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ABSTRACT

We have studied the influence of substrate temperature and hydrogen dilution ratio on the properties of silicon thin films deposited on single-crystal silicon and glass substrates. We varied the initial substrate temperature from 200° to 400°C and the dilution ratio from 10 to 100. We also studied the effectiveness of the use of a seed layer to increase the crystallinity of the films. The films were analyzed by atomic force microscopy, X-ray diffraction, Raman spectroscopy, and transmission and scanning electron microscopy. We found that as the dilution ratio is increased, the films go from amorphous, to a mixture of amorphous and crystalline, to nanocrystalline. The effect of substrate temperature is to increase the amount of crystallinity in the film for a given dilution ratio. We found that the use of a seed layer has limited effects and is important only for low values of dilution ratio and substrate temperature, when the films have large amounts of the amorphous phase.

INTRODUCTION

Nanocrystalline silicon (nc-Si) has been receiving special attention lately because it is cheaper to produce than crystalline silicon, does not seem to present the degradation problems of amorphous silicon (α-Si) [1], and can be doped p- and n-type [2,3]. Furthermore, because of its bandgap, it can be used in tandem solar cells with α-Si [4]. Among the deposition methods, hot-wire chemical vapor deposition (HWCVD) [5] has the advantage of higher deposition rates when compared to other conventional techniques, such as plasma-enhanced CVD.

In general, nc-Si is highly anisotropic, and it is deposited as a mixture of amorphous and crystalline phases. Furthermore, depending on the deposition conditions, the crystalline phase varies from nanocrystalline to large columnar grains [6]. Extensive work is still necessary before this material can be produced with controlled properties and is able to produce solar cells that can compete with more traditional ones. In the present work, we investigate the effects of different substrate temperatures and hydrogen dilution ratio on the structural properties of the films. We also investigate if the use of a very thin seed layer [7], deposited with a high value of dilution ratio, and different substrates (Si and glass) affect the growth process.

EXPERIMENTAL DETAILS

The films were grown by HWCVD, using a double filament, with a current of 13A passing through each filament, resulting in a temperature around 1850°C. Films were grown at three ranges of substrate temperatures, T_{sub}: 200°-320°C, 300°-383°C, and 400°-435°C. The first temperature is the one at the time when the shutter was open, and the last temperature is the one at the end of deposition. This increase in temperature is caused by the proximity between substrates and filaments. As expected, this effect is more pronounced at lower substrate temperatures. The dilution ratio (R) between hydrogen (H_2) and silane (SiH_4) was controlled by varying the flux of SiH_4. The flux of H_2 was kept around 250 sccm, while the flux of SiH_4 was varied from 25 to 2.5 sccm, for R varying between 10 and 100, respectively. The deposition pressure was 150 mTorr. The films deposited on seed layers were grown with similar parameters, and the seed layers (≅ 12 nm thick) were deposited with R equal to 100 and the above substrate temperatures. At the end of the deposition of the seed layer, the value of R was adjusted for the subsequent growth of the film. The films were deposited on 1737 Corning glass and (100)-oriented crystalline Si substrates. The films were characterized by atomic force microscopy, in tapping mode, with a Digital Instruments DI 3100 scanning probe microscope; X-ray diffraction, with a Scintag X1 diffractometer; Raman spectroscopy, with a single-grating Spex 270M spectrometer; and transmission and scanning electron microscopy (TEM and SEM), using a Philips CM30 TEM and a JEOL 6320F field-emission SEM, respectively.

RESULTS AND DISCUSSION

There is a considerable thickness variation of the films, that is, the film structure changes as the film grows, such that there can be a different type of film at the top surface from that at the substrate. For this reason, it is important to consider film thickness when comparing the properties of two films. Unless mentioned in the text, when we compare films, we make sure that the thickness is the same or that it is not playing a role in that analysis.

Deposition rate

Deposition rates were calculated from thickness values measured by SEM. As expected, the deposition rates decreased with an increase in the value of R. An interesting observation is that there was no major influence of the substrate temperature on the deposition rate, as shown in Fig. 1. Because temperature influences the surface diffusion of adsorbed species, in general it is a critical parameter on the nucleation and growth of thin films. The results shown in Fig. 1 indicate that, in the temperature range used in this work, the availability of the source material is the main factor in the deposition rate of nc-Si films.

