2 Experimental techniques

2.1 Plasma enhanced chemical vapour deposition (PECVD)

One of the widely used techniques to deposit $a$-Si:H is by plasma decomposition of silane. Other gases can be added to dope or to alloy the material or to dilute the plasma species. A field in the plasma can be created by direct current (DC), radio frequency (rf) or microwave frequency. The electrons gain their energy from this electric field. Dissociation of the gas molecules takes place through inelastic collision processes with energetic electrons. Thus, the plasma favors the gas phase dissociation reactions. The substrate temperature can be controlled independently from the plasma parameters. This enables one to reach lower substrate temperatures than with other techniques (thermal CVD), which is suitable for retaining hydrogen in the material.

The samples described along this study were deposited by rf-PECVD in the multi-chamber high vacuum deposition system PASTA (Process equipment for Amorphous Silicon Thin-film Application) [5,6]. The system consists of five independent deposition chambers interconnected through a load lock and by a transport system. In chambers 1 to 3, p-type, intrinsic and n-type PECVD layers are deposited, respectively. In chambers 4 and 5 the hot-wire CVD technique for deposition of intrinsic material is used. The maximum substrate side is $4'' \times 4''$. The background pressure in all the chambers is $10^{-8}$ mbar.

Typical deposition conditions used for $a$-SiGe:H material are listed in Table 2.1. For material characterization Corning glass and polished p-type crystalline wafer ($<100>$ orientation) were used as substrates. The solar cells were deposited on transparent conducting oxide (TCO) coated glass (Asahi U-type SnO$_2$:F).
Table 2.1: Typical deposition conditions for $a$-SiGe:H.

<table>
<thead>
<tr>
<th>Deposition parameter</th>
<th>Source gasses</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiH$_4$+GeH$_4$</td>
<td>Si$_2$H$_6$+GeH$_4$</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>170-200</td>
<td>170-220</td>
</tr>
<tr>
<td>Hydrogen dilution ratio ($f$)</td>
<td>60-80</td>
<td>80-150</td>
</tr>
<tr>
<td>(H$_2$/Source gasses)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rf power density (mW/cm$^2$)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Deposition pressure (mbar)</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

2.2 Characterization techniques

2.2.1 Material characterization

Reflection-Transmission (RT)

The analysis of the spectral reflectance and transmittance in the wavelength range 420-1035 nm (3-1.2 eV) determines the optical parameters and the thickness of the film. The light beam enters the film side of the glass/film structure. The solution of the Fresnel equations for the reflectance and the transmittance of the light beam in this structure as a function of the photon energy, $h\nu$, defines the refractive index, $n(h\nu)$, and the extinction coefficient, $k(h\nu)$. The absorption coefficient, $\alpha$, is determined from $k$ as $4\pi h\nu k/hc$, where $h$ is the Planck constant and $c$ is the speed of light. Another interesting parameter is the value of $n$ at low energies, $n_0$, which can be related to the density of the material. The value of $n_0$ is determined by extrapolating $1/(n(h\nu)^2-1)$ to $h\nu=0$ [7].

The optical band gap, $E_g$, can be found from the dependence of $\alpha$ on $h\nu$ for the photon energy region where the density of states distribution is significant. Equation 2.1 holds in this region.

\[
\alpha h\nu = a(h\nu - E_g)^{p+q+1}
\]  

Equation 2.1 holds in this region.

In this equation $a$ is a constant and the parameters $p$ and $q$ are related with the shape of the band edges. Since Tauc [4] reported a linear relation between $(\alpha nE)^{1/2}$ and the photon energy, the most usual value for $p$ and $q$ is 1/2, corresponding to a parabolic shape of the band edges. The band gap obtained solving Equation 2.1 with these values is called the Tauc’s band gap, $E_{Tauc}$. Several authors [8,9] have reported that a linear shape of the band edges has better linearity than a parabolic shape of the band edges. The value for $p$ and $q$ would be then equal to 1 and in this case the band gap obtained solving Equation 2.1 is called the
cubic band gap. An alternative method to define the optical band gap is the energy \(E_x\) at which \(\alpha(E_x)\) reaches a certain value, 10\(^x\). The band gap \(E_{3.5}\) and \(E_{0.4}\) are normally given for \(\alpha=10^{3.5} \text{ cm}^{-1}\) and \(\alpha=10^4 \text{ cm}^{-1}\), respectively. The band gap \(E_{0.4}\) shows values \(\sim 0.2 \text{ eV}\) higher than the Tauc band gap. This last convention has the advantage of being independent of the shape of the band edges. But for thick layers with pronounced fringes, the last method reduces its accuracy [10].

