3 Deposition of $a$-SiGe:H at low temperatures and high deposition rate

3.1 Introduction

Since the discovery of the light-induced degradation in $a$-Si:H, the Staebler-Wronski effect has been the subject of intensive studies. Understanding the process, improving the stability of the material under light exposure and developing solar cells with higher stable efficiencies have been the steps followed in order to overcome the principal obstacle of thin film solar cells. The models proposed to explain the Staebler-Wronski effect are reviewed in Chapter 5. Improved light-stability in $a$-Si:H has been observed for depositions under very high $H_2$ dilution conditions. It is suggested that these conditions promote the formation of microcrystals, improving the medium range order in the material [26]. In solar cells, reduction of the degradation can be achieved by using tandem structures where thinner solar cells are less sensitive to light-induced degradation. The top junction consist of $a$-Si:H. For the bottom junction, $\mu$-c-Si:H as well as $a$-SiGe:H is being used. The state of the art for $a$-SiGe:H has not reached, until now, the levels for $a$-Si:H. There is no report about $a$-SiGe:H where the medium range order has been improved.

Furthermore, the development of more stable materials must be achieved within technically friendly conditions. Lower substrate temperatures permit cheaper substrates and no material damage to previously deposited layer. At the same time, higher deposition rates reduce the time of production and the final cost of the solar cell.

In this chapter, processes leading to $a$-SiGe:H with high stability are studied for the low deposition temperature regime. Deposition conditions under the onset of crystalline formation are used to obtain a material with improved medium range order. This material will be addressed as protocrystalline material. The chapter presents results on higher deposition rates by employing $Si_2H_6$ as feed gas instead of $SiH_4$. 

27
3.2 Growth of $a$-Si:H by PECVD

The growth processes of $a$-Si:H determine to a large extent the optical, structural and electrical properties of the $a$-Si:H material and the performance of the $a$-Si:H devices. The understanding of these processes as well as the correlation between the deposition conditions and the final properties of the material, points to the optimization of the deposition conditions.

The deposition by an rf PECVD discharge can be divided into four steps:

1. Initially, electron-impact excitation, dissociation and ionization of the precursor gasses generate the primary constituents of the plasma, in which they react through gas phase reactions.

2. The gas phase reactions are determined by the plasma physics and chemistry. They can be divided into:
   - primary reactions, leading to neutral radicals together with ions
   - secondary reactions, leading to higher radicals (species with higher mass than the species of the feed gasses, formed by successive reactions) and nanoclusters.

These conditions define the flux and nature of the reactive species diffusing from the plasma to the substrate.

3. Plasma-surface interactions, such as physisorption and chemisorption, diffusion, etching and abstraction by reactive species, define the conditions on the growing surface that result in the film formation. Modification of the growth surface by atomic hydrogen is also part of this process.

4. The final step is the series of reactions taking place in the growing zone. Cross-linking reactions result in the formation of the film and relaxation of the matrix.

As a first step in understanding the growth process, it is necessary to define the growth chemistry that can lead to a predictable growth from only one kind of species. For a silane plasma at low pressures, low silane dissociation and at temperatures above 200 °C, primary reactions alone are sufficient to describe $a$-Si:H deposition. Ignoring the contribution of positive and negative ions, which is much smaller than the neutral radical contribution for pressures above $10^{-2}$ mbar [27], the primary SiH$_4$ dissociation involves energetic electron ($\geq 8$ eV) impact disso-
Deposition of a-SiGe:H at low temperatures and high deposition rate

ciation into SiH\textsubscript{m} (m \leq 3) radicals and H atoms. The dominant processes are [28]:

\[ e^- + SiH_4 \rightarrow SiH_2 + 2H + e^- \quad (\approx 0.85) \quad (3.1) \]
\[ \rightarrow SiH_3 + H + e^- \quad (\approx 0.15) \quad (3.2) \]

where the numbers in brackets represent the branching fractions. Both H and SiH\textsubscript{2} react with SiH\textsubscript{4}, leading to

- the H abstraction reaction, which increases the overall amount of SiH\textsubscript{3}
  \[ H + SiH_4 \rightarrow SiH_3 + H_2 \quad (3.3) \]
- and SiH\textsubscript{2} elimination, promoting higher radicals.
  \[ SiH_2 + SiH_4 \rightarrow Si_2H_6 \quad (3.4) \]

The species SiH\textsubscript{3} does not react with SiH\textsubscript{4}, and thus it becomes the dominant species in the growth process. Secondary reactions are significant for higher pressures, which promote chain reactions resulting in polymerization, or higher rf power, which promote reactions between SiH\textsubscript{3} with other SiH\textsubscript{3}, limiting the flux of SiH\textsubscript{3} towards the growing surface.

Even in the simplified settings of only one species contributing to the deposition, the growth process is still controversial. Several models have emerged to explain the optimum deposition condition for a-Si:H at \( \sim 250 \) °C. They attribute the growth to only SiH\textsubscript{3} species and usually emphasize the importance of the mobility of the radicals and H at the growing surface, but they differ in the physical and chemical details.

Matsuda et al. [29,30] proposed that the growth is controlled by a process at the surface. Once the precursor is physisorbed at the surface, the growth is limited by the diffusion of the precursor on the growing surface. The diffusion length of the precursor is defined by the activation energy of the surface reactions that the precursor undergoes. These reactions are the following:

\[ Si - H + SiH_3 \rightarrow SiH_4 (g) + D^0 \quad (abstraction) \quad (3.5) \]
\[ D^0 + SiH_3 \rightarrow Si - SiH_3 \quad (growth) \quad (3.6) \]
\[ SiH_3 + -SiH_3 \rightarrow Si_2H_6 (g) \quad (recombination) \quad (3.7) \]

where D\textsuperscript{0} represents a dangling bond. The diffusion length is then defined as:

\[ l = \left[2D_0\tau_s\right]^{1/2} \quad (3.8) \]
where \( D_s \propto e^{-E_s/kT} \) is the diffusion coefficient with \( E_s \sim 0.2 - 0.3 \text{ eV} \) and \( \tau_s \) is the residence time on the surface before the precursor reacts. Recently Vigneron et al. have proposed a higher value for \( E_s (~0.7 \text{ eV}) \) [31]. For low temperatures (below 250 °C) \( D_s \) decreases and therefore the diffusion length decreases. On the other hand, at high temperatures (above 300 °C) the surface H desorbs, creating dangling bonds which reduce \( \tau_s \) and therefore the diffusion length decreases. As a result, the optimum \( T_s \) is \( \sim 250 \) °C. In accordance with this model, enhancing the material properties would consist in finding new ways of improving the diffusion length of the precursor.

Winer [32] assumed that the quality of the material is determined by the thermodynamics of the following chemical reactions in equilibrium, taking place at or below the growth surface rather than in the plasma. These reactions are mediated through thermal diffusion of H.

\[
\begin{align*}
\text{SiH}_3 (g) + D^0 & \rightarrow \text{SiH} + \text{H}_2 (g) \quad (\text{SiH}_3 \text{ incorporation}) \quad (3.9) \\
\text{SiH} + \text{SiSi} & \rightarrow D^0 + \text{SiHSi} \quad (\text{defect formation}) \quad (3.10) \\
\text{SiHSi} + \text{SiSi}_{\text{weaker}} & \rightarrow \text{SiHSi} + \text{SiSi}_{\text{stronger}} \quad (\text{strain reduction}) \quad (3.11)
\end{align*}
\]

The plasma is seen as a source of reactive species. The optimal growth is obtained when the average rate of H diffusion \( \nu_H \), defined in the time interval \( \Delta t \), approximately matches the deposition rate \( R_d \)

\[
\nu_H \equiv \frac{4D_H}{\Delta t}^{1/2} \approx R_d \approx \frac{4D_H}{L} \quad (3.12)
\]

where \( D_H \) is the H diffusion constant, \( L \equiv R_d \Delta t \sim 1 \text{ Å} \) is the depth from the growing surface where the equilibrium growth process occurs and \( \Delta t \) is a time interval for equilibration. When the equilibrium is achieved, reactions 3.9 to 3.11 reach equilibrium during the deposition time, i.e. the H diffusion is high enough to allow thermal equilibrium conditions. The model predicts that the optimal \( T_s \) is given by the temperature at which \( \nu_H = R_d \), for a given rf power (deposition rate).

For a rf power of the order of 10 W the optimal \( T_s \) has a value of \( \sim 250 \) °C. In this model the plasma power and the deposition temperature determine the material properties.

