Nickel-induced crystallization of amorphous silicon

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Abstract. The nickel-induced crystallization of hydrogenated amorphous silicon (a-Si:H) is used to obtain large grained polycrystalline silicon thin films on glass substrates. a-Si:H is deposited by plasma enhanced chemical vapour deposition at 200 ºC, preparing intrinsic and slightly p-doped samples. Each sample was divided in several pieces, over which increasing Ni concentrations were sputtered. Two crystallization methods are compared, conventional furnace annealing (CFA) and rapid thermal annealing (RTA). The crystallization was followed by optical microscopy and scanning electron microscopy observations, X-ray diffraction, and reflectance measurements in the UV region. The large grain sizes obtained – larger than 100 µm for the samples crystallized by CFA – are very encouraging for the preparation of low-cost thin film polycrystalline silicon solar cells.

1. Introduction

After many years of research and development, the hydrogenated amorphous silicon (a-Si:H) technology acquired a degree of maturity that allows to deposit thin uniform films over large area glass substrates with a high velocity. However, problems with the stability and electrical quality of the material could not be overcome [1]. Recently, there has been a renewed interest in a-Si as a precursor to obtain polycrystalline silicon (poly-Si) for different applications like active-matrix liquid crystal displays, active-matrix organic light emitting diodes, and solar cells [2-5].

Among the different methods that allow a solid phase transformation from the amorphous to the polycrystalline state we have the conventional furnace annealing (CFA) and the rapid thermal annealing (RTA). CFA uses a conventional oven to heat the samples, and allows the crystallization of a-Si (non-hydrogenated, prepared by evaporation) at a temperature of 600 ºC in 48 h, providing a material with a grain size in the order of 1.5 µm [6]. RTA uses infrared radiation as a heating source, and has the advantage of the high heating speed (up to 60 ºC/s) that reduces the crystallization time. Besides, the radiation can be applied in pulses that heat the sample without heating the glass substrate (which is transparent to the infrared radiation). However, the grain size obtained in the crystallization of a-Si is also in the range of a few micrometers.

In an effort to reduce the crystallization temperature and crystallization time, and to increase the grain size, the effect of Nickel as an inductor of crystallization has been studied [2,3,7,8]. The addition of very small amounts of Ni (less than a monolayer) to the a-Si surface has a beneficial effect on the crystallization. Although there is an agreement about the formation of the nickel silicide NiSi2, which acts as a seed for the growth of crystalline silicon [9], the details of the crystallization mechanism are still under debate.
In this work, the Ni-induced crystallization of a-Si:H samples is studied by using the CFA and RTA methods. The results of both thermal treatments for a series of samples covered with different Ni concentrations are compared. A thermal process that induces a solid phase transformation from an amorphous to a polycrystalline material with the largest possible grain size is explored.

2. Experimental details

Samples were prepared on Schott AF-37 glass in a capacitively coupled Plasma Enhanced Chemical Vapor Deposition (PECVD) reactor. A relatively high frequency of 50 MHz and a power density of 120 mW/cm² were used, being the distance between electrodes of 1.1 cm. Intrinsic a-Si:H samples from pure silane (SiH₄), and slightly p-type samples adding some diborane (B₂H₆), were deposited without any hydrogen dilution. The substrate temperature was 200 ºC and the gas pressure was 600 µbar, leading to a deposition speed of 15-20 Å/sec. Nickel was deposited on top of the films by dc sputtering using a low power density of 95 mW/cm² and an Ar pressure of 70 mTorr. The Ni concentration was determined on test samples by atomic absorption spectroscopy [10], and varied between 8.7×10¹³ and 1.5×10¹³ atoms/cm², which means between 5 and 1 % of a monolayer.

Both CFA and RTA were performed at atmospheric pressure under nitrogen flow. CFA started with a dehydrogenation step at 400 ºC for 24 h, followed by an annealing at 550 ºC for different periods. The deposition of silicon by PECVD from SiH₄ gas leads to a-Si:H, a material with a hydrogen content in the range of 10%. The direct heating of this material to 550 ºC causes a violent hydrogen effusion that damages the samples. Therefore, a previous dehydrogenation step is needed. Some of the samples were dehydrogenated in the conventional furnace, and then crystallized by RTA. In this case, the samples were a) heated from room temperature to 350 ºC in 300 sec, b) heated from 350 to 630 ºC in 90 sec, c) kept at 630 ºC for 60 sec, and d) cooled from 630 to 350 ºC in 90 sec; repeating the sequence b) - c) - d) until full crystallization. Other samples were also dehydrogenated in the RTA furnace, applying a gradual heating from 350 to 550 ºC in 1800 sec between steps a) and b). The number of pulses required to fully crystallize the samples varied between 6 and 48 depending on the thickness of the samples and the Ni concentration.

Crystallization was controlled through optical microscopy, scanning electron microscopy, reflectance in the UV and X-ray diffraction.

