BACHELOR

On the influence of ICP-PECVD deposition parameters and annealing on the properties of a-Si:H passivation layers

Arts, K.

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On the influence of ICP–PECVD deposition parameters and annealing on the properties of a–Si:H passivation layers

K. Arts

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Eindhoven University of Technology
Department of Applied Physics
Plasma & Materials Processing (PMP) Group

Under the supervision of:
ir. B. Macco
prof.dr.ir. W.M.M. Kessels
Abstract

Hydrogenated amorphous silicon (a–Si:H) can be applied as a passivation layer in silicon heterojunction (SHJ) solar cells. In this project, depositions of a–Si:H thin films have been carried out using ICP–PECVD under several deposition conditions. This has been done to gain insight into the deposition process and how the properties of the deposited film can be controlled. To reach this goal, the deposition temperature, pressure and power have been varied to investigate the correlation between the plasma conditions and the properties of the deposited films. Also, an annealing series has been carried out to determine the influence of annealing on the properties of the a–Si:H film. The microstructure (i.e. porosity and hydrogen content) of the a–Si:H layers has been characterized by Raman spectroscopy, Fourier transformed infrared (FTIR) spectroscopy and spectroscopic ellipsometry (SE). By doing so, the influence of the deposition parameters and annealing on the properties of a–Si:H passivation layers has successfully been determined.
1 Introduction

1.1 The solar challenge

Environmental concerns about the use of fossil fuels and their limited availability has triggered the search for alternative, sustainable energy resources in the past decades \[3\]. Acid precipitation, stratospheric ozone depletion and the greenhouse effect are often seen as the most important environmental problems \[4\]. Possible emission–free energy resources, which do not contribute to these problems, are solar, hydroelectric, biomass, wind, ocean and geothermal energy \[6\]. Solar energy has the potential of being a major energy source for future generations, considering that the sun provides the Earth with more than 10000 times the power humans currently consume \[3\]. There are two ways to make the use of photovoltaic (PV) devices economically more profitable. One way is to reduce the costs of the used materials, for example by producing organic solar cells \[3\]. The second solution is to accept relatively high material costs and aim for high efficiencies \[4\]. Silicon based solar cells, which are discussed in this paper, reach efficiencies above 20% \[3\] and can be categorized in the second group.

1.2 Silicon heterojunction solar cells

The efficiency of solar cells can be improved by reducing electron–hole recombination. Dielectric passivation layers enable nearly recombination–free surfaces for c–Si solar cells. However, the efficiency is reduced with the use of highly recombination–active metal contacts. A solution for this problem is the use of heterostructure contacts, which fulfill the passivation and contacting roles simultaneously \[3\].

A sketch of an a–Si:H/c–Si heterojunction solar cell is given in figure 1.1, in which it can be seen that an intrinsic a–Si:H layer is used as a passivation layer and junction between the n–doped c-Si wafer and p–doped a–Si:H film. The a–Si:H (hydrogenated amorphous silicon) film is studied in this project and has an optimal thickness of approximately 10 nm. If the layer is thinner, it has poorer passivation properties. However, a thicker layer absorbs more photons, which should be absorbed by the c–Si (n) absorber to generate charge carriers.

The contacts of a heterojunction solar cell are electronically separated from the absorber by insertion of a buffer layer with a higher bandgap (such as a–Si:H). In this way the recombination activity at the surface is reduced, provided that the interface state density is minimized \[3\].
Since hydrogenated amorphous silicon has a slightly wider bandgap than that of c-Si, can be doped relatively easily and has excellent passivation properties, it is an attractive candidate to serve as a buffer layer for silicon heterojunction (SHJ) solar cells \[3\]. Among others, the relatively simple SHJ fabrication process and the high efficiencies cause the current interest in the commercialization of this technology \[3\].

### 1.3 Aim of this project

Surface passivation layers of a–Si:H can be produced with plasma enhanced chemical vapor deposition (PECVD). In this project an inductively coupled plasma (ICP) is used to deposit a–Si:H layers under several physical conditions: the deposition temperature, pressure and power are varied. The different deposited layers are characterized using spectroscopic ellipsometry, Fourier transformed infrared spectroscopy and Raman spectroscopy. This is done to investigate the influence of the deposition conditions on the properties of the deposited a–Si:H layer. By doing so, more insight is gained into the deposition process. Also, the properties of the deposited film can be controlled better and the investigated deposition conditions can be improved to reach superior passivation properties.

More specifically, it has been observed in earlier research that good passivation qualities are obtained with depositions at 50 °C followed by annealing at 200 °C, while device–grade films are normally grown at a deposition temperature of 200 °C without annealing afterwards. To investigate the difference between a–Si:H layers deposited in these two ways, the microstructure (i.e. hydrogen content and porosity) is characterized of films deposited at different temperatures and of films annealed for different annealing times. Concrete research questions of this project are:

- What is the influence of the deposition temperature, pressure, power and annealing time on the porosity and hydrogen content of the a–Si:H layer?
- What is the influence of the deposition temperature, pressure and power on the deposition rate?
- What is the uniformity of the thickness and porosity of a–Si:H films deposited using ICP–PECVD?
- Does the laser used in Raman spectroscopy have effect on the microstructure of the a–Si:H film?
- How do the a–Si:H properties correlate with the passivation quality?

Besides the scientific goal of gaining more knowledge about a–Si:H deposition, this project is carried out to learn how to do scientific research. A lot of experimental work is done to gain experience with different measurement techniques and provide empirical results. Literature studies are done to understand the basic deposition processes and to explain experimental observations.
2 Theory

2.1 Surface passivation with a–Si:H films

Electronic grade amorphous silicon is an alloy of silicon and hydrogen and is therefore called hydrogenated amorphous silicon, abbreviated with a–Si:H. Despite being amorphous and therefore lacking the long range order, it has been obtained from X-ray diffraction measurements that a–Si:H has the same short range order as c–Si \[18\]. Therefore, the semiconductor concepts such as the energy state bands can still be used in a–Si:H. However, there is no longer a well defined band gap. This is caused by the spread of energy states of the valence band and the conduction band into the bandgap, due to the long range disorder in the atomic structure of a–Si:H. Also, defects such as dangling bonds and floating bonds introduce energy states within the bandgap \[18\]. Therefore, the gap between the extended states and localized states is denoted by the term mobility gap rather than the bandgap. The mobility gap of a–Si:H has a typical value between 1.7 eV and 1.8 eV, which is larger than the bandgap of c–Si \[18\].

An a–Si:H film reduces the recombination activity at the surface of the crystalline silicon absorber in SHJ solar cells \[3\]. Recombination of charge carriers takes place when the carrier densities are departed of their equilibrium values \[19\]. The decay of excess charge carriers due to recombination is described by their recombinative lifetime $\tau_r$. There are three main mechanisms determining the recombinative lifetime, i.e. Shockley–Read–Hall recombination, radiative recombination and Auger recombination, characterized with lifetimes $\tau_{SRH}$, $\tau_{rad}$ and $\tau_{Auger}$ respectively \[19\]. These three mechanisms are illustrated in figure 2.1 and determine the recombination lifetime according to

$$
\tau_r = \frac{1}{\tau_{SRH}^{-1} + \tau_{rad}^{-1} + \tau_{Auger}^{-1}}.
$$

(2.1)

Figure 2.1: Recombination mechanisms: (a) SRH, (b) radiative, (c) direct Auger and (d) trap–assisted Auger \[19\].
2.1 Surface passivation with a–Si:H films

In SRH recombination, electron-hole pairs recombine through deep level impurities, in which the liberated energy is dissipated as phonons. Therefore the SRH recombination rate increases with a higher impurity density $N_T$ and $\tau_{SRH} \propto \frac{1}{N_T}$ \[19\].

When electron hole pairs recombine directly from band to band, it is called radiative recombination. In that case the energy is carried away by photon emission. Since both electrons and holes must be present simultaneously, the radiative lifetime is inversely proportional to the carrier density \[19\].