This model has been more elaborated in the hydrogen density of states model (HDOS) proposed by Street, taking into account the evolution of the chemical potential of the H in the plasma and on the growing surface [11], which tend to equalize. One important conclusion of the thermal equilibrium model is that the defect concentration in the material cannot be made arbitrarily small, but is limited by the disorder of the material (characterized by the Urbach energy).
Modifying the thermal equilibrium model, Hata et al. [33] proposed a quasi-equilibrium model where the surface defects formed during growth are annealed during deposition. The equilibrium is then developed through the entire thickness of the film and not only at the growing surface. The dependence of the defect density on the film thickness is explained by the depth dependent decay of the surface defects induced during deposition. The dependence of the defect density on the substrate temperature derives from the different annealing rate of defects by the substrate temperature.

Away from primary reactions conditions, technology demands for higher deposition rates to reduce production cost, and for low deposition temperatures, which are needed to avoid damage to the underlying deposited layers [34]. Under these deposition conditions, secondary reactions are no longer negligible and determine the film quality. The effect of secondary reactions is mainly the formation of clusters. Higher silane radicals (due to their slow diffusion) and negative ions (because they are trapped in the plasma) have a long residence time in the plasma bulk and can eventually react with other species leading to powder (negatively charged). As the powder is negatively charged and trapped in the plasma, it is expected that clusters undergo polarity changes to allow them to escape the plasma, contributing to growth. As a result, a whole range of small particle sizes in the bulk of the plasma reach the surface during deposition. There is no clear picture of the effect of these small particles on film properties, which may explain the different conclusions by different groups [35,36,37,38]. Thus, for example, Roca i Cabarrocas et al. [38] have deposited a-Si:H material (so called polymorphous) under plasma conditions where silicon clusters together with radicals contribute to the growth. The size of the clusters can be selected by modifying the pressure. They claim that the clusters help to create films with medium range order, thanks to the presence of microcrystallinity regions [39]. The medium range order improves the transport properties and stability with respect to standard a-Si:H (see Section 5.4). They are able to deposit amorphous as well as microcrystalline material.

### 3.3 Growth of a-SiGe:H by PECVD

In the previous section the complexity of the a-Si:H plasma was stressed. The variety of radicals generated can easily lead to inhomogeneous growth if the conditions are poorly controlled. For the growth of a-SiGe:H the process becomes more complex. The two primary precursors, SiH4 and GeH4, decompose at very
different rates. For 100 eV$^1$ electrons, the total dissociation cross section for GeH$_4$ is 2 times higher than for SiH$_4$ and the threshold for GeH$_4$ dissociation is 2 eV lower than for SiH$_4$, which enhances the dissociation of GeH$_4$ over SiH$_4$. A 2 to 6 times higher dissociation rate is expected for GeH$_4$ than for SiH$_4$ [28,42], depending on the deposition conditions and the measuring method used.

Following the work of Doyle [28], the most significant chemical reactions taking place in a SiH$_4$-GeH$_4$ plasma dominated by electron collisional dissociation are the following:

\[
\begin{align*}
\text{SiH}_2 + \text{SiH}_4 & \rightarrow \text{Si}_2\text{H}_6 & (3 - b) & (b) \\
& \quad \text{or} \quad \text{SiH}_2 + \text{GeH}_4 & \rightarrow \text{SiGeH}_6 & (3 - b) & (d) \\
& \quad \text{SiH}_2 + \text{GeH}_4 & \rightarrow \text{H}_2\text{GeSiH} + \text{H}_2 & (2 - b) & (e) \\
\end{align*}
\]

\[
\begin{align*}
\text{SiH}_3 + \text{H} + \text{e}^- & \rightarrow \text{SiH}_3 + \text{H} + \text{H}_2 + \text{e}^- & (0 - 20\%) & (g) \\
\text{Si} + \text{GeH}_4 & \rightarrow \text{SiGeH}_5 & (3 - b) & (h) \\
\text{SiH}_3 & \rightarrow \text{SiH}_3 + \text{H} + \text{e}^- & (< 10\%) & (i) \\
\text{SiH}_4 & \rightarrow \text{SiH}_4 + \text{H}_2 + \text{SiH}_3 & (80 - 90\%) & (a) \\
\text{GeH}_3 & \rightarrow \text{GeH}_3 + \text{H} + \text{e}^- & (80 - 85\%) & (k) \\
\text{GeH}_2 & \rightarrow \text{GeH}_2 + \text{H} + \text{e}^- & (15 - 20\%) & (m) \\
\text{GeH}_2 + \text{GeH}_4 & \rightarrow \text{Ge}_2\text{H}_6 & (3 - b) & (n) \\
& \quad \text{or} \quad \text{H}_2\text{GeGeH} + \text{H}_2 & (2 - b) & (o) \\
\end{align*}
\]

where 2-b and 3-b stands for 2-body and 3-body reaction. The complex H$_2$GeSiH$_2$ (reaction 3.13f) is expected to contribute to growth, while the other products of the 2-body reactions react with SiH$_4$ or GeH$_4$ to create higher radicals. Finally,

\footnote{In the range of 20-100 eV the total capture cross section for SiH$_4$ varies between 5-10$\times$10$^{-16}$ cm$^2$, for Si$_2$H$_6$ varies between 10-25$\times$10$^{-16}$ cm$^2$ while for GeH$_4$ at 100 eV it is 20$\times$10$^{-16}$ cm$^2$ [40,41].}
the H would react to produce:

\[ \text{H} + \text{SiH}_4 \rightarrow \text{H}_2 + \text{SiH}_3 \]  
\[ \text{H} + \text{GeH}_4 \rightarrow \text{H}_2 + \text{GeH}_3 \]  

Typical rate constants for neutral dissociation and dissociative ionization in rf plasmas for SiH\(_4\) are \(10^{-10} - 10^{-9} \text{ cm}^3\text{s}^{-1}\) and \(10^{-12} - 10^{-11} \text{ cm}^3\text{s}^{-1}\), respectively.

The growth of \(\alpha\)-SiGe:H can be described by considering first the reactions of SiH\(_4\) alone (reaction 3.1). When GeH\(_4\) is added, Doyle et al. have observed [28] that Si\(_2\)H\(_6\) production (reaction 3.13b) decreases because the radical SiH\(_2\) preferentially reacts with GeH\(_4\), producing SiGeH\(_6\) and H\(_2\)GeSiH\(_2\) (reactions 3.13d and 3.13f). This last radical is not very reactive and should reach the substrate, contributing to growth. The efficiency in Si incorporation in the material is thus increased by the addition of GeH\(_4\). On the other hand, most of the H (from reactions 3.13a, 3.13g, 3.13i, 3.13k and 3.13m) will react with GeH\(_3\), due to its higher rate constant\(^2\), compensating the losses of GeH\(_3\) due to the reaction of GeH\(_4\) with SiH\(_2\). In this way, the efficiency of Ge deposition remains roughly constant. The SiH is assumed to react with GeH\(_4\) contributing to growth (reaction 3.13h).

The final amount of Si and Ge incorporated in the film also depends on the sticking coefficient of each of the species. The sticking coefficient of GeH\(_3\) is 2 times higher than that of SiH\(_3\). The weaker Ge-Ge surface bond may react easier with GeH\(_3\), promoting the addition of Ge to the film, and possibly, the formation of Ge clusters. Moreover, H elimination from the Ge growing surface is much easier than from Si, which contributes to the higher density of defects in \(\alpha\)-SiGe:H alloys with respect to \(\alpha\)-Si:H. The structural properties and defect density will be discussed later.

From the discussion above, it is understandable that alloying \(\alpha\)-Si:H produces a material with electrical properties that are not as good as those of the original material; the properties deteriorate with the degree of alloying. Although the reasons are still not fully understood, the well accepted ideas are

- a preferential attachment of H to Si over Ge, which leads to an increase in Ge dangling bond density [45];
- formation of microstructure (voids, clusters) [46] and
- thermal equilibrium effects according to the thermal equilibrium model, which result in higher defect densities for low band gap material [32] (the rate constant for reaction 3.14 is in the range of \(4 \times 10^{-13} - 8 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\) [43], whereas for reaction 3.15 the rate constant varies around \(2 \times 10^{-12} - 4 \times 10^{-10} \text{ cm}^3\text{s}^{-1}\) [44].