3. Results and discussion

Figure 1 a) is a photograph, taken with an optical microscope in reflection mode, of a partially crystallized p-type 100 nm thick sample. The sample was covered with a Ni density of 4.4×10¹³ at/cm², which is less than 3% of a monolayer (1.61×10¹⁵ at/cm²). The crystallization was performed by CFA at 550 ºC for 24 h, after a dehydrogenation step as described in section 2.

A distribution of circular grains can be seen in figure 1, with an average diameter around 100 µm. In the lower-right corner it can be seen that the disk-shaped grains have collided, giving straight grain boundaries. Figure 1 b) is a detailed view of the previous one, taken with a higher magnification. A dense circular grain of ~ 150 µm – and still growing – can be appreciated. In the centre of the circle a dark spot can be seen, which is attributed to the NiSi₂ nucleus. It is known that the first stage of the crystallization process is the diffusion of Ni atoms to form a NiSi₂ precipitate, which should reach a critical size for the crystallization to proceed [9]. This NiSi₂ precipitates can be formed at as low as 350 ºC, in the initial stages of thermal annealing, and act as seeds for the growth of c-Si. In our case, the dehydrogenation step at 400 ºC for 24 h is enough to permit the Ni diffusion to form the silicide. NiSi₂ forms octahedral precipitates having eight {111} faces. The small lattice mismatch (0.4%) between NiSi₂(111) and Si(111) facilitates the formation of epitaxial c-Si on the {111} faces of the precipitates. In situ studies revealed that single-crystal Si needles grow in <111> directions from the NiSi₂ precipitates [9,11]. Only <110> oriented NiSi₂ precipitates, which have four {111} faces perpendicular to the a-Si surface, can lead to a long-range growth of crystallites. Depending on the thickness of the samples a mixture of vertical and lateral growth may occur, so it is important to study the crystallization of samples having different thicknesses.
Figure 1. a) Reflection optical microscope image of a p-type sample annealed at 550 ºC for 24 h by CFA, and b) detail of a region of the sample, showing a growing grain.

Figure 2 is a SEM image of a partially crystallized intrinsic layer (0.3 µm thick), focused on a grain boundary region. Inside the grains, some small pockets of amorphous material (etched away by a Secco solution) can still be appreciated. At the grain growing front, a network structure of branched crystallites can be seen. The width of the needlelike crystallites is about 100 nm. The primary and secondary arms’ directions of the needles have the regular angles of 70 or 110º (the so-called bi-directional needle network structure) [12]. This indicates that the crystal exhibits a preferential <110> orientation with respect to the film surface normal. The preferential orientation is confirmed by the X-rays diffraction spectrum shown in figure 3. From these data the relative integrated intensities 100:5 for the (111) and (220) peaks are obtained, which is a higher ratio than in previous reports [13]. The strong orientation of the grains is important for practical applications, since it promotes the uniformity of the material properties over the dimensions of the device.

Figure 2. SEM image of a partially crystallized intrinsic sample, where a grain growing front can be seen. The length of the bar is 1 µm.

Figure 3. X-ray diffraction patterns of the intrinsic sample (solid line) and of crystalline silicon powder (dashed line).

Figure 4 is a photograph, taken with an optical microscope in reflection mode, of the same film shown in figure 1, but now covered with a Ni density of 2.9×10¹³ at/cm². Both the dehydrogenation and the crystallization were performed by RTA, applying 18 heating pulses as described in section 2. The sample can be seen partially crystallized, with a mixture of some disk-shaped grains (~ 30 µm
diameter) and some small grains of irregular borders. The same result was obtained on samples that were dehydrogenated by CFA and then crystallized by RTA. When these samples were fully crystallized, after the application of ~36 heating pulses, a mixture of large and small grains was also observed. Large grains are ascribed to the Ni-induced crystallization, while small grains come from the spontaneous solid phase crystallization of a-Si at this elevated temperature of 630 ºC. Even when the sample reaches this temperature only for periods of 60 sec, it seems to be enough to promote the spontaneous crystallization of a-Si. Therefore, a lower peak temperature should be tried, which will be the subject of further research.

Figure 5 shows the UV-light reflectance spectra of a polished single crystalline silicon wafer (dashed line), of the sample of figure 1 after full crystallization by CFA (solid line), and of the sample of figure 4 after full crystallization by RTA (dotted line). The CFA sample shows a high degree of crystallinity, evidenced by the height of the peak at ~270 nm. The RTA sample, on the other hand, exhibits a lower crystallinity due to the defective phase present at the boundaries of the small grains. These results are in agreement with the optical microscope observations of figures 1 and 4.

4. Conclusion
The Ni-induced crystallization of a-Si by using the CFA and RTA methods has been studied. Although RTA has the great advantage of its high speed, the parameters still have to be adjusted to obtain a uniform distribution of grain sizes. CFA has proven to be a convenient method to crystallize a-Si, leading to disk-shaped grains with a diameter in excess of 100 µm. This is a very encouraging result towards the possible application of these films to semiconductor devices like solar cells.

Acknowledgments
This work was supported by ANPCyT (Projects 22-20267 and 22-25749), CONICET (Project PIP 5246) and UNL (Project CAI+D 28-158).

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