The Auger lifetime is inversely proportional to the carrier density squared, because three carriers are involved instead of two \[19\]. During Auger recombination the third carrier absorbs the momentum and liberated energy of the two recombining carriers \[12\].

In indirect bandgap semiconductors such as silicon, radiative recombination plays almost no role. Recombination in silicon is controlled by Auger recombination at high carrier densities and by SRH recombination at low carrier densities \[19\].
2.2 Layer growth of a–Si:H

Growth of a–Si:H layers with PECVD has been the subject of several studies in which different models have been proposed [9, 10, 8, 11, 14]. In this section a selection of models is presented which in particular explain the influence of the substrate temperature on the a–Si:H properties.

2.2.1 Thermodynamic model

In the thermodynamic approach initiated by the work of Winer and Street [15, 24], hydrogen equilibration is used to explain the effect of substrate temperature \( T_s \) and deposition rate \( R_d \) on the defect density of the deposited a–Si:H layer. The principle defects consist of dangling bonds, which are believed to be formed by the breaking of Si–Si bonds by mobile H that is released by Si–H bonds [10]. The concentration of dangling bonds is minimized at a sufficiently high \( T_s \), when H diffusion is fast enough to equilibrate the distribution of Si–Si and Si–H bonds. When \( T_s \) is too low, a large fraction of weak bonds are frozen into the network due to the insufficient H mobility. However, when \( T_s \) is too high, thermal disorder will cause a higher weak–bond density than optimal. The U–shaped dependence on \( T_s \) of the defect density in a–Si:H is explained by these two processes [10].

It is generally observed that at a higher deposition rate \( R_d \) a higher substrate temperature \( T_s \) is needed to obtain an optimal film quality. This is due to the fact that a large amount of bonded H must redistribute during the time in which a few atomic layers are grown. Therefore, the average rate of H diffusion should be equal to \( R_d \) [10].

2.2.2 Kinetic model

In the thermodynamic model, the actual process in which film growth takes place is not described in detail. A more detailed description is provided by the kinetic growth model, initially developed by Gallagher, Perrin et. al. and Matsuda et. al. [10, 17, 5]. In this model, called the MGP model, it is assumed that SiH\(_3\) is the only growth precursor. The basic film growth mechanisms proposed by the MGP model are given in figure 2.2.

In the MGP model it is presumed that a SiH\(_3\) radical can go into a weakly absorbed (physisorbed) state when reaching the a–Si:H surface. In this state a three–center Si–H–Si bond on a surface Si–H site is formed, after which the physisorbed radical can diffuse over the surface by hopping from one to another surface H. The diffusing SiH\(_3\) radical can be chemisorbed by sticking on a surface dangling bond, or abstract a surface H atom. In the first case film growth takes place. In the second case a surface dangling bond and gaseous SiH\(_4\) are created [10].
Since the created dangling bond can serve as a growth site for a second SiH\textsubscript{3} radical, the model explains that two SiH\textsubscript{3} radicals are needed per growth step at low $T_s$. It is also possible that two physisorbed SiH\textsubscript{3} radicals react with each other and form gaseous Si\textsubscript{2}H\textsubscript{6}. Either way, all physisorbed SiH\textsubscript{3} radicals either stick or form a gaseous species, since desorption is expected to be unimportant on the basis of energy considerations. At high $T_s$ ($>400$ °C, depending on $R_d$), surface dangling bonds can also be created by thermal desorption of surface H, in which gaseous H\textsubscript{2} is formed. However, at the commonly used $T_s$ of 200 °C, film growth according to this model is balanced by precursor-mediated sticking of SiH\textsubscript{3} and H abstraction by SiH\textsubscript{3} \[10\].

The proposed SiH\textsubscript{3} surface diffusion can also account for the relatively low surface roughness of a–Si:H \[10\]. Surface diffusion species with a high surface mobility may lead to a valley–filling effect. The fact that the surface roughness of a–Si:H generally decreases with increasing surface temperature can also be explained by the therewith increased surface mobility of the physisorbed radicals \[8\].

### 2.3 Characterization of the a–Si:H microstructure

The microstructure and hydrogen content of a–Si:H films can be characterized by spectroscopy measurements, for example absorption spectroscopy. Three characteristic absorption regions are present in the infrared spectrum of a–Si:H: wagging modes at 640 cm$^{-1}$, a doublet at 840–890 cm$^{-1}$ due to dihydride bending or scissors modes, and two stretching modes at 1980–2030 and 2060–2160 cm$^{-1}$ \[13, 22, 2\]. These two stretching modes are referred to as the low stretching mode LSM and the high stretching mode HSM, respectively. The exact physical origin and interpretation of the LSM and HSM has been discussed extensively in literature \[22, 21\]. It is claimed that two factors may cause the difference between the LSM and HSM, namely the hydride type and the bulk environment in which it resides \[21\].
The LSM is assigned to monohydrides, whereas the HSM is assigned to a stretching mode of dihydrides or to monohydrides which are clustered at internal void surfaces \[22, 13, 18\]. Experimental research (IR absorption spectroscopy on a–Si:H deposited by ETP) has confirmed that hydrides on a void surface contribute significantly to the HSM, while the LSM is dominated by the contribution of monohydrides in vacancies \[22\]. The lower and higher stretching modes are observed in standard hydrogenated amorphous silicon. However, hydrogenated micro- or nanocrystalline silicon (µc–Si:H or nc–Si:H, respectively) can have additional peaks: a small mode at 1895–1950 cm\(^{-1}\), a middle stretching mode (MSM) around 2030–2040 cm\(^{-1}\) and a second HSM at 2100–2130 cm\(^{-1}\) \[21\].

Since the LSM and HSM respectively originate from modes in a dense and void containing network, their magnitude is used to characterize the microstructure in the a–Si:H network. For this purpose, the dimensionless parameter \(R^*\) has been introduced \[18\]:

\[
R^* = \frac{I_{HSM}}{I_{LSM} + I_{HSM}},
\]

where \(I_{LSM}\) and \(I_{HSM}\) are the integrated absorption strengths of the two modes. A small value of \(R^*\) corresponds to a dense material. Generally, device quality a–Si:H is characterized with a \(R^*\)–value beneath 0.1 and contains less than 10 atomic % of hydrogen \[18\].

Besides giving information on the microstructure of the material, the absorption modes can be used to determine the hydrogen content in the a–Si:H film. The bond wagging band at approximately 640 cm\(^{-1}\) is best suited for this purpose, since every H bonded to silicon contributes to this mode \[22\]. The density \(N_x\) of a Si–H\(_x\) mode is calculated with

\[
N_x = A_x \int \omega^{-1} a(\omega) d\omega,
\]

with \(A_x\) as the proportionality constant and \(a\) as the absorption coefficient \[22, 13\]. The integral is over the absorption band of interest. Attempts to obtain the proportionality constant through theoretical analysis were not very successful. Therefore, they have been determined empirically by correlating the absorbance with H content measured by independent means \[13\]. The most widely used value of \(A_{640} = 1.6 \cdot 10^{19} \text{ cm}^{-2}\) \[13, 22\] has been calibrated with elastic recoil detection analysis \[22\]. The proportionality constant of the wagging mode at 640 cm\(^{-1}\), unlike those of the Si–H bond stretching modes, does not significantly depend on the sample preparation \[20\].
3 Experimental setup

3.1 Basic theory

The basic theory behind the used measurement techniques is given in this section. In section 3.2 the specific equipment and settings used in this project are given.

3.1.1 Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) is an optical measurement technique with which thin films can be characterized. The main feature of this technique is that it measures the change in polarized light after reflection on a sample. It is an indirect measurement method, since it requires an optical model (defined by optical constants and layer thicknesses) to extract physical properties [16].

The polarization of the incident lightwave can be decomposed in a component parallel with the plane of incidence (plane $p$) and a component perpendicular to the plane of incidence (plane $s$). The phase shift $\Delta$ between these two components and ratio $\tan(\Psi)$ of their amplitudes are measured with ellipsometry after reflection [16], as illustrated in figure 3.1. This is done as a function of wavelength $\lambda$, possibly at multiple oblique angles. In the case of a semiconductor the optimal angle of incidence is in the range of 70° to 80°. The measured $(\Psi, \Delta)$ spectra are analyzed with an optical model to determine parameters such as the film thickness, roughness and optical constants.

