Maximization of hydrogen incorporation on a-Si:H using optical emission spectroscopy

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Abstract. The use of hydrogenated amorphous silicon, a-Si:H, for improving heterojunction solar cell efficiency and decreasing cost has found increasing interest in recent years. Hydrogen incorporation in thin films of amorphous silicon is crucial for obtaining semiconductor quality because it passivates Si dangling bonds in the structure. In the present work the plasma optical emission during film growth by DC magnetron sputtering in Ar-H plasma was used to maximize hydrogen incorporation the a-Si and the effects of hydrogenation were evaluated, as part of a systematic investigation of different vapor a-Si:H deposition processes, physical and chemical. The experiments were performed using the Magnetron Sputtering technique varying the DC power and Ar-H gas rates. The grown films were characterized by Raman scattering, FT-IR spectroscopy and AFM. The results show that maximizing the plasma emission from Si-H species enhances hydrogen incorporation in amorphous films. The results also show the possibility of automatically controlling plasma composition for optimum hydrogen incorporation through optical emission spectroscopy (OES).

1. Introduction
In recent decades energy generation through the use of solar power has been becoming a significant and competitive supplier to the world’s electricity market. The generation of energy from solar radiation is becoming a mature technology, but its high cost limits its widespread use. Efforts have been made to make the technology more accessible, especially in developing countries like Brazil, and also to get more efficient devices. One example is a heterostructure based on the junction of an amorphous silicon layer grown on a crystalline silicon with an intrinsic a-Si:H layer between the p-n layers [1]. This kind of solar cells has achieved efficiency above 20% [2,3].

The use of amorphous silicon (a-Si) as an emitter layer in photovoltaic heterojunctions solar cells reduces production costs because the p-n junction can be produced at lower temperatures compared to crystalline silicon (c-Si) [3].

In pure a-Si, there is a large concentration of defects, in the order of 10³¹ per cm³, called dangling bonds. One way to reduce these defects is to passivate them with hydrogen which decrease the defect density from about 10¹⁵cm⁻³ to 10¹⁵ - 10¹⁶cm⁻³. In a-Si:H this represents less than one dangling bond per million of silicon atoms [4-6]. The understanding of the incorporation and stability of hydrogen in a-Si:H has been the subject of extensive research [3-6].
In this work optical emission spectroscopy has been used to study the behavior of active plasma species during Si sputtering in a Ar + H₂ atmosphere, to better understand the corresponding hydrogen incorporation in the a-Si:H thin films, that happens in such a process.

2. Experiment
The experiments were performed in a Balzers Magnetron Sputtering reactor BAS 450M (figure 1) with a 150W DC power supply, under different levels of gas Ar/H₂ flow, ranging from 100% Ar and 20% Ar/H₂. The substrate temperature was constant, at 100°C, while the base pressure of the chamber and the working pressure were set at 9.0×10⁻⁷ mbar and approximately 10⁻⁴ mbar, respectively. The films were deposited over glass and over electronic grade p-type Silicon substrates (100).

![Figure 1. Scheme of the magnetron BAS chamber.](image)

2.1. Optical emission analysis
The plasma optical emission analysis was carried out using a EP200Mmd from Verity Instruments, with a diffraction grating for spectral range between 200 and 900nm. The plasma emission under sputtering power of 150, 300 and 450W was monitored.

The observation of optical emission was concentrated on getting relevant information on the process of hydrogenation of amorphous silicon films, by means of the following transitions: ArI 4p – 4s, Hα (n=3), Hβ (n=4) and SiH A₂Δ – X²Π.

2.2. Thin film analysis
The surface morphology of the sample was investigated by Atomic Force Microscopy (AFM) using a MultiMode microscope with a Nanoscope II controller. It was equipped with a SiN tip and operated in tapping mode.

Raman scattering experiments were performed in the back-scattering geometry configuration, using the 632.8 nm line of an He–Ne laser at room temperature.

