating a less porous material. These dense materials were less prone to post deposition oxidation and thereby more stable.

Additionally, we found that hydrogen dilution plays a crucial role in the formation of nanocrystals in the material structure. A  $F(H2)/F(GeH_4)$  of 400 resulted in films with very crystal fractions of up to 60%. In addition, the samples processed at 275°C proved to have a higher crystal fraction than the samples processed at the same conditions but at a lower temperature of 200°C. However, no strong correlation was found between the crystallinity of the material and the desired device quality properties.

Another observation was that the photoconductivity was reduced for the samples processed at the high deposition temperature of 275°C. This might be due to a decrease of H incorporation in the bulk, resulting in voids rich of un-passivated dangling bonds. Also, the out diffusion of hydrogen and the resulting formation of dihydrides near the surface strongly increases the surface recombination velocity and thereby deteriorates the photo response.

No sample has met all requirements to be device quality. However, some samples have shown promising results. We have deposited films that have proven themselves to be very stable and an improved activation energy with respect to the films deposited at a higher electrode gap. The most tion energy. The most promising sample has an activation energy of 314 meV. a refractive index at 600nm of 5.25 and a  $E_{04}$  of 1.15 eV. However, the  $\sigma_{photo}/\sigma_{dark}$  is around 1, indicating a very poor photo response. This sample was processed at 275°C, 2.5W, 4mb and a hydrogen dilution ratio of 100. More research should be done to improve the photo response. The photo response of the films could not be improved by post deposition hydrogen plasma treatments despite our systematic approach.

The sample with the highest  $\sigma_{photo}/\sigma_{dark}$  and without significant oxidation has a  $\sigma_{photo}/\sigma_{dark}$  of 4.40 and an E<sub>04</sub> optical bandgap of 1.16 eV. Its refractive index is 4.77, E<sub>act</sub> of 163.9 meV and a hydrogen concentration of 8.73%. It has a small crystalline fraction of 10.08%. The deposition parameters were 10W, 4mbar, 200°C and a dilution ratio of 200. The activation energy of 163.9 meV is a limiting property for it to be a device quality film. New methods to counteract the formation

of donor dopants need to be further investigated. The boron doping experiment we conducted in this research was not conclusive on its effects.

# **6 DISCUSSION AND FUTURE RECOMMENDATIONS**

While this thesis gave further insights in the growth mechanisms of PECVD grown a-Ge:H films, it failed to produce device quality films. The photo response has not improved sufficiently. This might be due to the high defect density. Another point of consideration is the presence of carbides into the structure. This contamination deteriorates the electrical properties as well as the stability of the film. The origin of carbon contamination is not yet understood.

In this thesis, two deposition temperatures were used. Since the reactor was not able to go to higher temperatures, the temperature was limited at 275°C. It might be useful to repeat some experiments at higher temperatures. 275°C had some advantages over substrate temperatures of 200°C such as a higher refractive index and thereby less oxygen contamination; it also had a decreasing effect on the electrical properties. Temperature seems to have a strong effect on the hydrogen concentration inside the bulk of the material and at the film surface. The role of H in a-Ge:H is not yet fully understood. More emphasis on this part would be beneficiary to be able to optimize the deposition temperature and increase the electrical properties.

We aimed to increase the activation energy by boron doping. We tried to add boron radicals to the growth material by adding glass substrates with boron depositions next to our sample substrates. This method produced inconclusive results and further research should be done to investigate the effect of boron doping on the activation energy of the a-Ge:H films.

Lastly, it could be interesting to add another Group IV semiconductor element, tin, and to form the alloy GeSn. Alloying Ge with Sn, with a bandgap of 0 eV, would lower the bandgap substantially and might decrease the defect density and improve the photo response.