![Figure 3.1: Measured parameters in spectroscopic ellipsometry.](image)

An advantage of SE is that it is a non-contact and non-destructive measurement technique. Also, measurement and data acquisition is fast when assisted with a computer. Disadvantages are that measurements cannot be performed at normal incidence, the interfaces should be plane-parallel, thin films must be uniform in thickness and, in the case of multilayer samples, some optical constants have to be known in advance for the first iteration of the optical model. Furthermore, the value of the roughness must be limited to prevent the depolarization of light [16].
3.1.2 Raman spectroscopy

A popular scattering technique to identify vibration modes is Raman scattering. In this technique a material is irradiated with a single frequency of light [23]. This light can either be scattered or absorbed by the material. Electric charges within the material are set into an oscillating motion by the electric field of the incident light wave, after which electromagnetic energy is radiated by the accelerated charges. This secondary radiation is called scattered radiation. Light is absorbed by the material if part of the electromagnetic energy is converted into other forms of energy, such as thermal energy [1]. In Raman spectroscopy, the scattered photons are detected. If a phonon is excited, those scattered photons will have an energy shift that corresponds to the energy of a vibration mode of the material [23].

When interacting with a molecule, the light distorts (polarizes) the electron cloud and forms a short–lived state. Since this so–called virtual state is not stable, the photon is quickly re–radiated [23]. If the scattering only involves electron cloud distortion, the energy shift of the scattered photon will be very small, since the electrons are comparatively light. Therefore this process is regarded as elastic scattering. It is the most dominant process and is called Rayleigh scattering for molecules. Scattering will be inelastic if nuclear motion is induced. In that case, energy will be transferred from the photon to the molecule or vice versa. The scattered photon then has an energy that is shifted by one vibrational unit [23]. This inelastic scattering of light is called Raman scattering. Raman scattering is divided in Stokes and anti–Stokes scattering. In Stokes scattering, energy of the incident photon is absorbed by the molecule, promoting it to a higher excited vibrational state. In anti-Stokes scattering, energy is transferred from the molecule to the scattered photon. This is possible if the molecule is already in an excited state due to thermal energy. At room temperature, anti–Stokes scattering will be small since the number of molecules in an excited state is expected to be small [23].

![Figure 3.2: Schematic representation of the basic energy transitions in scattering processes](image)
A disadvantage is that Raman scattering is a weak process. Only one in every 106–108 scattered phonons are Raman scattered. Therefore, very high power densities have to be delivered to reach a high sensitivity, which may cause sample degradation. This will be experimentally shown in section 4.2.1. An advantage is that spectra of Raman spectroscopy are obtained with a single frequency light source [23].

3.1.3 Fourier transformed infrared spectroscopy

When a beam of polychromatic light is shone on a material, photons can be absorbed by the material if their energy corresponds to the energy gap between the ground state and an excited state of a molecular bond [23]. By measuring the transmitted spectrum with and without the material, its absorption spectrum can be calculated. Like in Raman spectroscopy, this provides information about the type of molecular bonds in the material.

Fourier transformed infrared spectroscopy (FTIR) is a technique in which the absorption spectrum is obtained by taking the Fourier transform of an interferogram. This interferogram is generated by a Michelson interferometer, which is the basic component of most Fourier transform spectrometers [7]. Suppose that a monochromatic light source with frequency $\nu$ is used in the interferometer. The detected intensity as a function of the mirror position $x$ is then given by

$$I(x) = B(\nu) \cos(2\pi x \nu),$$

where $B(\nu)$ is the spectrum of the source (i.e. the intensity of the emitted light as a function of its frequency) [7]. However, this is not a realistic view, as the sample is illuminated with polychromatic light. Since polychromatic light can be seen as a superposition of independent monochromatic components, the detected intensity can be calculated with

$$I(x) = \int_{-\infty}^{+\infty} B(\nu) \cos(2\pi x \nu) d\nu$$

in the case of a polychromatic light source [7]. The spectrum $B(\nu)$ of the light can thus be calculated with the measured interferogram, by taking the Fourier transform of equation 3.2. However, the interferogram and the spectrum must in general be related by the complex Fourier transform pair, because non-perfect compensation of the interferometer leads to sine components in the interferogram [7]. Thus, the spectrum and interferogram are generally coupled with

$$I(x) = \int_{-\infty}^{+\infty} B(\nu)e^{2\pi i x \nu} d\nu$$

and

$$B(\nu) = \int_{-\infty}^{+\infty} I(x)e^{-2\pi i x \nu} dx.$$  

An advantage of FTIR is that there is no need for a range of monochromatic light sources (like with a prism or grating instrument) to obtain the absorption spectrum [7].
3.2 Used equipment and settings

In this section the equipment and settings used in this project are specified. First, the deposition equipment and recipes are clarified. Secondly, the measurement equipment and measurement approaches are given.

3.2.1 ICP–PECVD

Figure 3.3 (source\textsuperscript{1}) shows the used equipment for the deposition of a–Si:H. It is a PECVD reactor in which the plasma is generated by an ICP-source. As can be seen in figure 3.3 the system (Oxford PlasmaLab System 100) is equipped with a loadlock with which wafers with a maximum diameter of 200 mm can be loaded (in this project 4” wafers are used). Also, \textit{in situ} spectroscopic ellipsometry monitoring is available, but this function has not been used.

Figure 3.3: Picture of an Oxford PlasmaLab System 100. This system is located in the cleanroom of NanoLab@TU/e and has been used for depositions of hydrogenated amorphous silicon films.

Several deposition conditions have been used in this project, of which all depositions are based on the standard recipe given on the following page. The varied parameters (temperature, pressure and power) with respect to the standard deposition conditions (50 °C, 10 mTorr, 400 W) are also given on the next page. The deposition time is adjusted so that the deposited film has a thickness of approximately 10 nm. Details of the samples and used deposition times are given in Table 3 in appendix D.

\textsuperscript{1}http://www.tue.nl/onderzoek/instituten-groepen-scholen/onderzoeksinstellingen/nanolabtue/list-of-equipment/processing-equipment/oxford-oxidenitride-icp-pecvd/ – on 13-06-14
3.2 Used equipment and settings

**Standard recipe of a–Si:H deposition with ICP–PECVD**

1. Load wafer and pump to base pressure

2. Heating of wafer to 50 °C during 300 s with helium backing

3. Ignition of the silane plasma
   - Argon flow: 20 sccm
   - Silane flow: 20 sccm
   - Temperature: 50 °C
   - Pressure: 10 mTorr
   - Power: 400 W
   - Time: 5 s

4. Deposition process
   - Argon flow: 20 sccm
   - Silane flow: 20 sccm
   - Temperature: 50 °C
   - Pressure: 10 mTorr
   - Power: 400 W
   - Time: 78 s

5. Pump to base pressure, purge and remove wafer

**Varied deposition parameters with respect to the standard recipe**

\[
\begin{array}{c|c|c|c|c}
\text{power series} & 800 \text{ W} & 600 \text{ W} & 200 \text{ W} \\
\hline
10 ^\circ \text{ C} & 50 ^\circ \text{ C}, 10 \text{ mTorr}, 400 \text{ W} & 100 ^\circ \text{ C} & 150 ^\circ \text{ C} & 200 ^\circ \text{ C} \\
\hline
15 \text{ mTorr} & 20 \text{ mTorr} & 30 \text{ mTorr} & 35 \text{ mTorr} \\
\end{array}
\]

**temperature series**

For temperatures of 50 °C and lower the chiller mode is used to reach and maintain the required temperature. The heater mode is used for temperatures above 50 °C.
3.2 Used equipment and settings

3.2.2 Spectroscopic ellipsometry

To check if the deposited layers have the desired thicknesses of ≈10 nm, the thicknesses are measured with a M–2000D Spectroscopic Ellipsometer of J.A. Woollam Co. shown in figure 3.4 (source\footnote{2}). The roughness, bandgap and refractive index of the film are also extracted from the modeling. Some specifications of this model are given in Table 1. In this setup, an EC–400 Electronics Control Box and M–2000D Detector Box are used in combination with a NIR or UV light source.