X-ray diffraction

All the films in this study had the cubic structure (JCPDS 27-1402). We found that, regardless of the growth temperature, the films had the same general behavior as the dilution ratio was varied. Films with very low R were amorphous. As R increased, a (220)-oriented phase would appear. As R continued to increase, the (220) orientation would decrease, and, for higher values of R, the film would become practically randomly oriented. This behavior, shown in Fig. 2, had been observed in a previous work for films grown at 400°C [8]. The value of R for which the film was amorphous was a function of the temperature (Fig. 2). Although films deposited with R equal to 14 and T_{sub} equal to 200° and 300°C did not show any diffraction

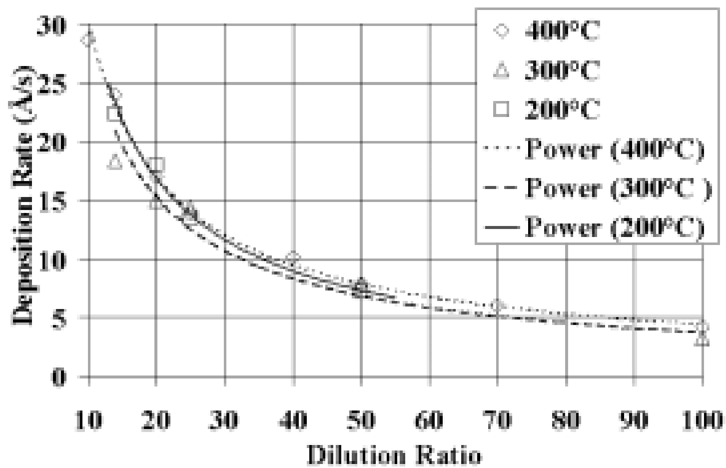

Figure 1. Deposition rate versus dilution ratio for Si films. The data were fitted to power functions, as denoted in the legends.

peak, an increase in T_{sub} to 400°C would produce films with a sharp (220) peak. A possible explanation is that at 400°C the adsorbed atoms have a higher surface mobility, and more atoms will be able to reach crystalline regions. Nevertheless, because at these low values of R, the nucleation of amorphous material still dominates the deposition process, the film will still be highly amorphous. For the 400°C films, a value of R equal to 10 would result in XRD patterns without any diffraction peak. For all the temperatures, films deposited with R equal to 20 already present a decrease in the (220) texture, and films deposited with R equal to 50 are already randomly oriented.

The effect of a seed layer was observed only in some situations when the film naturally would be amorphous (low R). For instance, for R equal to 14 and T_{sub} equal to 300°C, the seeded film had a small (220) peak, whereas the thicker unseeded film seemed to be completely

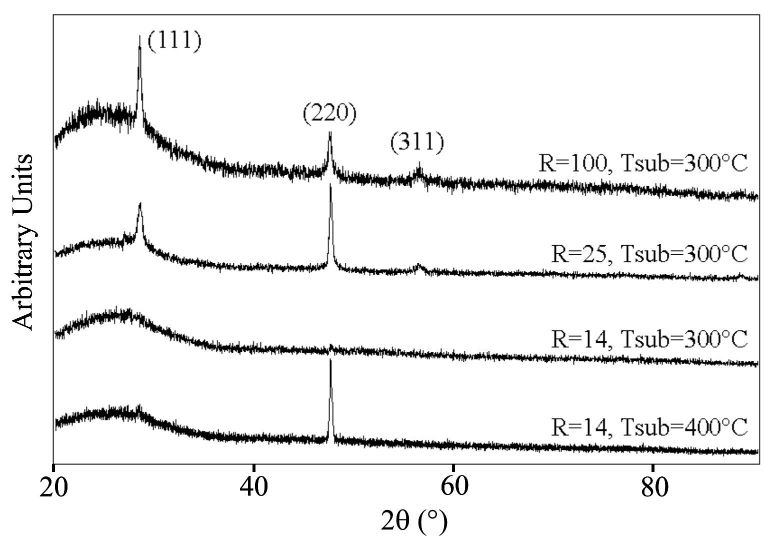

Figure 2. X-ray diffraction patterns for Si films grown at different conditions.

amorphous. For any other conditions, when a crystalline phase was already present, there were no significant differences between the results for unseeded and seeded films.