# **7 REFERENCES**

- [1] N. Sönnichsen, "Global cumulative installed capacity 2000-2019," 6 August 2020. [Online]. Available: https://www.statista.com/statistics/280220/global-cumulative-installed-solar-pvcapacity/#:~:text=Global%20cumulative%20solar%20photovoltaic%20capacity,installed%20 in%20that%20same%20year.. [Accessed 15th January 2021].
- [2] International Renewable Energy Agency, "Future Of Solar Photovoltaic: Deployment, investment, technology, grid integration and socia-economic aspects," IRENA, Abu Dhabi, 2019.
- [3] IEA, "Renwables Information Statistics Report," IEA, 2020.
- [4] E. Kabir, P. Kumar, S. Kumar and A. Adelodun, "Sp;ar emergy: potential and future prospects," *Renewable and Sustainable Energy Reviews*, vol. 82, pp. 894-900, 2018.
- [5] IRENA, "Renewable Power Generation Costs in 2019," IRENA, New York, 2020.
- [6] B. Jaskula, "Lithium," in 2017 Minerals Yearbook, U.S. Geological Sciences, 2020, pp. 1-11.
- [7] Hydrogen Europe, "hydrogeneurope," hydrogeneurope, 2017. [Online]. Available: https://hydrogeneurope.eu/electrolysers#:~:text=The%20efficiency%20of%20electrolysis%2 0is,based%20on%20the%20calorific%20value).. [Accessed 20 Feb 2021].
- [8] U.S. Department of Energy, "Fuel Cell Technologies," Energy Efficiency and Renewable Energy, Washington DC, 2015.
- [9] B. Bouazatta, A. Ravichandran and T. d. Vrijer, "Development of a-/nc-Ge:H," Delft, 2020.
- [10] A. Smets, K. Jager, O. Isabella, M. Zeman and R. v. Swaaij, Solar Energy: The Physics and Engineering of Photovoltaic Conversion Technologies and Systems, UIT Cambridge, 2016.
- [11] A. Rind, "Photovoltaic Applications of Si and Ge Thin Films Deposited by PECVD," Faculty of Engineering, Science and Mathematics School of Electronics and Computer Scienc, Southampton, 2014.
- [12] Y. Liu, "High growth rate deposition of hydrogenated amorphous silicon-germanium films and devices using ECR-PECVD," Iowa State University, Ames, 2002.
- [13] A. Amato, S. Terreni, M. Granata, C. Michel, B. Sassolas and L. Pinard, "Observation of a correlation between internal friction and urbach energy in amorphous oxides thin films," *Scientific reports*, vol. 10, no. 1670, pp. 1-9, 2020.
- [14] B. Ebersberger and W. Krühler, "Equilibrium defect density in hydrogenated amorphous germanium," *Applied Physics Letters*, vol. 65, pp. 1683-1685, 1998.
- [15] J. Wang, "Novel concepts in the PECVD deposition of silicon thin films: from plasma chemistry to photovoltaic device applications," Paris, 2018.

- [16] H. Kim and P. Cabarrocas, "Irreversible light-induced degradation and stabilization of hydrogenated polymorphous silicon solar cell," *Solar Energy materials and Solar Cells*, vol. 105, pp. 208-212, 2012.
- [17] V. Dalal, S. Kaushal, J. Xu and K. Han, "A critical reveiw of the growth and properties of a-(si,ge):h," *Proceedings of 1994 IEEE 1st World Conderence on Photovoltaic energy Conversion*, pp. 464-467, 1994.
- [18] V. Dalal, "Growth Chemistry of amorphous silicon and amorphous silcon-germanium alloys," *Current Opinion in Solid State & Materials Science,* vol. 6, no. 5, pp. 455-464, 2002.
- [19] J. Marra and J. A. M. Huethorst, "Physical Principles of Marangoni Drying," Philips Research Laboratories, Eindhoven, 1991.
- [20] T. d. Vrijer, A. Smets and B. Bouazatta, "The impact of processing conditions and postdeposition oxidation on the opto-electrical properties of hydrogenated amorphous and nanocrystalline Germanium films," *Journal of Non-Crystalline Solids*, 2020.
- [21] J.A. Woollam, "What is ellipsometry," J.A. Woollam, Lincoln, 2020.
- [22] D. Bermejo and M. Cardona, "Raman Scattering in Pure and Hydrogenated Amorphous Germanium ANd Silicon," *Journal of Non-Crystalline SOlids*, pp. 405-419, 1979.
- [23] V. Volodin, G. K. Krivyakin, G. G. Ivlev, S. L. Propopyev, S. V. Gusakova and A. A. Popov, "Crystallization of amorpous germanium films and multilayer a-Ge/a-Si Structures upon exposure to nanosecond laser radiation," *Semiconductors,* vol. 53, pp. 400-405, 2019.
- [24] Y. Chou and S. Lee, "Structural, optical, and electrical properties of hydrogenated amorphous silicon germanium alloys," *Journal of applied Physics*, vol. 83, no. 8, pp. 4111-4123, 1998.
- [25] V. Volodin, D. Marin, V. Sachkov, E. Gorokhov, H. Rinnert and M. Vergnat, "Applying an improved phonon confinement model to the analysis of raman spectra of germanium nanocrystals," *Journal of experimental and theoretical physics*, vol. 118, no. 1, pp. 65-71, 2014.
- [26] P. Klement, C. Feser, B. Hanke, K. v. Maydell and C. Agert, "Correlation between optical emission spectroscopy of hydrogen /germane plasma and the raman crystallinity factor of germanium layers," *Applied Physics letters*, vol. 102, no. 15, pp. 1-3, 2013.
- [27] W. Paul, "Structural, optical and photoelectronic properties of improved pecvd a-ge:h," *Journal of Non-Crystalline Solids*, pp. 803-808, 1991.
- [28] G. Dushaq, M. Rasras and A. Nayfeh, "Hydrogen-Induced Crystallization of Germanium Films at Low Temperature using an RF-PECVD Reactor," *The Electrochemical Society*, pp. 213-217, 2017.
- [29] E. Johnson and P. Cabarrocas, "High Quality a-Ge:H Fiilms and Devices Through Enhanced Plasma Chemistry," *MRS Proceedings*, 2011.