In this study, the band gap of the thin films (\(\sim 100 \text{ nm}\)) is defined as \(E_{3.5}\) for accuracy reasons, while for thick films (\(\sim 500 \text{ nm}\)) the band gap is determined through \(E_{3.5}\) and the Tauc band gap.

**Electrical conductivity and activation energy**

The photo- \((\sigma_p)\) and dark- \((\sigma_d)\) conductivity as well as the activation energy \(E_A\) of the dark-conductivity are measured on thick films deposited onto Corning glass. Aluminium coplanar contacts are evaporated on the film.

The \(\sigma_d\) is measured in the vacuum after annealing the samples at 160 \(^\circ\)C for 90 minutes. A voltage of 100V is applied during the measurement. The \(E_A\) is determined from the slope of the \(\ln(\sigma_d)\) against the inverse of the temperature during the controlled cooling process.

The \(\sigma_p\) is determined from the current measured under AM1.5 condition generated by a WACOM dual source solar simulator. Measuring the photocurrent, the \(\sigma_p\) is obtained through the relation

\[
\sigma_p = \frac{I}{Vwl}
\]

where \(I\) is the photocurrent, \(l\) is the length of the contacts, \(V\) is the applied voltage, \(w\) is the distance between the contacts and \(d\) is the thickness of the film.

**Constant photocurrent method (CPM)**

Due to the absorption of \(a\)-Si:H, the small thickness of the film (\(\leq 1 \mu\text{m}\)) does not permit one to measure \(\alpha\) for energies below 1.2 eV by R-T techniques. The sub-band gap absorption spectrum (where the \(\alpha\) is below \(10^4 \text{ cm}^{-1}\)) is then measured by other techniques as photothermal deflection spectroscopy (PDS) and constant photocurrent method (CPM). For CPM, the intensity of a monochromatic light is adjusted in order to keep a constant photocurrent, while the photon energy of the monochromatic light is varied between 0.8 and 2.2 eV. The \(\alpha\) is measured in a relative scale from the relation \(\alpha(E)\times 1/F(E)\), where \(F(E)\) is the photon flux. This provides a relative value for \(\alpha\) that must be adjusted with the absolute \(\alpha\) obtained
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Figure 2.1: Absorption coefficient spectra of \(a\)-SiGe:H measured by RT (black line) and by CPM (\(\triangle\)). \(\alpha_k\) represents the cross point where a deviation from the pure exponential trend of the Urbach tail is found.

by RT measurements at the photon energy region. The region where both the \(\alpha\)s overlap depends on the alloy composition. For the material presented in this study, this region is between \(1 \times 10^3\) and \(8 \times 10^3\) cm\(^{-1}\).

Two important parameters can be deduced from the analysis of \(\alpha\):

- the Urbach energy, \(E_U\), which characterised the disorder and can be related to the number of weak Si-Si bonds [11];

- the midgap defect density, \(N_D\), which can be estimated from the crossover point, \(\alpha_k\), where a deviation from the pure exponential trend of the Urbach tail occurs (see Fig. 2.1). The defect density is determined by

\[
N_D = 10^{16} \alpha_k \tag{2.3}
\]

where the calibration constant is from [12].
Steady-state photocarrier grating technique (SSPG)

The photocarrier grating technique is based on the creation of a small-amplitude photocarrier grating on a uniform photocarrier background. The electronic transport of the photogenerated carriers is dominated by the less mobile carrier, normally the minority carrier (holes). The ambipolar diffusion length can be measured reliably with an accuracy better than 10% for diffusion lengths between 50-200 nm [13]. In addition to the ambipolar diffusion length, the value of $\gamma$ is also obtained. The photo-conductivity in amorphous alloys follows a power law relation with the generation rate, $G (\sigma_p \propto G^\gamma)$. The exponent $\gamma$ is related to the slope of the conduction band tail of the density of states (DOS) [14].