\(^2\)The rate constant for reaction 3.14 is in the range of \(4 \times 10^{-13} - 8 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\) [43], whereas for reaction 3.15 the rate constant varies around \(2 \times 10^{-12} - 4 \times 10^{-10} \text{ cm}^3\text{s}^{-1}\) [44].
defect density increases when the difference between the energy level of the defect and the valence band edge decreases; in low band gap materials this difference is smaller than in wider band gap materials).

All the processes mentioned above modify the electronic properties through a change in the $\mu_T$ product.

To overcome these limitations various alternative deposition methods to the standard ones have been used (for example by remote electron-cyclotron-resonance (ECR) or higher frequencies than the standard PECVD techniques (VHF)), and different dilution gases or deposition conditions have been tried (dilution gases as F$_2$ or Ar or deposition conditions near the powder regime).

In this research, the development of better and technologically friendly $a$-SiGe:H material is pursued by using high dilution with H$_2$ of the precursor gasses, by depositing at low substrate temperatures, and by using Si$_2$H$_6$ instead of SiH$_4$. In the following sections the influence of these parameters is discussed and the experimental results presented. In the next subsections, the motivation for changing these deposition parameters is given.

### 3.3.1 Hydrogen dilution of $a$-SiGe:H

The Ge-related radicals have a smaller surface diffusion coefficients on the growing surface than the Si-related radicals [45]. Moreover, the H bound to Ge thermally dissociates at lower temperatures than bound to Si. These two characteristics make Ge rich surfaces very reactive, reducing the surface diffusion of adsorbed radicals.

Supposing that the surface diffusion coefficient of precursors is the limiting parameter (as in the surface diffusion model [29,30]), an increase in the atomic H flux towards the surface would cover the growing surface better. This would increase the diffusion coefficient and decrease the number of Ge clusters. A higher H$_2$ dilution would provide this extra amount of atomic H by the dissociation of H$_2$ which in turn promotes the reactions 3.14 and 3.15 over the electron dissociation [47]. Nevertheless, this idea is under discussion due to the experiments of Matsuda [48] and Tachibana [49]. They observed how the density of atomic H in a SiH$_4$ plasma decreases upon dilution with H$_2$. Taking into account the lower dissociation energy of GeH$_4$ with respect to SiH$_4$, this result would be directly applicable to the SiH$_4$-GeH$_4$ plasma.

It is therefore proposed that a higher H$_2$ dilution prevents the formation of radicals with a short lifetime due to the reaction with H$_2$ instead of with other radicals. This applies in particular to Ge-related radicals because of the preferential depletion of GeH$_4$ [50].
Finally, Street’s model (modified thermal model) explains the improvement with H\textsubscript{2} dilution as follows [51]. Increasing the dilution causes an increase in the atomic H at the growing surface and the chemical potential of the H thus becomes closer to the energy of mobile H. At the same time, the deposition rate decreases. This gives time to optimize the local bonding configuration by the interaction of H with the network until the density of weak bonds at the surface and the H content is minimized for the deposition conditions. As a result, the defect density decreases with an increase in dilution.

Another important role of H\textsubscript{2} dilution is its influence on the microstructure; as H\textsubscript{2} dilution increases, the material changes from amorphous (short range order) to microcrystalline (long range order). Mobile H atoms can diffuse deeply into the lattice at the growth temperature and can extract excess H, that otherwise would lead to voids and columnar growth. A higher density of atomic H removes the excess H more efficiently. The same results could be achieved by ion bombardment with energies not exceeding 5 eV. (Higher ion energy would damage the material). Xu et al. [52] corroborated the creation of oriented microstructures (related with the formation of crystals) with H\textsubscript{2} dilution and the reduction in the void density.

In summary, the effects of H\textsubscript{2} dilution on a-SiGe:H are

1. an increase in H coverage of the growing surface [53],
2. a selective etching of Ge-Ge weak bonds [22],
3. the production of a more homogeneous structure [54] and
4. the suppression of gas phase polymerization in the plasma [55].

A drawback of high H\textsubscript{2} dilution is the decrease in deposition rate, mostly due to suppression in the radical production and etching processes during growth.

With respect to the stability, recent studies [52,26] have shown that a-Si:H solar cells, which intrinsic layer was deposited under very high H\textsubscript{2} dilution conditions of the SiH\textsubscript{4}, exhibit higher stability values than a-Si:H solar cells under lower H\textsubscript{2} dilution conditions. Several groups [52,56] have proposed the presence of a more ordered nanocrystalline network induced by the atomic H as the cause of the higher stability. The material grown near the transition to microcrystalline phase is known as protocrystalline material. No study has been reported on the stability of protocrystalline a-SiGe:H. In Section 3.4.1 the growth of protocrystalline a-SiGe:H is studied, and in Chapter 5 the stability against light exposure of the material itself and in solar cell structure is presented.
3.3.2 Low substrate temperature deposition of $a$-SiGe:H

The substrate temperature is an important parameter related to the problem of surface mobility of growth species and desorption of H. Even though a minimum in the defect density has been observed at a temperature around 250 °C for $a$-Si:H, a review of the literature dealing with the substrate temperature shows that the substrate temperature has to be optimized for each individual deposition process and alloy composition. Winer [32] proposed that the optimal deposition temperature varies with the rf power. However, the necessity of higher deposition temperature when the deposition rate is higher is well accepted [57].

The surface temperature during deposition affects the H content in the film. High temperature results in a lower H content and a lower $E_g$. However, the H and Ge contents of $a$-SiGe:H films do not independently influence $E_g$, as observed by Terakawa et al. [58].

Two factors related to the deposition temperature govern the growing surface defect density and therefore the quality of the material. On the one hand, the surface mobility of precursors increases with the substrate temperature. As mentioned before, the Ge-related precursors are expected to limit the film quality due to their lower surface mobility. Increasing the substrate temperature, the mobility would be enhanced resulting in a better quality material (higher photosensitivity). Perrin et al. observed a sharp increase in the surface reaction probability, $\beta$, above 200 °C [59] supporting this previous supposition. Similar results are obtained if the amount of Ge-related precursors on the surface is reduced.

On the other hand, the H surface coverage increases with a reduction in the substrate temperature. The thermal desorption of H from the growing surface occurs principally from Ge-H bonds, due to a lower activation energy for H desorption than for Si-H bonds (desorption occurs even at 110 °C for Ge-H compared with the 350 °C needed for Si-H). If the amount of Ge-related precursors at the surface is reduced the H desorption would be reduced at the same time.

With these ideas in mind, Matsuda et al. [60] and Middya et al. [61] proposed essentially the use of feed gasses at a low flow (to reduce the amount of Ge precursors on the surface), high H$_2$ dilution (to increase the H coverage of the growing surface) and high temperatures (to promote the mobility of Ge precursors). They observe a maximum in photosensitivity at a deposition temperature of 200 °C.

However, a high deposition temperature during the fabrication of solar cells may result in degradation in the previously deposited layers, in particular when they are deposited at lower temperature. TCO coated glasses also degrade at high temperatures [34] in a H$_2$ plasma. Some groups have opted for n-i-p solar cell structures deposited on stainless steel substrates, due to the higher deposition temperature of the n-doped layer [62].
Deposition of a-SiGe:H at low temperatures and high deposition rate

Zeman et al. [63] have recently shown how during the band gap profiling of a-SiGe:H solar cells, the initial layers deposited at lower dilution may have a higher Urbach energy than expected for a device quality material with a band gap of \( \sim 1.7 \) eV. In computer simulations of solar cells with a graded intrinsic layer, the same high values for the Urbach energy of these materials are needed to simulate the external parameters. By decreasing the deposition temperature, the Urbach energy can be reduced to a value closer to device-quality material.

To avoid damage to the previously deposited layers during multijunction solar cell deposition as well as to prevent the inclusion of possible low quality material during the band gap profiling of a-SiGe:H solar cells, deposition at low substrate temperature is required.

### 3.3.3 Deposition of a-SiGe:H with \( \text{Si}_2\text{H}_6 + \text{GeH}_4 \)

An advantage of using \( \text{Si}_2\text{H}_6 \) instead of \( \text{SiH}_4 \) is that the dissociation rates of \( \text{Si}_2\text{H}_6 \) and \( \text{GeH}_4 \) are very similar (see footnote on page 32). The difference in the dissociation rates of \( \text{GeH}_4 \) and \( \text{SiH}_4 \) is a factor between 2 and 6 [28,42], whereas the difference between \( \text{GeH}_4 \) and \( \text{Si}_2\text{H}_6 \) dissociation rates is reported to be only 0.8 [42].