![Figure 3.4: Used setup (M–2000D Spectroscopic Ellipsometer of J.A. Woollam Co.) for the spectroscopic ellipsometry measurements.](image)

A vertical base is used on which the sample is mounted via a vacuum chuck. The measurements are done under angles of 65°, 70° and 75° with an accuracy of ±0.02° or better. Data analysis is done with the CompleteEASE software provided by J.A. Woollam Co. A three layer model is used (c–Si substrate – native oxide – a–Si:H) to fit the measured (Ψ, Δ) and calculate the layer parameters.

Table 1: M–2000D Spectroscopic Ellipsometer specifications, taken from source\footnote{2}.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral Range</td>
<td>193 nm to 1000 nm, 500 wavelengths</td>
</tr>
<tr>
<td>Spectral Resolution Bandwidth</td>
<td>1.6 nm pixel resolution ~ 5 nm bandwidth</td>
</tr>
<tr>
<td>Data Acquisition Rate</td>
<td>Maximum of 20 Hz, typically 1–5 s measuring time</td>
</tr>
<tr>
<td>Beam Diameter</td>
<td>2 mm to 5 mm</td>
</tr>
<tr>
<td>Beam Divergence</td>
<td>Less than 0.3°</td>
</tr>
<tr>
<td>Typical Accuracy</td>
<td>Ψ = 45° ± 0.075°, Δ = 0° ± 0.05°</td>
</tr>
</tbody>
</table>

\footnote{2}{https://depts.washington.edu/ntuf/facility/docs/M2000_Spec_Sheet.pdf – on 13-06-14}
3.2 Used equipment and settings

3.2.3 Raman spectroscopy

The Raman spectroscopy measurements have been done with an Invia Raman Microscope of Renishaw, displayed in figure 3.5 (source[^3]). A 50x/0.75 objective is used and the power rotary switch is turned to half power during all measurements.

Figure 3.5: Used equipment (Renishaw Invia Raman Microscope) for the Raman spectroscopy measurements.

Since it has been observed that the laser affects the properties of the film (see section 4.2.1), the laser intensity and measurement time are not the same for all measurements. Laser exposure on the sample has been limited by averaging the spectra measured at multiple (200–300) spots with distances of 10 µm and using 10% laser intensity during 10s. This is done with the mapping function of the used WiRE 2.0 software. In this way the laser intensity is high enough to obtain a clear spectrum and the laser exposure time is low enough to limit annealing of the film by the laser. Also, the total measurement time of ~1 hour is more practical than the ~17 hours needed with 1% laser intensity. The script with which the measured spectra of the mapping series are separated and filtered is given in appendix E. In Table 2, some of the frequently used measurement settings are given.

Table 2: Frequently used laser intensities and measurement times in the Raman spectroscopy measurements

<table>
<thead>
<tr>
<th>Laser intensity</th>
<th>Measurement time</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>17 hours</td>
</tr>
<tr>
<td>1%</td>
<td>17 hours</td>
</tr>
<tr>
<td>10%</td>
<td>1000 s</td>
</tr>
<tr>
<td>50%</td>
<td>300 s</td>
</tr>
<tr>
<td>100%</td>
<td>300 s</td>
</tr>
<tr>
<td>10% mapping</td>
<td>10 s, ~250 times</td>
</tr>
</tbody>
</table>

3.2.4 Fourier transformed infrared spectroscopy

In figure 3.6, the equipment used for the FTIR measurements is shown (source:
http://chemlabz.com/?procom=tensor-27-2 – on 13-06-14). It is a TENSOR27 FTIR spectrometer of Bruker, with a spectral range of 340 cm$^{-1}$ to 8000 cm$^{-1}$.

![Figure 3.6: Used setup (TENSOR27 of Bruker) for the FTIR measurements.](image)

The absorption spectra of the deposited a–Si:H layers have been determined by measuring the transmitted intensity of a c-Si wafer with a deposited a–Si:H film ($T_{\text{sample}}$) and a blank reference wafer ($T_{\text{ref}}$). Double sided polished wafers are used to get a clear spectrum. The absorption spectrum $A(\lambda)$ is calculated with

$$A(\lambda) = -\log\left(\frac{T_{\text{sample}}}{T_{\text{ref}}}\right)$$  \hspace{1cm} (3.5)

Because the IR lamp of the used setup does not always have the same intensity, the absorption spectrum measured at day $b$ is corrected with respect to the reference transmission measured at day $a$ by measuring the emitted spectrum $T_{\text{air}}$ of the lamp alone during both days. In this way the reference transmission $T_{\text{ref}b}$ at day $b$ is determined:

$$T_{\text{ref}b} = T_{\text{ref}a} \cdot \frac{T_{\text{air}b}}{T_{\text{air}a}},$$  \hspace{1cm} (3.6)

so that

$$A(\lambda) = -\log\left(\frac{T_{\text{sample}}}{T_{\text{ref}a} \cdot T_{\text{air}a}} \cdot \frac{T_{\text{air}b}}{T_{\text{air}b}}\right).$$  \hspace{1cm} (3.7)

An advantage of this approach is that the reference spectrum of the blank c–Si wafer has to be measured only once. Because of internal reflections between the layers, there is a large baseline on the measured signal. Like in the Raman spectroscopy measurements, the baseline is corrected during data analysis in Origin. Hydrogen content is calculated using a Mathematica notebook created by Pim Veldhuizen: Easy Peak Fitting – version 0.95 beta – 23-06-2014 (see appendix B for more details).

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4 Results and discussion

4.1 Deposition rate

In this section the results of the spectroscopic ellipsometry measurements are presented. With this measurement technique the deposition rate has been determined under several deposition conditions (i.e. temperature, pressure and power). Also, the uniformities of three samples with different deposition pressures have been measured. The formulas with which the uncertainties of the measurements are calculated are given appendix A.

4.1.1 Temperature series

Layers of a–Si:H have been grown at deposition temperatures of 10, 50, 100, 150 and 200 °C. The pressure and power have been kept constant at 10 mTorr and 400 W in this temperature series. In figure 4.1 the measured deposition rates of these samples have been plotted. The measurements show that the deposition rate decreases with increasing deposition temperature. As stated in section 2.2.2, a higher surface temperature $T_s$ causes a higher surface mobility of the physisorbed radicals. This may lead to a denser deposited film, since voids can be filled by diffusing SiH$_3$ radicals in a higher rate. In section 4.2.3 it is shown that the deposited films indeed seem to be denser when the deposition temperature is higher. Since it takes longer to grow a dense film than a void containing network, this may be one of the reasons why the deposition rate decreased as a function of temperature.

![Figure 4.1: Measured deposition rate as a function of the deposition temperature.](image-url)
4.1 Deposition rate

4.1.2 Pressure series

A similar procedure as for the temperature series has been carried out to determine the dependence of the deposition rate on the deposition pressure. The results are given in figure 4.2, in which it can be seen that the deposition rate decreases when the pressure is increased. This observation could be explained by the fact that the mean free path of the electrons within the plasma decreases when the pressure is increased. As a result, the electrons reach lower kinetic energies when accelerated by the electric field and less reactive radicals are created. The lower \( \text{SiH}_3 \) concentration will then cause a lower deposition rate. Also, more deposition could take place on the walls of the deposition chamber instead of on the wafer when the pressure is increased.

4.1.3 Power series

When the power input in the plasma is increased, so does the deposition rate. This can be seen in figure 4.3, in which the deposition rates are given of samples deposited with 200, 400, 600 and 800 W of power. This relation is tentatively explained by the presumption that the electron density within the plasma increases when the power is increased. As a result, more reactive radicals could be produced, which would cause a higher deposition rate.
4.1.4 Thickness uniformity

To investigate whether the deposition rate is uniform along the sample, the uniformities of three samples have been measured with spectroscopic ellipsometry. In figure 4.4, the thicknesses of the deposited layers are plotted against the measurement position on the wafer. In order to compare the deposition rates of the three samples, the measured thicknesses are divided by the thickness measured near the edge.