The SSPG experimental setup used in this study is explained in reference [15]. We only mention here the intensity of the HeNe laser (5 mW) and the DC voltage applied to the sample (10 V).

Fourier-transform infrared spectroscopy (FTIR)

The Fourier-transform infrared spectroscopy (FTIR) determines the content of bonded H and the silicon-hydrogen and germanium-hydrogen bonding configurations. A Digilab FTS-40 spectrometer equipped with a liquid-nitrogen cooled HgCdTe detector is used to perform FTIR measurements. The samples are deposited on polished highly resistive $c$-Si wafer, which is suitable due to its low oxygen content. The measurements were corrected for both incoherent and coherent multiple reflections in the films [16,17]. The infrared transmission is measured in the wave number range of 400-4000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. This region contains all the relevant $\text{SiH}_x$, $\text{GeH}_x$ and silicon-oxide bonding configurations.

The FTIR spectrum was deconvoluted with Gaussian absorption profiles for the desired vibrational modes. The number of one kind of bond $N$ at a discrete frequency $\omega$ is calculated from the absorption spectra following the equation

$$N = A_k I_k = A_k \int \frac{\alpha(\omega)}{\omega} \, d\omega$$  \hspace{1cm} (2.4)

where $A_k$ is a proportionality constant for the vibrational mode $k$ and $I_k$ is the integrated absorption of a peak corresponding with the vibrational mode $k$.

The bonding configurations surveyed in this study together with their proportionality constants are displayed in Table 2.2.

The vibrational mode at 2080-2090 cm$^{-1}$ is cause of debate [19]. Clustered H atoms or hydrogen at internal surfaces of the voids are more tightly bounded
Table 2.2: Characteristic vibrational modes and proportional constants for a-SiGe:H used in this study.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>$A_k$ (10$^{20}$ cm$^{-2}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH</td>
<td>2000</td>
<td>Stretching</td>
<td>1.2</td>
<td>[17]</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>2080-2090</td>
<td>Stretching</td>
<td>1.7</td>
<td>[17]</td>
</tr>
<tr>
<td>GeH</td>
<td>1880</td>
<td>Stretching</td>
<td>0.6</td>
<td>[18]</td>
</tr>
<tr>
<td>GeH$_2$</td>
<td>1980</td>
<td>Stretching</td>
<td>0.6</td>
<td>[18]</td>
</tr>
</tbody>
</table>

to the Si, shifting their stretching mode to higher frequencies ($\sim 2080$ cm$^{-1}$). Therefore it is not possible to distinguish between SiH on voids and SiH$_2$. The hydrogen-bonding configuration is characterized by the microstructure parameter $R^*$, defined as

$$R^* = \frac{I_{2080}}{I_{2000} + I_{2080}}.$$  (2.5)

A high microstructure parameter is often a sign of high void density material.

Raman spectroscopy

The Raman effect consists of an inelastic scattering of a photon by a solid material with the creation or annihilation of one or two phonons. The local environments in the material influence the scattering processes. Thus, in the a-SiGe:H material case, the phonon peak frequency is affected by the composition of the alloy as well as by structural strain. This permits one to correlate the amount of Ge in the material with the position of the vibrational mode for Si-Si bonds, the most sensitive to the alloying process [20].

The Raman spectra were decomposed into the characteristic amorphous or crystalline transverse optical modes (TO) for Si-Si, Si-Ge and Ge-Ge bonding. Together with these modes, three extra modes were necessary to fit the Raman spectra. The new modes are the following: a mode at 200-230 cm$^{-1}$ associated with a resonant mode or to an extent to induced disorder associated with the Ge LA band [21]; two weak modes at 430 cm$^{-1}$ and 450 cm$^{-1}$ related to the Si-Ge and Si-Si phonon bands, respectively [20]. The fitting of one of the spectrum is shown in Figure 2.2. By comparing the ratio Ge-Ge/Si-Ge of the measured material with a theoretical random distribution, the degree of Ge clustered in the material can be evaluated [22].