The study presented by Doyle et al. [28] proposed that the initial radical mix in the plasma remains similar to the \( \text{SiH}_4 + \text{GeH}_4 \) discharge. Thus, the flux of radicals contributing to growth is expected to be dominated by the same monoradicals (\( \text{SiH}_3 \) and \( \text{GeH}_3 \)) and higher radicals as in the \( \text{SiH}_4 + \text{GeH}_4 \) plasma. The study of \( \text{Si}_2\text{H}_6 \) dissociation predicts a lack of disilicon radicals contributing to growth [28]. The reactions that may take place with \( \text{Si}_2\text{H}_6 \) are the following:

\[
\begin{align*}
e^- + \text{Si}_2\text{H}_6 & \rightarrow \text{SiH}_3 + \text{SiH}_3 + \text{H} + e^- & (3.16) \\
\text{H}_3\text{SiSiH} + 2\text{H} + e^- & (3.17) \\
\text{H} + \text{Si}_2\text{H}_6 & \rightarrow \text{SiH}_4 + \text{SiH}_3 & (3.18) \\
\text{Si}_2\text{H}_5 + \text{H}_2 & (3.19)
\end{align*}
\]

While the \( \text{Si}_2\text{H}_6 + \text{GeH}_4 \) plasma kinetics are similar to the \( \text{SiH}_4 + \text{GeH}_4 \) plasma, the explanation for the observed difference in the film quality between these two methods is not straightforward [64,65]. Using feed gases with similar dissociation rates avoids the preferential depletion of one of them, in this case \( \text{GeH}_4 \). Under deposition conditions where the \( \text{GeH}_4 \) is depleted, the presence of higher radicals and powder increases (see Equation 3.13). These higher radicals have surface reaction probabilities close to unity, and it can be expected that the sticking probabilities are also close to unity, i.e. the higher radicals can insert directly...
into the SiH or GeH surface bonds. If these conditions are not optimized by ion bombardment or high hydrogen dilution, the presence of voids will create shadowed regions with unsaturated dangling bonds, a more disordered network and finally a highly defective material. By replacing SiH$_4$ with Si$_2$H$_6$ the depletion of GeH$_4$ can be prevented, reducing the density of deep states.

Another source of difference between SiH$_4$ and Si$_2$H$_6$ as feed gas could be a difference in the ion bombardment, due to the different optimal deposition conditions for SiH$_4$ and Si$_2$H$_6$. As will be shown in Section 3.5, other radicals than in SiH$_4$ plasma, such as Si$_2$H$_5$, must be contributing to the growth, which could affect the film properties.

An advantage that comes as a consequence of the similar dissociation rates, is the possibility of reaching a higher deposition rate while maintaining low structural disorder in the deposited material [66] as well as better uniformity in large area deposition.

### 3.4 Results in deposition of $a$-SiGe:H at low temperature

This section contains the characterization results of materials deposited with GeH$_4$+SiH$_4$ at different substrate temperature. First, the results are presented to be discussed subsequently.

#### 3.4.1 Material properties

In order to investigate the influence of the deposition temperature on the properties of $a$-SiGe:H material at the edge of microcrystallinity, several series of materials were deposited in which the flow of hydrogen was changed for different substrate temperatures. The band gap was kept constant for all the series. The deposition temperature, $T_s$, was controlled by heating the substrate holder. We have studied the range from 200 °C to 170 °C, because it was expected that this deposition temperature would best match that of the $a$-SiC:H p-doped layer of 160 °C.

The GeH$_4$+SiH$_4$ flow was kept constant at 2.7 sccm. Hydrogen dilution, defined as $f = H_2/(GeH_4+SiH_4)$, was varied from $f = 65\%$ to $f = 85\%$, the latter being the maximum value reachable by the deposition system. The very high dilution condition is expected to lead to material near the microcrystalline regime. The dilution could have been increased by decreasing the GeH$_4$+SiH$_4$ flow. This procedure was not followed because it has the disadvantage of reducing the deposition rate and more importantly, it creates depletion of the source gasses (specifically GeH$_4$), which would degenerate in higher radical formation (reactions 3.13) and low quality material [67,68].
Two different film thicknesses were deposited: thin films (~100 nm) as well as thick films (~500 nm).

Figures 3.1a and b show the deposition rate ($R_d$) for three different dilutions as a function of the substrate temperature, for thin as for thick samples, respectively. Figure 3.1c and d show $n_0$ for the same samples. The thin films show a deposition rate that is not dependent on the temperature. On the other hand, the dilution decreases the deposition rate, ascribed to the reduction of the fraction of the silane as well as of the germane gas. All the series for thin materials have a similar density, related with $n_0$, which is independent of $T_s$.

For the thick samples, $R_d$ as well as $n_0$ depend on $T_s$ and on the H$_2$ dilution ratio. The increase in H$_2$ dilution reduces $R_d$ (similar to the thin films case) except for the highest diluted series ($f=85\%$), for which $R_d$ is unexpectedly higher again at all the temperatures than for $f=75\%$. The values of $n_0$ follow an inverse trend when compared with the microstructure factor, $R^*$ (Fig. 3.3d) (more compact materials, high $n_0$, have lower $R^*$). These differences are discussed in Section 3.4.2.

**Structural properties**

The structural properties were characterised by IR and Raman spectroscopy and by Rutherford Backscattering Spectrometry (RBS).

Figure 3.2 shows the Raman shift for the series under study. The Raman spectra were decomposed into the characteristic amorphous and crystalline transverse optical modes for Si-Si, Si-Ge and Ge-Ge bonding. An example of decomposition is shown on page 21.

By Raman spectroscopy, the presence of crystal structure and clusters, due to preferential Ge-Ge or Si-Si bonding, is investigated. The existence of these clusters is suggested (Section 3.3) as one of the causes of the poor electronic transport properties of a-SiGe:H [54].

Starting with the lowest dilution series ($f=65\%$), no significant changes in the structure are observed by varying the $T_s$. The materials are amorphous with no clear sign of crystallinity, for both thin and thick films. The width of the amorphous peaks is too broad to distinguish the crystalline peaks, if any.

Increasing H$_2$ dilution ($f=75\%$) the crystalline peaks become visible. The variations in the Raman spectra in Fig. 3.2 show the genesis of the transition from amorphous to microcrystalline, in two ways. Firstly, the transition to microcrystalline structure is seen with the increase in the thickness. The material starts being amorphous (thin sample at $T_s=190 ^\circ C$) to exhibit some microcrystalline structure in the thick sample (~500 nm). (The Raman spectra of the thin sample is virtually the same as that for the material deposited at $T_s=170 ^\circ C$, thus it is not shown.
Figure 3.1: Deposition rate and n$_0$ value for thin (a and c) and thick (b and d) films respectively as a function of T$_s$ for three different H$_2$ dilutions.

for clarity). Secondly, there is a transition to microcrystalline structure with T$_s$. The sample deposited at T$_s$=180 °C does not have signs of microcrystalline structure, however at T$_s$=190 °C the TO modes for crystalline Si-Si, Si-Ge and Ge-Ge clearly appear as shoulders at lower frequencies compared with the amorphous Raman spectrum of the sample at T$_s$=180 °C.

When H$_2$ dilution is further increased (f=85%), pronounced resonance modes of crystalline Si-Si, Si-Ge and Ge-Ge appear. When the temperature is over 170 °C, the material steeply changes from being amorphous to display Raman peaks at the crystalline TO modes, indicating the presence of crystalline structure.

In summary, by increasing the dilution of source gases with hydrogen during the deposition, the material has become partially microcrystalline. This is explained by the hydrogen etching the growing surfaces, which eliminates parts
of the disordered configuration and strained or weak bonds. Thus the crystalline phase, with a lower energy configuration, remains in the structure. Low $T_s$ reduces the H diffusion rate to values below the limit to allow changes in the bonding configurations. On the other hand, the hydrogen density of states model (HDOS) proposed by Street [11] suggests that lowering the $T_s$ would raise the H chemical potential, accelerating the transition to crystalline growth. Section 3.4.2 will discuss the results in detail.