Figure 4.4: Measured uniformities of a–Si:H films deposited at different pressures. The thicknesses have been divided by the measured thickness near the edge.

Figure 4.4 shows that the deposition rate can be up to 35% higher at the middle of the wafer than at the edge. It can be seen that the deposition rate is more uniform when the deposition pressure is lower. This could be explained by the fact that the expansion of the plasma can be larger when the pressure in the chamber is lower, resulting in more uniform plasma conditions at the surface of the wafer.
4.2 Microstructure of the a–Si:H layer

The density of voids of the a–Si:H layers has been investigated by measuring the $R^*$ values of the samples using Raman spectroscopy. In this way the correlation between the porosity and the deposition conditions has empirically been obtained. Also, the influence of the laser used in Raman spectroscopy on the deposited layer has been studied.

4.2.1 Influence of the Raman laser on a–Si:H

When measuring the vibrational spectrum of a–Si:H with Raman spectroscopy, a lower and higher stretching mode of Si–H bonds as given in figure 4.5 are typically observed. To determine the peak ratio (i.e. the value of $R^*$), the measurement data is fitted with two Gaussian peaks, which is done after subtraction of the baseline. Since the a–Si:H films (deposited on c–Si Czochralski–grown wafers) are approximately 10 nm thick, a long measurement time or a high laser intensity is needed to obtain a spectrum with a proper signal to noise ratio. The spectrum given in figure 4.5 is obtained with a laser intensity of 100% and a measurement time of 300 s.

![Figure 4.5: Typical spectrum of a–Si:H on c–Si, measured with Raman spectroscopy after baseline correction.](image-url)
This recipe (100% laser intensity during 300 s) has been used for most samples, after it had been concluded that the laser has no significant influence on the a-Si:H layer. This conclusion had been made based on measurements with different laser intensities on a single sample (see figure C.1 in appendix C). However, it has been observed that the measured spectrum does change when the measurement is repeated continuously on the same spot. This can be seen clearly in figure 4.6, in which repeated acquisitions at 100% laser intensity are given. The measurements in this section have been performed on the same sample (sample 16, see Table 3 in appendix D).

Figure 4.6: Repeated Raman measurements of an a-Si:H layer at 100% laser intensity. It can be seen that the shape and size of the spectrum changes with increasing laser exposure.

In figure 4.6 it can be seen that the signal decreases as a function of laser exposure time. It may be the case that Si–H bonds are broken when the film is annealed by the laser. In that case, the hydrogen content decreases and therewith the area of the measured LSM and HSM peaks. The second observation is that the shape of the spectrum changes due to laser exposure: the HSM peak seems to decrease with respect to the LSM peak. This could be caused by a reduced amount of higher hydrides at the internal surface of voids or by a decreased porosity of the film.
Based on the measurements given in figure 4.6, it has been concluded that the measurements of $R^*$ at 100% laser intensity are not fully reliable. To test how low the laser intensity should be to prevent layer modification, repeated acquisitions have also been performed at 50%, 10% and 1% laser intensity. In figure 4.7, the measurements at 1% intensity are given, along with the averaged spectrum. Figure 4.7 shows that the ratio between the HSM and LSM peak is higher when measured with 1% than with 100% laser intensity. Clearly, the laser is of less influence on the layer when a lower intensity is used. This can also be seen by the fact that the shape and strength of the signal changes less at 1% laser intensity.

Figure 4.7: Repeated Raman measurements of an a–Si:H layer at 1% laser intensity and the average spectrum of all acquisitions.

In figure 4.8a the loss of counts as a function of energy input of the laser is displayed for all tested laser intensities. The cumulative number of counts of the LSM and HSM peak seems to drop exponentially, at least at 100% and 50% laser intensity. The signal strength drops more slowly when a lower laser intensity is used. However, when using a lower laser intensity a longer measurement time is needed to obtain a proper signal to noise ratio. As a result, the laser exposure time is larger and the total signal loss increases. When comparing the signal drop at 50% and at 100% intensity, it can be seen that the total loss is approximately the same.
To further investigate the effect of the laser on the density of voids, the measured values of $R^*$ are plotted as a function of added energy in figure 4.8b. As a general trend it can be seen that the value of $R^*$ drops when the sample is exposed to the laser, but seems to saturate after the first or a few accumulations. The rate ($s^{-1}$) at which the value of $R^*$ decreases, increases with the laser intensity.

(a) Number of counts of the cumulative LSM and HSM peak as a function of energy input of the laser, measured at different laser intensities. The number of counts have been normalized with the amount of counts during the first acquisition.

(b) Measured values of $R^*$ as a function of energy input of the laser. Indicated is the value determined with the averaged spectrum measured at 1% laser intensity. The $R^*$–values seem to drop with respect to this value when the sample is heated by the laser.

Figure 4.8: Investigation of the laser influence on a–Si:H films during Raman spectroscopy measurements.

The individual measurements done at 1% laser intensity are inaccurate because of too short measurement times. However, the $R^*$–value determined with the averaged spectrum at 1% intensity (indicated in figure 4.8b) is the most reliable value, since the influence of the laser is limited the most. The decrease of $R^*$–values at higher laser intensities is on the order of 40% with respect to this value.

With the data given in this section, it can be concluded that the laser used in Raman spectroscopy significantly influences the properties of the film and can therefore affect the measurements. To prevent this, it is recommended to carry out short measurements at several spots so that annealing of the film is prevented (see section 3.2.3).
4.2 Microstructure of the a–Si:H layer

4.2.2 Uniformity of $R^*$

Using spectroscopic ellipsometry measurements, it has been observed that the thickness of the deposited layer is not uniform. Therefore, the determined thickness of a certain sample depends on the measurement position. In order to check if the determined value of $R^*$ is also position–dependent, Raman measurements have been done at several positions on the wafer. The results are given in figure 4.9a, in which it can be seen that the measured $R^*$–values are, within the measurement accuracy, independent of the position. Thus, it seems that the porosity of the deposited film is uniform and the measurement position has no significant effect on the determined value of $R^*$.

(a) Measured values of $R^*$ as a function of the position on the wafer. The measurements have been done at 100% laser intensity during 100s.

(b) Normalized areas of the cumulative LSM and HSM peak and relative thickness of the deposited a–Si:H film, as a function of the position on the wafer.

Figure 4.9: Uniformity check of the Raman spectroscopy measurements.

It has been observed that the total number of counts of a single measurement is not uniform across the wafer. In figure 4.9b it can be seen that this is a result of the fact that the thickness of the deposited film is not uniform. When the a–Si:H layer is thicker, more photons are scattered with a Raman shift within the LSM and HSM region and the measured area of the cumulative peak is larger.
4.2.3 Temperature series

Even though the laser used in Raman spectroscopy affects the properties of the deposited a–Si:H layer, a trend of $R^*$ as a function of deposition temperature can still be seen. This is shown in figure 4.10, in which measurements with 1%, 50%, 100% and a mapping series with 10% laser intensity are given. It can be seen that the value of $R^*$ decreases when the deposition temperature is higher. In other words, a higher temperature results in a denser deposited film. This could be explained by the theorem that a higher surface temperature $T_s$ causes a higher surface mobility of the physisorbed radicals, resulting in a void–filling effect as stated in section 2.2.2 on page 9.

![Figure 4.10: Measured values of $R^*$ as a function of the deposition temperature.](image)

The mapping series has been done to reduce the laser exposure on the sample, as explained in section 3.2. In figure 4.10, it can be seen that the trend is more leveled when the laser exposure is higher. Since the measurements with the smallest laser exposure are the most reliable, it is likely that the actual value of $R^*$ decreases from at least 0.4 to 0.075 when the deposition temperature is increased from 10 °C to 200 °C.