Raman spectra were measured using the 514.5 nm line of a Spectra-Physics Ar$^+$ laser, a Spex triple-grating monochromator, and a liquid-nitrogen cooled
Figure 2.2: Decomposition of the Raman scattering spectrum for a-SiGe:H. Three amorphous peaks and three crystal peaks (filled in grey) are shown. The two extra peaks around 450 cm\(^{-1}\) are filled with lines.

CCD detector (Roper Scientific). The probing depth with this wavelength is \(\sim\)60 nm for amorphous material.

2.2.2 Solar cell characterization

Current-voltage characterization (J-V)

Solar cell characterization is usually done studying the dependence of the output current on an applied voltage, known as J-V characteristic. The measurement can be carried out in the dark or under light conditions. The most important parameters obtained from the J-V characteristic under illumination conditions are the following (see Fig. 2.3):

- the short circuit current \((J_{sc})\), is the current of the solar cell in short circuit conditions. The \(J_{sc}\) is equal to the photogenerated current \((J_{ph})\) in an optimal solar cell,

- the open circuit voltage \((V_{oc})\), is the applied voltage for which the current is zero,
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Figure 2.3: The J-V characteristics of an a-SiGe:H solar cell under AM 1.5 and dark conditions.

- the fill factor (FF), is a measurement of the "squareness" of the J-V characteristic, being defined as

\[ FF = \frac{J_m V_m}{J_{sc} V_{sc}} \]  

(2.6)

where \( J_m \) and \( V_m \) are the current and voltage at the maximum power point \( (P_{MAX}=J_m V_m) \).

- the energy conversion efficiency \( (\eta) \), is defined as

\[ \eta = \frac{P_{MAX}}{P_{in}} \]  

(2.7)

where \( P_{in} \) is the power of the incident radiation.

An electrical approach to describe the J-V characteristic of an ideal solar cell is reached applying the superposition principle. In accordance with this principle the light J-V characteristic is the result of translating downward the dark J-V
characteristic by the magnitude of the light generated current. In real solar cells there are power losses due to the resistance at the interfaces between the different layers that form the solar cell or current leakage paths. The superposition principle is then corrected with the incorporation of series ($R_s$) and parallel ($R_p$) resistance. The solution of this electric circuit gives the total current density through the solar cell as

$$J = J_0 \left( \exp \left[ \frac{e(V - JR_s)}{nk_B T} \right] - 1 \right) + \frac{V - JR_s}{R_p} - J_{ph} \quad (2.8)$$

where $J_0$ is the reverse-bias saturation current density, $n$ is the diode quality factor, $k_B$ is Boltzmann’s constant, $T$ the absolute temperature and $e$ the elementary charge. The diode quality factor takes a value close to 1 in the case of diffusion-drive current or to 2 in the case of pure recombination-drive current. The value of $J_0$ and $n$ is determined by the dark J-V characteristic. A detail description of the origin of these parameters can be found in reference [2].

The dark and light J-V characteristics can be numerically obtained by solving the basic semiconductor transport equations, i.e. the hole and electron continuity equations and the Poisson’s equation. This approach permits one to obtain an estimation of other solar cell characteristics not easily measured by existing methods.

The illumination condition for measuring the J-V characteristic under illumination were created with a WACOM dual source solar simulator, in which illumination from a halogen lamp and a xenon lamp are mixed. The simulator provides illumination with an AM 1.5 spectrum at an intensity of 100 mW/cm$^2$.