In order to calculate the hydrogen percentage in the thin film we used the infrared spectroscopy technique, through which it is possible to determine the percentage of hydrogen bonded in the a-Si:H structure. The process consists of calculating the area between the stretching modes for SiHx (2000 – 2090 cm⁻¹) [7]:

\[ \text{Hydrogen percentage} = \frac{A_{2000-2090}}{A_{2000-2090} + A_{2000-2090}} \times 100 \]

where \(A_{2000-2090}\) is the area under the stretching modes for SiHx.
Where the absorption coefficient $\alpha$ is obtained using the intensity ratio for a given thickness $d$:

$$\alpha = \frac{1}{d} \ln \left( \frac{I_0}{I} \right)$$  \hspace{1cm} (2)$$

Then the sample density in the substrate is:

$$N_s = A_w \cdot S$$ \hspace{1cm} (3)$$

Where: $N_i$ is the film density, and $A_w$ is a proportionality constant. Using these expressions we can calculate the hydrogen percentage formula by means of [7]:

$$C_x = \frac{N_x}{N_s + N_x}$$ \hspace{1cm} (4)$$

Where $c_x$ is the percentage of the material in the film and $N_s$ is the substrate density.

The microstructure factor defined as the ratio between the intensity related to the stretching mode of monohydrits ($I_{2090}$) with respect to the sum of monohydrits and polyhydrits ($I_{2000} + I_{2090}$) is given by the equation 5 [8].

$$R_{2090} = \frac{I_{2090}}{I_{2000} + I_{2090}}$$ \hspace{1cm} (5)$$

The hydrogen incorporation at the film and the microstructure factor were performed using FTIR spectroscopy.

3. Experimental results

3.1. The light emission from the plasma

We carried out monitoring of the main peaks in order to infer about the process of hydrogenation of amorphous silicon films, namely the peaks ArI 4p – 4s, Ha (n=3), Hβ (n=4) and SiH A2Δ – Χ2Π. Figure 2 shows the evolution of these peaks with the variation of both, the Ar percentage and the power.

The effect of the power source in the behavior of the optical emission lines was observed for the case in which both gases vary. Figure 3 shows the changes in intensity for different gas percentages and power source used in the system. The relevant effect of power source on the intensity can be also observed.

For each power source the behavior of the curves are similar. Intensity variation is greater for the greater powers source as might be expected from the analysis of the graphs in figure 3. Only the behavior of the curve for SiH has a small difference from the others. It is noted that below 50% of Ar the variation of the Power source of 300W becomes greater than for a power of 450W and the variation the 150W curve is much lower compared to the others. These are important indicators for the production of films of a-Si:H in which the points of greatest emission intensity of SiH line lead to higher rates of H bonded to the structure of amorphous Si, which consequently passivate more dangling bonds [9].

Figure 3 shows the rate of variation of the optical emission intensity for the data presented in figure 2. The idea of these graphs is to analyze the “speed” with which the emission intensity varies for each percentage of gas and energy. It will be important to support the analysis of the power effect on the growth of the films.
Figure 2. Effect of power on the intensity of the Hα, Hβ, Ar e SiH peaks.

Figure 3. Rate of variation of the optical emission intensity with the %Ar.
The pattern of the SiH line emission, increasing the intensity reaching a maximum and decreasing changing the Ar-H ratio determined the range of gases to grow the films as shown in figure 4 for the power of 150W.

![Figure 4](image)

**Figure 4.** Evolution of the normalized optical emission lines with the Ar-H\textsubscript{2} concentration in the process for 150W.

### 3.2. Thin film properties

The following analysis are related to properties of the films grown at the highlighted region on figure 4. The surface morphology and the root-mean-square roughness (RMS) were obtained from AFM images. The AFM images showed a rough (film) and compact thin films. Figure 5 shows the topography images of the samples.

![Figure 5](image)

**Figure 5.** Topography image for: (a) 40%, (b) 50%, (c) 60% of H\textsubscript{2} content and the section analysis of a step to get the thickness.
The RMS of the sample with higher flow (60%) was approximately 0.5 nm and the thickness of the film was 220 nm, for a sample with 50% the RMS was 0.3 nm and the step was 73.5 nm, and for a sample with 40% 0.4 nm to RMS and 72 nm thickness. The increasing of the rugosity corresponds to the high flux of the H\textsubscript{2}. A possible meaning for it should be that when the hydrogen partial pressure increases, it induces crystallization as previously showed [10].