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The observed decrease of the value of $R^*$ as a function of deposition temperature indicates that the layer is denser when deposited at higher temperatures. To support this statement, the refractive indexes of the films deposited at different temperatures have been measured with spectroscopic ellipsometry at 1.96 eV. A denser film is believed to have a higher refractive index, so it is expected that the refractive index increases as a function of deposition temperature. As can be seen in figure 4.11, this is indeed the case.

![Figure 4.11: Measured refractive indexes of a–Si:H layers deposited at different temperatures.](image)
4.2 Microstructure of the a–Si:H layer

4.2.4 Annealing

An annealing series has been done using sample 5 (see appendix D). The film has been deposited at the defined standard conditions (50 °C, 10 mTorr, 400 W and 78 s). Pieces of this sample have been annealed using the Jipelec JetFirst located at the cleanroom of Nanolab@TU/e. A temperature of 200 °C and a N₂ flow of 150 sccm have been used.

(a) Measured values of \( R^* \) as a function of annealing time at 200 °C. The measurements have been done at 100% laser intensity during 100 s.

(b) Measured thickness and refractive index of the deposited film for different annealing times at 200 °C. The measurements have been done consistently at 1.3 cm to the edge of the wafer.

Figure 4.12: Investigated influence of annealing on the porosity of the film.

The measured \( R^* \)-values as a function of annealing time are given in figure 4.12a. Within the measurement accuracy, the value of \( R^* \) does not seem to change due to annealing. This may be caused by the influence of the laser, which could be checked by carrying out a mapping series as explained in section 3.2. A mapping series has not been done because of limited time. In figure 4.12b it can be seen that refractive index seems to increase as a function of annealing time, which could indicate that the porosity of the film decreases by annealing. However, this change is only on the order of 10% and may be insignificant within the accuracy of the measurement. Also, a clear decrease in layer thickness cannot be observed in figure 4.12b. Thus, based on the measurements given in this section, annealing seems to have a small influence on the porosity of the film, at least compared to the investigated influence of the deposition temperature.
4.2.5 Pressure series

As can be seen in figure 4.13, the deposition pressure does not seem to have a significant influence on the value of $R^*$ of the deposited a–Si:H films. In section 4.1.2 it had been observed that a lower pressure results in a higher deposition rate. A higher deposition rate could in turn result in a higher density of voids, as the physisorbed SiH$_3$ radicals have less time to diffuse at the surface and fill the voids. However, a decrease of $R^*$ as a function of deposition pressure is not clearly observed.

![Figure 4.13: Measured values of $R^*$ as a function of the deposition pressure.](image)

It could be the case that the deposition rate has a small influence on the density of voids, for example because of a comparatively high diffusion rate of physisorbed radicals (i.e. a lower diffusion time than the typical time in between radicals arriving at the surface). However, the observed independence may also be caused by the ‘trend–leveling’ effect of the laser. Nevertheless, it can be claimed that the deposition pressure has an insignificant influence on the void concentration compared to the deposition temperature, at least within the used ranges.
4.2.6 Power series

The values of $R^*$ have also been measured of the samples deposited with different powers. In figure 4.14 the measured values are given of depositions at 200 W, 400 W, 600 W and 800 W. A few values have been measured twice with 100% laser intensity to check their consistency. Mapping series with 10% laser intensity and 10 s per spot have also been done to limit laser exposure.

![Figure 4.14: Measured values of $R^*$ as a function of the deposition power.](image)

Like the deposition pressure, the power does not seem to significantly affect the void concentration. If anything, there seems to be a U–shaped dependence between $R^*$ and the deposition power. The increase of $R^*$ between 600 W and 800 W could be caused by the increased deposition rate. Also, a higher power can cause a higher plasma potential. This could lead to more sputtering due to ion bombardment and an increased void concentration in the a–Si:H film.
4.3 Hydrogen content of the a–Si:H layer

As mentioned in section 2.3, the bond wagging band around 640 cm\(^{-1}\) can be used to determine the hydrogen content in the a–Si:H film, since every Si–H bond contributes to this mode. These peaks are measured using Fourier transformed infrared spectroscopy (FTIR), which is an absolute measurement method and is therefore suitable to determine the hydrogen content, in contrary to Raman spectroscopy.

4.3.1 FTIR measurements

A typical absorbance measurement of a–Si:H with FTIR is given in figure 4.15. The Si–H wagging peak at 640 cm\(^{-1}\) and cumulative peak of the lower and higher stretching modes of Si–H between 1980 cm\(^{-1}\) and 2160 cm\(^{-1}\) can clearly be seen. In spite of purging with N\(_2\), several sharp peaks can be seen due to gaseous H\(_2\)O (1300–1800 cm\(^{-1}\) and 3500–4000 cm\(^{-1}\)) and CO\(_2\) (around 2600 cm\(^{-1}\)) in the measurement chamber.

Figure 4.15: Typical spectrum of a–Si:H on c–Si, measured with FTIR.

The FTIR measurements have been used to compare the hydrogen content of the different deposited layers. Also, the shapes of the cumulative LSM and HSM peaks are compared. The values of \(R^*\) have not been determined with FTIR, since the data could not be fitted reliably. This is due to the fact that multiple local minima can be found and the fitting is very dependent on the baseline correction.
4.3 Hydrogen content of the a–Si:H layer

4.3.2 Temperature series

In figure 4.16 the measured absorption peaks at 640 cm\(^{-1}\) of layers deposited at different temperatures are given. It can be seen that the area of the peaks decreases when the deposition temperature is increased, which indicates a decreasing hydrogen content. This decrease is confirmed in figure 4.17 in which the calculated hydrogen content is plotted against the deposition temperature. The way in which hydrogen content is calculated is explained in appendix B.

![Figure 4.16: Measured H–wagging peaks at different deposition temperatures.](image)

The spectrum of the layer deposited at 10 °C is not presented, because this film has been deposited on a single sided polished wafer. As given in figure C.5 in appendix C the measured spectra on single sided polished wafers are rather craggy and unreliable. Therefore these measurements have not been used in the determination of hydrogen content.

Notable in figure 4.16 is the additional peak around 620 cm\(^{-1}\). This peak is believed to be caused by surface bonded H because of two reasons. Firstly, the peak is sharper than the 'bulk–wagging' peak around 640 cm\(^{-1}\), indicating better defined degrees of freedom of the Si–H bonds. Secondly, the additional peak decreases in size in the timespan of several weeks, which could be explained by surface oxidation (see figure C.6 in appendix C).
The observed decrease in hydrogen content as a function of deposition temperature can be caused by various reasons. First of all, at a higher surface temperature more thermal desorption of surface H can take place. However, according to literature [10], surface desorption of hydrogen is expected to be unimportant at the used temperatures. The decreasing hydrogen content is therefore likely to be caused by other reasons. For example, the mobility of surface and subsurface hydrogen is larger when the substrate temperature is higher. As a result, diffusing H can react more frequently and form gaseous H₂ in a higher rate.

When looking at the measured LSM and HSM peaks of layers deposited at different temperatures, as given in figure 4.18, the HSM peak seems to decrease with respect to the LSM peak when the temperature is increased. This trend has also been observed with Raman spectroscopy (section 4.2.3) and is believed to be caused by a higher surface mobility of physisorbed radicals.

Figure 4.17: Calculated hydrogen content of a–Si:H layers as a function of the deposition temperature.

Figure 4.18: Measured LSM and HSM peaks with different deposition temperatures.
4.3 Hydrogen content of the a–Si:H layer

4.3.3 Annealing

Pieces of sample 5 (deposited at 50 °C, see appendix D) have been annealed at 200 °C during different annealing times. The FTIR measurements of these pieces are given in 4.19. It can be seen that the shape of the cumulative LSM and HSM peak does not seem to change due to annealing. This is consistent with the measurements given in section 4.2.4, where it has been observed that the value of $R^*$ is not significantly changed by annealing. However, the H–wagging peak around 640 cm$^{-2}$ decreases due to annealing, indicating a decreased hydrogen content.