Spectral response (SR) characterization

When a monochromatic light at a wavelength $\lambda$ probes the solar cell, biased at a voltage $V$, the number of carriers collected per incident photon at $\lambda$ can be derived from

$$\eta_{col}(\lambda, V) = \frac{J_{ph}(\lambda, V)}{e \phi_0} \quad (2.9)$$

where $\phi_0$ is the number of photons per unit area per second and $e$ is the elementary charge. The parameter $\eta_{col}$ is known as external collection efficiency or spectral response. The generation rate ($G$) of electron-hole pairs in the solar cell has an inverse exponential dependence on $\lambda$ and on the distance inside the solar cell.
from the surface on which the light enters the solar cell \((G \sim e^{-\alpha x})\). This property allows the spectral response technique to distinguish the contribution to the photocarrier collection from different regions of the solar cell. The short wavelengths are absorbed more strongly than the long wavelengths, generating carriers in the front and the bulk of the solar cell, respectively.

The measurement of tandem solar cells was done following the work of Burdick et al. [23]. A 1000 W xenon lamp was filtered to obtain bias light in the desired spectrum range. The blue bias light was obtained with a BG25 filter, while the red bias light was obtained with an OG570 filter. With the suitable spectrum range in the bias light, one of the cells that forms the tandem is saturated, generating a current close to the \(J_{sc}\) of the individual cell. The SR is measured under short circuit conditions, which creates a negative voltage on the limiting cell in opposition to the voltage created due to the bias light in the saturated cell. Applying to the tandem cell a positive voltage close to the \(V_{oc}\) of the saturated cell, the SR will measure the spectral dependence of the limiting cell.

The investigation of the SR for high energy photons, which do not reach the back surface, provides information about the effective diffusion length, \(L_{\text{eff}}\). To study this internal process, SR must be corrected from the external optical effects (the total reflectance of the cell), leading to the fraction of photons absorbed in the solar cell that are collected under short circuit conditions. The corrected SR is known as internal quantum efficiency (IQE). The inverse of the IQE shows a linear relation with the inverse of \(\alpha\), which slope is proportional to \(L_{\text{eff}}\) (Eq. 2.10) [24]. The proportionality constant depends on the surface roughness defined as the average path angle of the photons with respect to the cell’s normal vector, \(\theta\).

\[
\text{IQE}^{-1} = 1 + \alpha^{-1} \frac{\cos(\theta)}{L_{\text{eff}}} 
\]  

(2.10)

### 2.3 Degradation

The light induced degradation facility used in this study consists of a large box with dimensions of \(1 \times 1 \times 1.35\) m\(^3\). A fixed glass platform serves as a holder for the samples. The samples are illuminated from underneath the platform by a series of lamps and a mirror system in a housing. The housing is box type with the horizontal size of \(30 \times 40\) cm and a height of 60 cm, and it is located 5 cm below the platform. It is made from four vertically and one horizontally (at the bottom) placed mirrors.

The housing encloses a system of Osram halogen lamps with a power of 150 W each and two Philips MHN-TD 250 W metal halide lamps aligned sym-
Experimental techniques

Figure 2.4: Comparison of the standard solar spectrum (AM 1.5) with the spectrum generated by the lamps of the light soaking facility with and without the filter used with the $a$-SiGe:H solar cells

metrictically with respect to the mirrors. These lamps are located at the bottom of the housing a few centimeters above the horizontal mirror. The lamps are easily accessible and replaceable. Within the spectral sensitivity of amorphous silicon solar cells, the light provided by these lamps approximates the standard spectrum of AM1.5. Figure 2.4 shows the comparison of the standard solar spectrum (AM1.5) with the spectrum generated by the lamps of the light soaking facility. The spectrum is measured using a Hamamatsu reference detector with and without the filter used for the $a$-SiGe:H solar cells [25].

The light intensity at the sample platform is around 90 mW/cm$^2$ over an area of $\pm 0.1$ m$^2$. To determine the uniformity of illumination, the light intensity was measured over the entire area of the sample platform using the Hamamatsu reference detector and an amorphous silicon solar cell. The uniformity is achieved by multiple reflections provided by the mirror arrangement. A mechanism that ensured stable temperature of the samples within the range of $50 \pm 2$ °C was designed. The mechanism consists of heat sinks directly attached to the mirror housing and supported by blowers. The cell temperature was continuously monitored through thermocouples attached to a reference cell on the sample platform.