With respect to the H bonding configuration, Figures 3.3a to 3.3c show the infrared vibrational spectra for the three dilution series. The vertical lines in Figure 3.3a represent the position of the stretching mode for Si-H. Figure 3.3d shows the microstructure factor, $R^* = I_{2080}/(I_{2000} + I_{2080})$, for the three series. The shift in the position of the stretching mode for Si-H in $a$-Si:H has been related to the presence of microcrystalline structure [69]. In $a$-Si:Ge:H deposited at 200 °C...
Figure 3.3: Infrared-absorption spectra of hydrogenated vibrational modes in \( \alpha \)-SiGe:H grown at different \( T_s \) under several \( H_2 \) dilution ratios: a) \( f=65\% \), b) \( f=75\% \) and c) \( f=85\% \). d) Microstructure factor for the same samples.

and \( f=85\% \), the shift in the position of the stretching mode for Si-H can be related as well with the presence of microcrystalline structure, as Raman measurement corroborates (Fig. 3.2).

The H content in different bond configurations, for the dilution series under study, as a function of \( T_s \), is shown in Figure 3.4. The total H and Ge contents in the material are shown in Figure 3.5. The materials with \( f=65\% \) exhibit no variation in \( C_{H(Si-H)} \), \( C_{H(Si-H_2)} \) or \( C_{H(Ge-H)} \) with \( T_s \), as well as in the total H and Ge content. For fully amorphous material at low \( T_s \) and high \( H_2 \) dilution Shima et al. [70] have observed similar behaviour. When \( H_2 \) dilution is increased to \( f=75\% \), the dihydride bonds decrease with respect to Si-H bonds. This is reflected in a lower microstructure factor with respect to \( f=65\% \) (Fig. 3.3d). The
Deposition of a-SiGe:H at low temperatures and high deposition rate

Figure 3.4: H content in different bond configurations of a-SiGe:H deposited at three different flows as a function of $T_s$.

Figure 3.5: Total H and Ge content of a-SiGe:H deposited at three different flows as a function of $T_s$. 
hydrogen content decreases with increasing $T_s$. Crossing the microcrystalline edge, $f=85\%$, the material shows as well a decrease in H content with increasing $T_s$ at the Si-H peak. As a result, the material becomes more porous ($n_0 \sim 2.90$ at $T_s=180^\circ C$). At the lowest $T_s$ ($170^\circ C$), the variation in dilution does not modify the amorphous structure of the material, showing for every $f$ the same values for $C_{H(Si-H)}$, $C_{H(Si-H_2)}$ and $C_{H(Ge-H)}$. The low temperature on the surface may be limiting the diffusion of radicals and H; it is necessary to have an even higher $H_2$ dilution.

Figure 3.6 shows a cross-sectional transmission electron microscopy (TEM) image of a material grown at the onset of microcrystallinity ($f=75\%$ and
Deposition of a-SiGe:H at low temperatures and high deposition rate

Figure 3.7: Raman ratios a) $I_{Ge-Ge}/I_{Si-Ge}$ and b) $I_{Si-Ge}/I_{Si-Si}$ as a function of Ge content for a-SiGe:H deposited under three different H$_2$ dilutions. The solid curve represents the ratios for random alloys. The error bars are inside the size of the points.

$T_s=180$ °C. Columnar void structures are observed along the thickness of the material. Hydrogens bonded at the internal surfaces of the voids are more tightly bound to the Si. This produces a shift of their stretching mode to higher frequencies ($\sim 2080$ cm$^{-1}$), which contributes, together with the Si-H$_2$ stretching mode ($\sim 2090$ cm$^{-1}$), to the vibrational mode at 2080-2090 cm$^{-1}$ observed in Fig. 3.4. The structural strain induced by Ge incorporated into the material is released through the creation of these columnar void structures.

With respect to the presence of homo- or heteronuclear bonds, Figure 3.7a shows the ratio $I_{Ge-Ge}/I_{Si-Ge}$, while Figure 3.7b shows the ratio $I_{Si-Ge}/I_{Si-Si}$ as a function of the germanium concentration in the material. The vibrational modes measured by Raman spectroscopy are TO peaks of Si-Si, Si-Ge and Ge-Ge. Assuming a perfect random network, the amount of these bonds will be represented by the fractions $(1-x)^2$, $2(1-x)x$ and $x^2$, respectively, where $x$ is the germanium concentration. Comparing the measured ratio ($I_{Ge-Ge}/I_{Si-Ge}$ and $I_{Si-Ge}/I_{Si-Si}$) with the predicted for random alloys ($x/2(1-x)$ and $2x/(1-x)$), an estimation of the presence of clusters can be found, knowing the Ge concentration ($x$). The random alloy is calibrated by fitting the predicted bond density ratio, $x/2(1-x)$ and $2x/(1-x)$, with the fractions $I_{Ge-Ge}/I_{Si-Ge}$ and $I_{Si-Ge}/I_{Si-Si}$ of a sample with very high concentration of Ge ($\sim 70$ at.%). This material with high Ge concentration is expected to have a randomly mixed state [22]. The calibration of the ratio $I_{Si-Ge}/I_{Si-Si}$ in the random distribution is less accurate than for the ration $I_{Ge-Ge}/I_{Si-Ge}$, due to the small peak at TO mode for Si-Si in the
material with high germanium concentration used for the calibration.

The amorphous materials (made at low dilution conditions \( f \leq 75\% \) and low \( T_s \) or high \( H_2 \) dilution and very low \( T_s \)) exhibit a preferential formation of Ge-Ge bonds, and consequently formation of Ge clusters, as Figure 3.7a shows. Materials deposited under amorphous conditions show higher cluster formation (higher values of \( I_{Ge-Ge}/I_{Si-Ge} \) with respect to the random distribution). This indicates that the plasma chemistry conditions to grow amorphous material are unsuitable for promoting the formation of Si-Ge heterobonds. The presence of microcrystalline structure in the material promotes the formation of more ordered material. Small amounts of microcrystalline structure, obtained by depositing on the edge of the microcrystalline detection, are sufficient to reduce the cluster formation and promote the growth of more order regions. Materials with \( f=85\% \) and \( T_s \) over 170 °C present clear microcrystals, as Fig. 3.2a shows, and a ratio \( I_{Ge-Ge}/I_{Si-Ge} \) lower than the expected for random distribution. At the same time, the material deposited under \( f=75\% \) and \( T_s=190 \) °C, exhibits the same higher amount of heterogeneous Si-Ge bonds as the more microcrystalline material. On the other hand, the material deposited under \( f=75\% \) and \( T_s=180 \) °C presents the bond heterogeneity structure of an amorphous material with high Ge content and a random structure.

In Figure 3.6 it was shown a transmission electron microscopy imagine of the total thickness of the \( a_{-} \)-SiGe:H material previous to the microcrystalline formation (protocrystalline material). To study in more detail the structure of the protocrystalline material, high resolution electron microscopy (HREM) was used. Figure 3.8 shows the HREM images taken at different positions along the thickness of the film. The HREM image of the amorphous glass substrate (Figure 3.8a) shows an homogeneous structure typical for amorphous material. The fast-Fourier transform (FFT) of the image (inset figure) exhibits the diffuse halo ring confirming the amorphous structure of the glass substrate. An HREM image of the material deposited close to the substrate is shown in Figure 3.8b, while Figures 3.8c and 3.8d show images of the material close to the surface. The FFT of the image in Fig. 3.8b (inset figure) exhibits a ring slightly sharper than for pure amorphous material. The ring becomes sharper as the material grows, indicating a more ordered structure (inset Fig. 3.8c). This is also observed by selected-area diffraction pattern (inset Fig. 3.8d). We speculate that the improvement of the medium range order is due to the formation of small structures inside the material. These microstructures are visible in Fig. 3.8c and more clearly in Fig. 3.8d as darker regions with sizes of several tenths of Angstroms. The Raman spectrum of the protocrystalline material (at \( f=75 \) % and \( T_s=180 \) °C in Fig. 3.2) shows that these microstructures are not in crystalline phase. At the same time, the microstruc-
Deposition of a-SiGe:H at low temperatures and high deposition rate

Figure 3.8: High resolution electron microscopy (HREM) images from different areas of the protocrystalline a-SiGe:H material. a) Area from glass substrate (amorphous); the inset shows the fast-Fourier transform (FFT). b) Area from material close to substrate; inset: FFT. c) Area from material close to surface; inset: FFT. d) Area from material close to the surface; the inset figure shows the selected-area diffraction pattern (SADP).