The decrease in hydrogen content as a function of annealing time is given in figure 4.20. In the calculations of the hydrogen content, it has been taken into account that the thickness of the film is affected by annealing (section 4.2.4). It can be seen that the decrease is the strongest during the first minutes, after which the H content seems to saturate. When the a–Si:H layer is annealed, gaseous H$_2$ could be formed due to surface diffusion of bonded H. This could explain the observed decrease in hydrogen content due to annealing.

![Absolute measurements](image)

Figure 4.19: Measured absorption peaks of the a–Si:H film of sample 5 (see appendix D), at different annealing times at 200 °C.

![Hydrogen content](image)

Figure 4.20: Calculated hydrogen content as a function of the annealing time at 200 °C.
4.3 Hydrogen content of the a–Si:H layer

4.3.4 Pressure series

The characteristic peaks (wagging peak around 640 cm\(^{-1}\) and LSM and HSM peak) of a–Si:H films deposited at different pressures on double sided polished c–Si samples are presented in figure 4.21. Though the layer thickness is of influence on the absorption, it seems to be the case that the peak around 640 cm\(^{-1}\) is larger when the deposition pressure is lower, which would indicate an increased hydrogen content. The deposition pressure seems to have no effect on the value of \(R^*\), since the shape of the cumulative LSM and HSM peak is constant. This observation is consistent with the observed independence in section 4.2.5.

![Figure 4.21: Measured characteristic peaks at different deposition pressures.](image)

In figure 4.22 the calculated hydrogen content is given as a function of the deposition pressure. It can be seen that the hydrogen content indeed decreases when the pressure is increased. This could be explained by the observed decrease in deposition rate as a function of pressure (see section 4.1.2). When the deposition rate is lower, surface and subsurface diffusing H has more time to combine and form gaseous H\(_2\), which would result in a lower hydrogen content.

![Figure 4.22: Calculated hydrogen content as a function of the deposition pressure.](image)
4.3 Hydrogen content of the a–Si:H layer

4.3.5 Power series

FTIR measurements have also been done on samples deposited at different power. The measurements of the double sided samples are given in figure 4.23. In order to compare the peaks, the spectra are divided by the layer thicknesses. It can be seen that the shape of the LSM and HSM peak does not significantly change, which confirms the insignificant influence of the deposition power on the porosity of the film.

The calculated hydrogen content of films deposited at different powers is given in figure 4.24. It seems to be the case that the hydrogen content increases as a function of deposition power. This could be caused by the increased deposition rate (see section 4.1.3), as surface diffusing H has less time to form gaseous H$_2$. However, no clear correlation between H content and deposition power can be seen based on these three measurements.
5 Conclusions

In this project, the influence of the deposition temperature, pressure power and annealing on the properties (i.e. porosity and hydrogen content) of the a–Si:H film has successfully been determined. However, in the introduction 1.3 it is stated that another goal of this project was to correlate the passivation quality of the film with the investigated properties. This has not been done because of time limitations and is therefore advised to be done in future research (see section 6). The main conclusions of this project are now presented.

5.1 Deposition rate

By performing SE measurements on a–Si:H layers deposited at varied temperature, pressure and power, the following conclusions have been made:

- The deposition rate decreases with increasing temperature, possibly because of a higher surface mobility of physisorbed SiH$_3$ radicals. This could result in a denser deposited layer and therewith a lower deposition rate.

- A higher pressure leads to a lower deposition rate. This is believed to be caused by a lower SiH$_3$ radical production rate, since the mean free path and therewith the maximum energy of the electrons in the plasma is reduced when the pressure is increased.

- When the power input is increased, so does the deposition rate. This is expected to be caused by a higher SiH$_3$ radical production rate, since the electron density within the plasma could be increased when the plasma power is increased.

- The deposition rate is not uniform along the wafer: deposition of a–Si:H with ICP–PECVD can be up to 35% larger at the middle of a 4” wafer than at the edge. This percentage depends on the pressure in the chamber. A better uniformity is reached with a lower pressure, because of the larger expansion of the plasma.

5.2 Microstructure of the a–Si:H layer

Raman spectroscopy measurements have been done to investigate the microstructure of the deposited a–Si:H layers. For this purpose the ratios $R^*$ of the HSM and LSM peaks have been determined of all samples. A high value of $R^*$ indicates that the film is porous. The main conclusions are:

- The deposited layer is more dense when the deposition temperature is higher. This is believed to be caused by a higher surface mobility of physisorbed SiH$_3$ radicals, resulting in void–filling along the surface.

- Within the investigated ranges, the deposition pressure and power seem to have no significant influence on the void concentration of the deposited a–Si:H film.
• Annealing of the a–Si:H film does not significantly change the value of $R^*$. Also, no clear trend can be seen in the layer thickness and refractive index as a function of annealing time. Therefore, the porosity of the film does not seem to be affected by annealing.

• The used laser in Raman spectroscopy anneals the deposited film during the measurement. As a result, the signal strength decreases and the value of $R^*$ decreases. The decrease in signal strength may be caused by breaking of Si–H bonds and a resulting decreased hydrogen content.

• The value of $R^*$ of the deposited a–Si:H is uniform within the measurement accuracy.

5.3 Hydrogen content of the a–Si:H layer

The hydrogen content of the deposited a–Si:H films has been calculated after measuring the absorption peak of the H–wagging mode around 640 cm$^{-2}$. By doing so, these observations have been made:

• An increased deposition temperature causes a decrease in hydrogen content (in the range of 50 °C to 200 °C). Among others, this may be caused by an increased rate at which gaseous H$_2$ is formed, as the mobility of hydrogen is increased when the substrate temperature is higher.

• The hydrogen content seems to decrease as a function of deposition pressure, which could be caused by the decreased deposition rate as surface diffusing H has more time to react and form gaseous H$_2$.

• No convincing trend of the hydrogen content as a function of deposition power has been measured. However, it seems to be the case that the H concentration increases with power, possibly because of the increased deposition rate.

• When the c–Si sample with a–Si:H film is annealed, the hydrogen content of the a–Si:H layer decreases. This could be caused by the forming of gaseous H$_2$ due to hydrogen diffusion.
6 Outlook and recommendations

6.1 Spectroscopic ellipsometry

By measuring the thickness of deposited a–Si:H films at several positions, it has been observed that the thickness of the deposited films is not uniform. As a result, the determined deposition rate at certain deposition conditions is dependent on the measuring spot on the wafer. Therefore, it is recommended to measure the thickness of the wafer consistently at the same distance from the edge of the wafer, for example at the center.

6.2 Raman spectroscopy

The measurements of the $R^*$-values with Raman spectroscopy of the deposited a–Si:H layers have not been fully reliable because of the following reasons:

- The hydrogen content and density of voids are changed when the layer is heated by the laser. Therefore, certain differences in porosity may not have been observed if different samples have undergone similar crystallization during the measurement. Also, the amount of heating is subject to the laser intensity, measurement duration and to thermal contact of the sample with the environment. These differences can cause a variation in the measured values of $R^*$.

- The determined value of $R^*$ is subject to the baseline correction which depends on personal interpretation of the acquired data, especially in the case of a low signal to noise ratio.

- Despite the fact that the samples are stored in a vacuum vessel, oxidation takes place, which can affect the measurements.

For future Raman spectroscopy measurements on thin films, it is recommended to test the influence of the laser before starting with a measurement series. Based upon these tests, a laser intensity and measurement duration can be chosen with which a clear signal is obtained without influencing the layer. If the sample is uniform, a 'mapping–method' as used in this project is a good option. The chosen conditions should be used in the entire measurement series to prevent variations caused by the laser. Baseline correction should be carried out in a consistent manner, especially if the signal is small compared to the baseline. This could be done with the use of modeled baseline detection. Finally, measurements should be done soon after deposition to prevent oxidation of the films. A practical advise is to save multiple acquisitions separately, so that peaks caused by cosmic rays can be removed from the individual spectra instead of being added to the averaged spectrum.
6.3 FTIR

For FTIR measurements, it is recommended to use sufficiently high purging times to eliminate gaseous CO$_2$ and H$_2$O in the measuring chamber, especially when the IR absorption of the film is small compared to the absorption of CO$_2$ and H$_2$O at standard concentrations. In this project, purging has been done for approximately 15 minutes with a N$_2$ flow of 30 L/min before each measurement.