Figure 7 shows the Raman shift of the samples (a) and the de-convolution of the vibrational modes (b). The pattern showed is due the TA, LA, LO and TO1 vibrations mode related to a-Si phase.

![Figure 6. Roughness as a function of the flow for different powers.](image)

![Figure 7. Raman shift for all samples (a) and the de-convolution for the sample 2.](image)

The FTIR analysis is presented on figure 8 with the complete spectrum (a), the range related to the Si-H stretching modes (b) and the de-convolution of the samples grown at 150W (c). From the figure 8 (b) one can see the centre of the peaks varying from 2000 to 2100 cm\textsuperscript{-1}, and (c) the amplitude de-convoluted for each sample is changing. This gives rise to the microstructural factor (R\textsubscript{2090}) and is related to the polyhydrides (Si – H\textsubscript{x}) and monohydrides (Si – H) presented on the structure of the a-Si.

Figure 9 presents the hydrogen incorporation at the films for the different parameters. As we can see the pattern of the hydrogen at the film e similar to the pattern of the optical emission line related to the SiH emitting at the plasma. One can see a high level of incorporation of hydrogen 20 e 30%.
Figure 10 shows the microstructure factor at the studied range of atmosphere plasma composition. This graph means that highest $R_{2090}$, more polyhydrides (Si – $H_x$) is present at the structure of the film. Which is worst for good electrical properties in the film.

Figure 8. (a) Absorbance spectrum as a function of the wavenumber (b) Si-H / Si – $H_x$ stretching modes (c) de-convolution of the samples grown at 150W.

Figure 9. $H\%$ incorporated on the a-Si:H thin films as a function of the $H_2$ at the deposition atmosphere and the power.
3.3. Discussions

The pattern of the SiH line emission at the plasma was repeated in the pattern of incorporation of hydrogen in the film grown in the same range of the partial pressure of the gases. Comparing the figures 6, 9 and 10 one can see that at higher partial pressure of hydrogen more polyhydrates incorporate to the film, but the total hydrogen at the structure of the films gets a maximum for 50%. In other words, the excess of hydrogen that increase the deposition rate, damage the topology of the film and increase the microstructural factor. If the partial pressure of hydrogen is increased one can induce the crystallization of the film, as previously showed [10]. This can indicate some aspect related to the growth mechanism of the a-Si:H thin film. As showed by Abdesselem et al. [11], at low temperature the growth mechanism is governed by the incorporation of SiHx (x=0-1) coming from the plasma, but the ratio between mono-poly hydrides is very important to high performance. In this way the role of the excess of Hydrogen at the plasma is very important and the optical emission coming from the plasma helped to found it.

On the graph of incorporation of hydrogen in the film (figure 9), note that at the highest partial pressure of Hydrogen (60%), there is no difference at the amount incorporated for the extreme powers of 450 and 150. The power of 300W at 50% of the gases showed slight difference. Comparing with Figure 3, where one can see a higher decay rate for the powers of 300 and 450W, we can associate the more abrupt decrease in the light emission of species of interest (Si-H) with the reduction of incorporation of the same.

4. Conclusions

A sputtering process that allows high H content in the a-Si:H has been done. The study showed that monitoring of plasma species is effective to predict the pattern of hydrogenation of a-Si. It is also shown that maximum hydrogenation is mainly a function of the H content in the atmosphere and there is an optimum level of H dilution in the H-Ar plasma that corresponds to a maximum in the SiH species plasma emission. It is also shown that the H content corresponding to this optimum dilution, as well as the level of silicon hydrogenation, increases with sputtering power for low partial pressure of H but it does not change significantly for high partial pressure of Hydrogen. It is shown that the excess of hydrogen significantly affects the topography of the film and increases the microstructural factor. Finally it is shown that the effects of changing process variables on the hydrogenation can be
monitored by the optical emission from plasma, which makes this technique a potential tool to control the production of a-Si:H.

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