...do not consist of only Ge atoms (which would be observed as Ge clustering formation) but as an heterogeneous mix of Ge and Si atoms. This is observed in Fig. 3.7a, where the measured $I_{Ge-Ge}/I_{Si-Ge}$ ratio for the protocrystalline material has the same value as for a random alloy. Moreover, when the conditions lead to crystalline formation (see the change in material grown at $f=75\%$ from $T_s=180^\circ C$ to $190^\circ C$ in Fig. 3.7a), the amount of Ge in the material decreases and the material shows a higher structural order (reduction of Ge-Ge cluster below the random level). Thus, the a-SiGe:H material starts growing amorphous with a high amount of Ge and changes to a material with a more ordered microstructure during growth. The crystallization begins at higher thickness (possibly at the site of...
Figure 3.9: The absorption coefficient spectra measured by CPM versus $T_s$ for $a$-SiGe:H deposited with several $H_2$-diluted ratio: a) $f=65\%$, b) $f=75\%$ and c) $f=85\%$.

the ordered microstructures), reducing the amount of Ge in the material [71]. This has important consequences for the growth of $\mu$-SiGe, as the structural strain in the network induced by high Ge concentration retards the crystalline nucleation.

**Optical characteristics**

The optical band gap determined by Tauc’s plot or by a cubic relation (as described in Section 2.2.1) remains constant for all series, amounting to 1.50-1.54 eV for the Tauc’s gap and 1.20-1.25 eV for the cubic band gap.

Figures 3.9a to c show the absorption coefficient spectra for $f=65\%$, 75\% and 85\% respectively, as a function of the deposition temperature. The higher dilution series leads to a high Urbach energy (Fig. 3.10c), which could have been caused by a high concentration of Ge in the material or by microcrystals inserted in the
Deposition of a-SiGe:H at low temperatures and high deposition rate

Figure 3.10: Urbach energy (a) and midgap density of states (b) as a function of $T_s$ for three different $H_2$ dilutions.

amorphous phase. The Raman spectra (Fig. 3.2) and the concentration of Ge in the material measured by RBS (Fig. 3.5) were obtained to identify the cause of the exceptionally high Urbach energy values. The Ge concentration in the material for the higher dilution series is comparable with the other dilution series. On the other hand, the Raman spectra show crystalline structures that is not seen when the dilution is decreased (Fig. 3.2). This indicates that the microcrystals are the cause of the higher Urbach energy. For materials with a microcrystalline structure, the high defect density in the band gap contributes to the sub-band gap absorption. This excess absorption makes the Urbach energy higher, often over 100 meV [72].

If these microcrystals together with the presence of other phase, vary in a volume smaller than the volume under the illuminated area (10 mm$^2$ during the CPM measurement) the CPM measurement averages all the optical transitions within the illuminated volume. Thus, the high Urbach energy does not correspond with the conduction or valence band tail of the homogeneous alloy. A thinner layer of the material (to be applied in a solar cell) may show different properties than the more heterogeneous thick material, as the microcrystalline structure grows with the thickness of the film. For example, Xu et al. [73] observed for amorphous a-SiGe:H materials weak or no relation between material properties and solar cell performance. They observed that the decrease in the $\mu_T$ product with alloying is not reflected in the solar cell output, together with a lack of correlation between the defect density (that remains constant) and the fill factor (FF) (that decreases) with light soaking. The existence of a relation between the defect density and the FF is discussed in Chapter 4.
The Urbach energy and the midgap defect density measured by CPM are shown in Figures 3.10a and 3.10b, respectively. The value of both the parameters decreases when \( T_s \) is decreased, until the lower \( T_s \) limit of 170 °C. The Raman spectra of the materials that do not have clear crystalline peaks, correspond to a low Urbach energy and density of defects. They were deposited with \( f \leq 75\% \) at any of the \( T_s \) used. Higher dilution than 75\% is clearly detrimental for the material, corresponding to higher defect density and Urbach tails. In Section 3.4.2 these results will be discussed in detail.

Photo- and dark-conductivity

Figure 3.11 shows the photo- and dark-conductivity for the various dilution series as a function of \( T_s \). The photo-conductivity increases as the \( \text{H}_2 \) dilution decreases (the material becomes more amorphous). At the same time, the conductivity of the amorphous material exhibits a higher sensitivity to \( T_s \), more significant for materials made at low dilution conditions. This is manifested in the drop of photo- and dark-conductivity at 170 °C. At this temperature all the dilution series produced are amorphous (Fig. 3.2), but only the most diluted series do not show a pronounced drop at 170 °C. An explanation could be found in the extra atomic H that is formed in the plasma at high dilution conditions. The bombardment of the atomic H to the surface imparts enough energy to the growing precursor on the surface to compensate the energy deficiency by decreasing \( T_s \). At the same time, the atomic H eliminates excess of H from the \( a\)-SiGe:H film [74].

3.4.2 Discussion

The difference in the deposition rate between thin and thick samples is an issue normally overlooked but to which it is worthwhile to pay attention due to the plasma processes responsible for it. The growth model proposed by Winer does not explain properly this difference. According to this model (described in Section 3.2) the rf power (directly related with \( R_d \)) and \( T_s \) control the material properties, while the plasma only provides the reactive species. If neither the rf power nor the \( T_s \) is changed and the material properties change with the deposition time, other processes than thermal diffusion of surface H are needed.

In accordance with the model proposed by Hata et al. [33] (see Section 3.2) the surface defects are buried into the bulk as the film grows. If the temperature and the annealing time are adequate, the bulk defects are annealed. The annealing time depends on the kind of defects created at the surface. Moreover, when the dilution is changed, the conditions in the plasma change at the same time, specially through the amount of atomic H probing the surface. As a result, the local
bonding configurations at the surface are significantly influenced by the plasma conditions. Then, the surface defect density depends on the plasma conditions (H₂ dilution). For very high dilution conditions, f=85%, the amount of atomic H bombarding the growing surface promotes a change in phase (creation of crystalline structures). The amount of surface defect density will be higher than that for lower H₂ dilutions. If the deposition time is the same for materials created with different dilutions and long enough to cause observable differences, the material with higher dilutions will have more buried defects. More H is attached at the boundaries of the crystalline structure, resulting in the higher $R^*$ observed in Fig. 3.3d and consequently an increase in $R_d$, not expected with increasing dilution. Porous materials exhibit higher thickness than more compact materials (for the same deposition time), which is observed as a higher deposition rate. The material exhibits lower density, as defined through $n_0$ (Fig. 3.1d).

The results described in the previous section present the interesting characteristics of the materials made under different hydrogen dilutions of the plasma gasses and for different deposition temperatures. These are the principal parameters in the hydrogen density of states model (HDOS) proposed by Street [11], which makes it attractive to test the model for explaining the previous results.
According to this model the optimum conditions for growing $a$-Si:H material strongly depend on the hydrogen chemical potential ($\mu_H$) in the plasma. The principal dependence of $\mu_H$ lies on the concentration of H in the plasma (dilution) and in the temperature on the growing surface ($T_s$). The model has succeeded in explaining the deposition of fully amorphous $a$-SiGe:H [75]. In this section, the model for material at the edge of the microcrystalline growth at low deposition temperatures will be discussed.

The model considers that the bonding structure in the film is to a large extent controlled by $\mu_H$ in the plasma. The H chemically reacts with the bonds at and beneath the growing surface, altering the distribution of weak and broken bonds. At high enough temperatures the structure will reach an equilibrium state defined by the match of $\mu_H$ in the plasma and in the film. The process is mediated by the interchange of H between the plasma and the surface as well as by the diffusion of H on the surface, promoting changes in the bonding configuration as defined in the weak bond model [76] (Eq. 4.1). The equilibrium is reached locally by minimizing the free energy of small volumes constrained by the long-range disorder in the amorphous network. When the equilibrium is reached, the structure will present the lowest weak bond and dangling bond density, limited by the amorphous network.