- [30] Y. Bouizem, A. Belfedal and J. D. Sib, "Optoelectronic properties of hydrogenated amorphous germanium deposited by rf-PECVD as a function of applied rf-power," *Journal of Physics: Condensed Matter*, pp. 5149-5158, 2005.
- [31] M. Moreno, A. Torres and R. Ambrosio, "Deposition and characterization of polymorphous germanium films prepared by low frequency PECVD," *Journal of Non-Crystalline Solids,* pp. 2099-2102, 2011.
- [32] Q. Sheng-Hua, C. Cheng-Zhao and L. Cui-qing, "Effect of hydrogen dilution on crystalline porperties of nano-crystalline silicon thin films in fast grwoth," *Acta Physica Sinica*, vol. 58, pp. 656-569, 2009.
- [33] C. Godet, V. Chu, B. Equer and L. Chahed, "Density of States of Amorphous Germanium Thin Films Deposited by the PECVD of H2-Diluted Germane," in *Materials Research Society Symposium*, Paris, 1990.
- [34] J. Weber, H. Miller and E. Lavrov, "Hydrogen in Germanium," *Materials Science in Semiconductor Physics*, vol. 9, pp. 564-560, 2006.
- [35] M. STUTZMANN, J. STUKE and H. DERSC, "Electron Spin Resonance of Doped Glow-Discharge Amorphous Germanium," *Solid State Physics*, pp. 141-152, 1983.
- [36] S. a. p. o. h.-i. p. i. e. semiconductors, "P.J.H. Denteneer; C.G. van de Walle; S.T. Pantelides," *Physical Review Letters*, vol. 62, no. 16, pp. 1884-1889, 1989.
- [37] G. C, I. E. Zawawi and M. Gauthier, "Improvement of plasma-deposited a-Ge:H Thin films by hydrogen dilution of germane," *Solid State Communications*, vol. 74, no. 8, pp. 721-725, 1990.
- [38] A. Bhaduri, P. Chaudhuri and D. Williamson, "Strucutural and optoelectronic properties of silicon germanium alloy thin films deposited by pulsed radio frequency plasma enhanced chemical vopor deposition," *Journal of Applied Physics*, vol. 104, pp. 1-10, 2008.
- [39] N. Posthuma, G. Flamand, W. Geens and J. Poortmans, "Surface passivation for germanium photovoltaic cells," *Solar Energy Materials and Solar Cells*, pp. 37-45, 2004.
- [40] T. A. Abtew and D. Drabold, "Ab initio models of amorphous Si1-xGex:H," *Physical Review B*, vol. 75, pp. 1-9, 2007.
- [41] W. Turner and S. Jones, "Structural, optical, and electrical characterization of improved amorphous hydrogenated germanium," *Journal of Applied Physics*, pp. 7430-7440, 1990.
- [42] A. H. M. Smets, W. M. M. Kessels and M. C. M. v. d. Sanden, "Surface-diffusion-controlled incorporation of nanosized voids during hydrogenated amorphous silicon film growth," *Applied Physics Letters*, 2005.
- [43] S. Guha, J. Yang, J. Jones, Y. Chen and D. L. Williamson, "the Effect of microvoids on initial and light-degraded efficiencies of hydrogenated amorhpus silicon alloy solar cells," *Applied Physics Letters*, pp. 1444-1446, 1992.

- [44] D. Debaiyoti and A. Dey, "Optimization in the nanostructural evolution of hydrogenated thin film in RF-PECVD," *Physica E; Low dimensional systems and nonastructures,* pp. 20-28, 2019.
- [45] T. Nakashita and A. Inoue, "Dependence of Electronic Properties of Hydrogenated Amorphous Ge on Deposition Condition," *Japanese Journal of Applied Physics*, pp. 1730-1736, 1992.
- [46] A. Chowdhury, S. Mukhopadhyay and S. Ray, "Effect of electrode separation on PECVD deposited nanocrystalline silicon thin film and solar cell properties," *Solar Energy Materials* & *Solar Cells*, vol. 94, pp. 1522-1527, 2010.
- [47] D. Staebler and C. Wronski, "Revirsible changes in conductivy in discharge produced a-Si:H," *Applied Physics Letter*, vol. 4, no. 31, pp. 292-294, 1977.