6.4 Future research

In this project, the influence of the deposition conditions (temperature, pressure and power) and the influence of annealing on the properties (i.e. value of $R^*$ and hydrogen content) of the a–Si:H film has been investigated. However, the influence on the recombinative lifetime has not yet been studied, because Czochralski–grown wafers have been used which have a high Shockley–Read–Hall recombination rate compared to the more expensive Float–zone wafers.

Future research can consist of depositions on FZ wafers at different temperatures (and possibly different pressures and powers) followed by annealing and measuring of the recombinative lifetime. This can be done with a Sinton Lifetime Tester containing a heating stage. In this way the influence of the deposition temperature and annealing on the passivation quality of the a–Si:H film can be investigated.
7 Acknowledgments

For the last two months I have worked with pleasure at the PMP group. The research has been interesting and it was nice to work independently with some advanced measuring and deposition techniques available at this faculty. Also, the working atmosphere at PMP is very nice and I am glad that I joined the Plasma Enhanced Soccer Team.

I would like to thank Bart for his good supervision, help and informal communication. When my grandfather died two weeks before the end of this project, I was free to take my time and support my family.

Furthermore, I would like to thank Wytze for the technical support with the Raman spectroscopy measurements and Pim for providing the Mathematica model with which the hydrogen contents have been calculated. Also, I would like to thank Tjibbe for the ICP instructions and Erwin for the feedback on this report.
References


A  Error calculations

The used errors are 68% intervals calculated with

\[ S_x^2 = \sum_{i=1}^{n} \left( \frac{\partial f}{\partial x_i} S_{x_i} \right)^2, \quad (A.1) \]

where \( S_x \) is the error of measurement \( x \), which is a function of \( n \) variables \( x_i (x = f(x_1, x_2, \cdots, x_n)) \).

- Error in \( R^* \)

\( R^* \) is calculated with \( R^* = \frac{A_{HSM}}{A_{HSM} + A_{LSM}} \). Using equation (A.1) gives:

\[ S_{R^*} = \frac{1}{A_{LSM} + A_{HSM}} \sqrt{A_{HSM}^2 S_{LSM}^2 + A_{LSM}^2 S_{HSM}^2}. \quad (A.2) \]

- Error in deposition rate and relative thickness layer

Both the deposition rate and relative layer thickness are calculated by taking the ratio between two variables \( a \) and \( b \), so \( y = \frac{a}{b} \). The error \( S_y \) is calculated with

\[ S_y = \frac{a}{b} \sqrt{\left( \frac{S_a}{a} \right)^2 + \left( \frac{S_b}{b} \right)^2}. \quad (A.3) \]

All other errors given in this report are determined numerically by fitting measurement data.
B Calculation hydrogen content

The hydrogen contents of the films deposited at single sided polished wafers have been calculated with equation 2.3, in which a proportionality constant of $A_x = 1.6 \cdot 10^{19}$ cm$^{-2}$ has been used. However, the difficult part is the calculation of the absorption coefficient $a(\omega)$. This is done using the Mathematica notebook created by Pim Veldhuizen: Easy Peak Fitting – version 0.95 beta – 23-06-2014. A screenshot of the procedure is given in figure B.1.

Figure B.1: Screenshot of the Mathematica notebook with which the hydrogen content of the deposited a–Si:H films has been calculated.

First, the baseline of the absorption signal is subtracted if this has not yet been done in Origin. Secondly, the program calculates the absorption coefficient as a function of wavenumber. For this calculation the measured thickness of the film is provided, along with the transmission of the double sided polished wafer. A transmission of 0.84 has been measured in the region around 640 cm$^{-2}$. Then the absorption peak at 640 cm$^{-2}$ is fitted with two Gauss peaks, so the observed ‘surface peak’ is included. Finally, equation 2.3 is evaluated.

With equation 2.3 the amount of H atoms per cubic cm is calculated. In this report, hydrogen contents are given in atomic percentages. These percentages have been calculated with

$$At.\% = \frac{[H]}{[H] + [Si]} \cdot 100\%,$$  \hspace{1cm} (B.1)

where a silicon concentration $[Si]$ of $5 \cdot 10^{22}$ cm$^{-3}$ has been used.
C Additional graphs

Figure C.1: Several values of $R^*$ of a deposited a–Si:H layer, measured on different spots and with different laser intensities.

Figure C.2: LSM and HSM peaks measured with Raman spectroscopy of a–Si:H layers deposited at different temperatures.
Figure C.3: Measured refractive index at 1.96 eV at different deposition pressures.

Figure C.4: Measured refractive index at 1.96 eV at different deposition powers.
Figure C.5: Absorption spectra of single sided polished samples, measured with FTIR.

Figure C.6: Absorption spectra of sample 11, measured with FTIR on different times. It can be seen that the ‘surface peak’ at approximately 610 cm$^{-1}$ decreases, which may be caused by surface oxidation. The wagging peak measured at June 19$^{th}$ is too large because of a steep baseline which has not been properly corrected.
# Sample logbook

Table 3: Deposition data samples

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Time (s)</th>
<th>Temperature (°C)</th>
<th>Pressure (mTorr)</th>
<th>Power (W)</th>
<th>Thickness (nm)</th>
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<td>10</td>
<td>400</td>
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<td>10</td>
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</tr>
</tbody>
</table>
E Matlab script for Raman data conversion

```matlab
% This file the Raman mapping measurements are converted

clear all;
clsc;
format long;

% Load data

filename='S16 map 12 June.txt';
Data = load(filename);
Wav1 = Data(:,3);
Counts1 = Data(:,4);

% Convert data

%%%%% Spot separation %%%%%

1 = length(Wav1);

Wav2 = zeros(1); % Array with wavenumbers
Counts2 = zeros(1,1); % Matrix with spectra in separate columns
j=1;
spot=1;

for i = 1 : 1
    if spot == 1
        Wav2(i) = Wav1(i);
        end
    Counts2(j,spot) = Counts1(i);
    j=j+1;
    if 1<i & Wav1(i+1)-Wav1(i)>100
        spot = spot+1;
        j = 1;
        end
end
```
% MATLAB SCRIPT FOR RAMAN DATA CONVERSION

% Delete wrong spectra

[waves,Spots] = size(Counts2);
Counts3 = zeros(1,1); % Matrix with correct spectra in separate columns
% A spectrum is considered incorrect if the average or maximum number of
% counts is too high, see *

for sp = 1 : Spots
    Sum(sp) = sum(Counts2(:,sp));
    Max(sp) = max(Counts2(:,sp));
end
mean = 1;
for sp = 1 : Spots
    if Sum(sp)<15000 && Max(sp)<100 %
        for i = 1 : waves
            Counts3(i,mean) = Counts2(i,sp);
        end
        mean = mean + 1;
    end
end

% Calculate average spectrum

AvSpec = zeros(waves,1); % Array with average number of counts
for i = 1 : waves
    AvSpec(i) = sum(Counts3(i,:))/(mean-1);
end

% Plot data

subplot(3,1,1);plot(wav2,Counts3(:,10),'y',wav2,AvSpec,'r');
xlim([700 2500]);xlabel('Wavenumber (cm^{-1}));ylabel('Counts');
subplot(3,1,2);plot(Max);xlabel('Spot');ylabel('Max counts');
subplot(3,1,3);plot(Sum);xlabel('Spot');ylabel('Sum counts');

disp('Number of spectra removed:');disp(mean-1);

% Write data in new .txt file

fileID = fopen('AvSpec_S16_map1.txt', 'w');
fprintf(fileID,'%.8f\n',AvSpec);
fclose(fileID);

fileID = fopen('Wavenumbers_map1.txt', 'w');
fprintf(fileID,'%.2f\n',wav2);
fclose(fileID);

% 

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