Figures 3.12b, c and d show the HDOS distribution, $N_H(E)$, as a function of the H bonding energy relative to the vacuum level, $E_{HV}$. Hydrogen is present in Si-H and Ge-H bonds, below $\mu_H$, represented by two broad bands indicating the different environment around the H bond. The Ge-H bond is weaker than the Si-H bond, so the energy needed to make the H mobile is smaller. $E_M$ represents the minimum energy at which the H can diffuse freely, and is estimated to be 0.5 to 1 eV below $E_{HV}$. The energy difference between $E_M$ and $\mu_H$ corresponds to the activation energy for H diffusion (1.5 eV). Above $\mu_H$, the states are unoccupied and they include weak and stronger Si-Si bonds where the H can be inserted with different energies. The redistribution energy, $E_R$, is defined as the minimum energy at which the atoms can be redistributed in a time $t_s$ by interacting with H, before they are definitely included in the film structure. The position of $\mu_H$ in the plasma and $E_R$ are defined by

$$E_{HV} - \mu_H = kT \ln \left( \frac{N_{H0}}{N_{HP}} \right)$$  \hspace{1cm} (3.20)
$$E_M - E_R = kT \ln (\omega_0 t_s)$$  \hspace{1cm} (3.21)

where $N_{HP}$ is the H concentration in the plasma, $N_{H0}$ is the inverse of the H quantum volume (the effective density of states, $3 \times 10^{24}$ cm$^{-3}$), $t_s$ is the deposition time and $\omega_0 = 10^{13}$ s$^{-1}$. The limiting step in the growth process is the
Deposition of a-SiGe:H at low temperatures and high deposition rate 53

Figure 3.12: Hydrogen density of states distribution, $N_H(E)$, as a function of the H bonding energy correlated with a dilution of b) 65%, c) 75% and d) 85%, at $T_s=190\,^\circ C$. A) shows the temperature dependence of $\mu_H$ and $E_R$.

excitation of H to a mobile state. The most ordered structure is obtained when $E_R$ lies deep below the Si-H band (longer $t_s$). In other case the growth process will be kinetically limited by the H diffusion, broadening the weak bond distribution.

Figures 3.12b, c and d show the HDOS distribution which will be correlated with the dilution, $f$, of 65%, 75% and 85%, respectively, at $T_s=190\,^\circ C$. Figure 3.12a together with 3.12b, 3.12c or 3.12d show the temperature dependence of $\mu_H$ and $E_R$ for the different HDOS. The $T_{\text{min}}$ and $T_{\text{max}}$ define the limits at which a low temperature shifts $E_R$ inside the Si-H band and freezing the H in the Si-H bonds, unable to restructure. This case would produce a high density of weak bonds. The higher temperature limit is reached when $\mu_H$ moves deeper into the Si-H band. In this case all the Ge-H bonds would be unoccupied together with many of the Si-H bonds, growing a highly defective material.

The material diluted at $f=65\%$ presents a constant deposition rate, superior to the most diluted series. In these conditions the relaxation time during growth will be smaller than for series with $f=75\%$ and 85%. The redistribution energy is
shifted to higher energies, but it is still low enough to allow for structural relaxation. The high H concentration in the material together with a low microstructure parameter (Fig. 3.3d) suggests that the greatest part of the dangling bonds would be passivated and the weak bonds relaxed. The weak bond band would be narrow with a small overlap with the Ge-H bond band. At the same time, $\mu_H$ would lie above the Ge-H bond band ensuring that the Ge bonds are occupied with H (Fig. 3.12b). This is observed in the low Urbach energy and defect density (Fig. 3.10). Decreasing $T_s$ to 180°C moves $\mu_H$ closer to $E_M$, helping the redistribution of atomic H that needs lower energy to become mobile. The probability of dangling bond formation and the amount of weak bonds decreases. If $T_s$ is decreased to 170 °C the model predicts a further improvement in the structure through the shift of $\mu_H$ to $E_M$. But the diffusion of H to deeper states is critically reduced. This implies that the time available for redistribution processes decreases generating more weak bonds. This time the Urbach energy increases oppositely with $T_s$ ($E_R$ is shifted closer to the Si-H band).

At $f=75\%$ the amount of atomic H in the plasma increases, providing the plasma with more energetic bombardment over the surface. The first bonds to feel this extra energy are the weaker bonds (Si-H$_2$ $\sim$2.8 eV compared with Ge-H$\sim$3 eV and Si-H$\sim$3.4 eV). Figure 3.13 shows the ratio of Ge-H bonds in the material with respect to the weakest bonds (Si-H$_2$ and Ge-H). Together with Fig. 3.4, where the H content in different bond configurations is shown, one can observe how at these dilution conditions the Si-H$_2$ is preferentially removed from the material, leading to low microstructure fraction (Fig. 3.3d). On the other hand a larger extent of H on the subsurface may form small microcrystals, creating at the boundaries inhomogeneities and weak Si-H bonds. The weak bond band consequently will have a wider overlapping with the Ge-H band (Fig. 3.12c). The beneficial effect on $\mu_H$ due to the higher dilution partially compensates the increase in defect density. The material exhibits slightly more pronounced Urbach energy and very similar defect density. A decrease in $T_s$ decreases the deposition rate (shifting $E_R$ downward) creating less disorder and lower Urbach energy (Fig. 3.10). At the same time, the H desorbs less from the surface, growing a material with higher H content (Fig. 3.5). A lower temperature, $T_s=170$ °C, has the same effect as for the previous series.

When the dilution is increased to $f=85\%$, the formation of microcrystals is clearly observed by Raman spectroscopy (Fig. 3.2). The shift in the Si-H IR peak is correlated too with the presence of microcrystals [69]. The boundaries at the microcrystals and other microstructures will increase the density of weak bonds (broader weak bond band in Fig. 3.12d). The high amount of Si-H$_2$ observed could be located at these boundaries, passivating the bonds created by the
Deposition of a-SiGe:H at low temperatures and high deposition rate

Figure 3.13: Ratio of Ge-H bonds to Ge-H/Si-H as a function of Ts of a-SiGe:H deposited under three different H2 dilution ratios.

mismatch of the amorphous and crystal networks. The broad weak bond band extensively overlaps the Ge-H and may be even the Si-H band. This would generate more Ge and Si dangling bonds than in the previous cases, which could be interesting to verify by ESR. In summary, the Urbach energy sharply increases at the same time as the density of defects (Fig. 3.10). Decreasing Ts avoids the desorption of H from the surface (Ge-H bonds), increasing the final amount of H incorporated in the material specially in the bond configuration Ge-H (Fig. 3.13) or as voids or clusters (Fig. 3.3d). The deposition rate decreases with decreasing Ts, which shifts ER downwards. This implies that the time available for structural changes increases reducing the weak bonds band. This is observed in a reduction of the Urbach energy and the defect density with decreasing Ts (Fig. 3.10). Under Ts=170 °C, the material behaves the same as for the previous dilutions. At this temperature the depth at which the H can promote structural changes kinetically limits the system, and even a higher dilution than f=85% may be necessary to help the diffusion of H. In this case, the increase in dilution should be accompanied by a decrease in the deposition rate (by the higher dilution itself or through the rf power) to provide time for avoiding the insertion of higher radicals.
By modifying the thickness of the film and the $T_s$ we have observed a phase transition in the $a$-SiGe:H material. The influence of the hydrogen dilution and the substrate temperature on this process has been studied. As a result, the deposition parameters to obtain a material before the formation of microcrystals (protocrystalline material) were determined for different deposition conditions. The material which presents clear macrocrystalline structure (observed from Raman spectroscopy), exhibits an improvement in the medium range order with respect to amorphous material (Fig. 3.7). We speculate that the protocrystalline material exhibits similar improvement. This will ameliorate the stability of the material, fundamental for the stability of the solar cell (see Chapter 5).

3.5 Results in deposition of $a$-SiGe:H at high deposition rates

Several works have proposed the advantage of replacing SiH$_4$ with Si$_2$H$_6$ in order to provide the plasma with species dissociating at closer rate to GeH$_4$. Lundszein et al. [65] have obtained a considerable improvement in microstructure factor and Urbach tail in this way with very high H$_2$ dilution. They suggested that once in this stage, the deposition rate ($R_d$) could be easily increased through the rf power without adverse effect on the material properties. Sakata et al. [66] have observed for materials deposited with $a$-Si:H that when depositing at high deposition rates, the use of SiH$_4$ gas results in material with higher structural disorder than when Si$_2$H$_6$ is used as feed gas.

The work presented below have a goal of depositing $a$-SiGe:H material at high deposition rate and low temperatures. We present here a series of films made with Si$_2$H$_6$+GeH$_4$ where the band gap was kept constant at 1.52±0.02 eV (Tauc’s band gap). The H$_2$ dilution was varied from $f=40\%$ to 150$\%$ by changing the total flow of Si$_2$H$_6$+GeH$_4$ and keeping H$_2$ flow constant at 185 sccm (the maximum permitted by the system).

All the materials obtained with Si$_2$H$_6$ gas contain a higher concentration of hydrogen than for SiH$_4$ as source gas (for the same band gap). The Ge concentration is also appreciably higher. The trends obtained show a general increase in $R_d$ when the dilution is decreased, which comes along with a general deterioration of the photo- and dark-conductivity, Urbach energy and diffusion length.

Figure 3.14a, b, c and d show the H and Ge content, the photo- and dark-conductivity, the Urbach energy and the microstructure factor as a function of the deposition rate and for two different $T_s$ (180 °C and 200 °C).

It has been suggested that a high amount of Ge in the material inhibits the mi-
Deposition of a-SiGe:H at low temperatures and high deposition rate

Figure 3.14: Germanium and hydrogen content (a), photo- ($\sigma_p$) and dark- ($\sigma_d$) conductivity (b), Urbach energy (c) and microstructure factor (d) for two series of a-SiGe:H material deposited with Si$_2$H$_6$+GeH$_4$ at $T_s$ of 170 °C and 200 °C, as a function of the deposition rate. The variation in deposition rate is obtained by changing the Si$_2$H$_6$+GeH$_4$ flow.

crystallinity formation due to the introduction of extra structural strain in the network [77]. On the other hand, the interaction of H within the material is expected to produce structural relaxation, promoting the microcrystalline formation. But when H is introduced as higher hydrides, the effect is the opposite, retarding the microcrystalline formation.

As shown in Figures 3.14a, the amount of Ge and H is higher for the case of Si$_2$H$_6$ than in the case of SiH$_4$ (Fig. 3.5). At the same time, the microstructure factor exhibits a high presence of higher hydrides (Fig. 3.14d). Therefore the material growth with Si$_2$H$_6$ as source gas is amorphous, even at the highest dilution
(lowest \( R_d \)), confirmed by Raman spectroscopy measurements. An increase in \( T_s \) helps to decrease the presence of high hydrides but not enough to create nucleation. For very low dilution (high \( R_d \)), the higher \( T_s \) helps to grow a more compact material, improving the surface diffusion of radicals and the H elimination from the surface and the bulk [78].

For the same dilution as in the case of \( \text{SiH}_4+\text{GeH}_4 \), the material deposited with \( \text{Si}_2\text{H}_6+\text{GeH}_4 \) as source gasses (material with \( R_d=1.2 \) Å/s in Fig. 3.14), exhibits a 2 times higher deposition rate. The Urbach energy and the photo- and dark-conductivity show for both the cases very close values, and the defect density is one order of magnitude higher for the case of disilane compared to silane. But the most important drawback is the instability of this material to illumination. In Section 5.4 a degradation study of the protocrystalline material deposited with \( \text{SiH}_4+\text{GeH}_4 \) is compared with two amorphous materials deposited with \( \text{Si}_2\text{H}_6+\text{GeH}_4 \) at the same and two times higher \( R_d \) and \( T_s \) of 200 °C. These are the materials deposited with \( \text{Si}_2\text{H}_6+\text{GeH}_4 \) with the best properties.

In summary, the change in plasma chemistry when \( \text{SiH}_4 \) is replaced with \( \text{Si}_2\text{H}_6 \) as feed gas seems to be responsible for the significant increase in insertion of higher hydrides for the same dilution conditions. Under higher dilution conditions obtained at low \( \text{Si}_2\text{H}_6+\text{GeH}_4 \) flow, a possible depletion of both gasses could be contributing to the deposition of higher radicals, with detrimental influence of the Urbach energy and defect density. To improve the formation of microcrystalline structure, the concentration of higher hydrides must be reduced. This can be achieved through a higher H\(_2\) dilution in those cases where the depletion of \( \text{Si}_2\text{H}_6 \) and \( \text{GeH}_4 \) gasses is at the same time avoided. Other possibility is through strong ion bombardment resulting in a release the strain in the network by H elimination. The use of \( \text{Si}_2\text{H}_6 \) as a source gas towards higher deposition rates must go together with the growth of protocrystalline \( a-\text{SiGe:H} \) material which exhibits high stability against the Staebler-Wronski effect. As mentioned before, higher H\(_2\) flows (not reachable in this study) are necessary when \( \text{Si}_2\text{H}_6 \) is used as a source gas.

### 3.6 Conclusions

The influence of the deposition temperature and H\(_2\) dilution on the formation of microcrystalline phase in \( a-\text{SiGe:H} \) material has been studied in detail. The H\(_2\) dilution was varied along with the \( T_s \) to promote the formation of microcrystalline phase at low deposition temperature (\( T_s=180 \) °C), with the aim of depositing \( a-\text{SiGe:H} \) at the edge of this transition. The material obtained exhibits a reduction in the amount of Ge-Ge cluster to values lower than amorphous material, pro-
Table 3.1: Material properties of fully α-SiGe:H, amorphous before crystalline formation (protocrystalline), deposited with SiH4+GeH4 at low T_s, and α-SiGe:H deposited with Si2H6+GeH4.

<table>
<thead>
<tr>
<th>Material property</th>
<th>Amorphous SiH4+GeH4</th>
<th>Proto SiH4+GeH4</th>
<th>Amorphous Si2H6+GeH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_s (°C)</td>
<td>180</td>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td>Dilution (f)</td>
<td>65 %</td>
<td>75 %</td>
<td>75 %</td>
</tr>
<tr>
<td>Deposition rate (Å/s)</td>
<td>0.6</td>
<td>0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Tauc band gap (eV)</td>
<td>1.55</td>
<td>1.52</td>
<td>1.52</td>
</tr>
<tr>
<td>Activation energy (eV)</td>
<td>0.73</td>
<td>0.7</td>
<td>.74</td>
</tr>
<tr>
<td>H content (at.%</td>
<td>12.5</td>
<td>13.4</td>
<td>13.5</td>
</tr>
<tr>
<td>Ge content (at.%</td>
<td>40</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Microstructure R0</td>
<td>0.27</td>
<td>0.21</td>
<td>0.37</td>
</tr>
<tr>
<td>Urbach energy (meV)</td>
<td>50</td>
<td>65</td>
<td>70</td>
</tr>
<tr>
<td>CPM defect density (cm⁻³)</td>
<td>1 x 10¹⁶</td>
<td>2 x 10¹⁶</td>
<td>1 x 10¹⁶</td>
</tr>
<tr>
<td>Ambipolar diffusion length (nm)</td>
<td>95</td>
<td>94</td>
<td>96</td>
</tr>
<tr>
<td>Dark-conductivity (S/cm)</td>
<td>1 x 10⁻⁹</td>
<td>9.7 x 10⁻¹⁰</td>
<td>8.9 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Photo-conductivity (S/cm)</td>
<td>1 x 10⁻⁵</td>
<td>2.7 x 10⁻⁶</td>
<td>2.9 x 10⁻⁶</td>
</tr>
<tr>
<td>Photosensitivity S</td>
<td>1 x 10⁴</td>
<td>2.8 x 10³</td>
<td>3.3 x 10³</td>
</tr>
</tbody>
</table>

promoting the growth of more ordered material. We speculate that the improvement in the medium range order is generated by heterogeneous microstructures of Si and Ge atoms with more ordered amorphous structure than the α-SiGe:H network where they are immersed. Below a temperature of 180 °C a steep transition is observed where, independently of the dilution ratio, the material grows amorphous. The HDOS model was invoked to describe the results. At the same time, conditions for higher deposition rate were investigated. Replacing SiH4 with Si2H6 as a feed gas, the deposition rate was doubled. The different radical formation in the plasma degenerates in an amorphous material with higher H content. On the other hand, in high deposition rate conditions the deposition temperature must be increased to promote diffusion of radicals at the surface.

From this can be concluded that the deposition of protocrystalline α-SiGe:H is possible at low temperatures over a minimum T_s. At the same time, higher deposition rate conditions obtained with Si2H6 are incompatible with the growth of protocrystalline α-SiGe:H at low substrate temperature. Table 3.1 shows the summary of the characteristic parameters for three different materials: an fully amorphous α-SiGe:H material obtained at low T_s; an α-SiGe:H material deposited below the crystalline formation (protocrystalline material) and a fully amorphous
$a$-SiGe:H material deposited with $\text{Si}_2\text{H}_6+\text{GeH}_4$.

The stability of those materials against the Staebler-Wronski effect as well as their influence when implemented in a solar cell structure is studied in Chapter 5.