We also did not find any significant effect of substrate on the XRD measurements. This result is not so surprising, because the crystalline phase has (220) texture or is randomly oriented, whereas the Si substrate has a (100) orientation. This means that, if there is epitaxial growth, it is not extensive. Indeed, in spite of some limited epitaxial growth observed in TEM analysis, we have not noticed any substantial influence of the substrates on the properties of the films.

We observed a peak at 26.9° in samples grown at 400°C, for both seeded and unseeded films. Because it was present only in films grown with R larger than 14, it must be associated with the randomly oriented phase. Nevertheless, this peak was not observed for films deposited at 200° or 300°C, and its origin is at the moment unknown, due to the nature of XRD analysis, which in general requires few peaks for the identification of a crystalline structure.

Raman spectroscopy

We observed that the crystallinity in the films improves for higher substrate temperatures and dilution ratios. Nevertheless, as for XRD, an increase in R seems to be more effective than an increase in T_{sub}. Also, an increase in R affects the film more strongly at the lowest T_{sub}. As shown in Fig. 3, samples go from amorphous to highly crystalline as R and T_{sub} increases. It is important to mention that the samples deposited at 200°C, in Fig. 3, were about 25% thinner than the ones deposited at 400°C. This probably results in the latter samples seeming to be relatively more crystalline than they would if all samples had the same thickness. Comparison of the results using red and green lasers indicates that, in general, the crystallinity increases with sample thickness. Nevertheless, because the measurements were done on the films deposited on

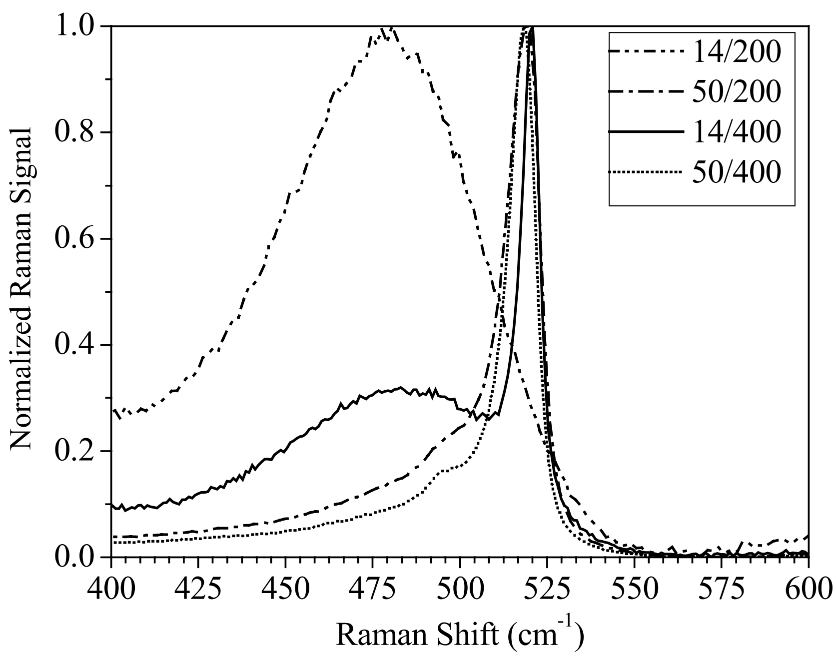

Figure 3. Raman spectra for Si films deposited at different conditions. In the legend, the number on the left is the dilution ratio and the one on the right is the substrate temperature.

Si, and because many of the films deposited at 200° and 300°C were not thick enough to prevent the red laser from reaching the substrate, we cannot confirm that this behavior occurs for all films analyzed in this work.

We have only analyzed seeded films deposited at 400°C. As in the XRD measurements, we only found evidence of the effectiveness of the use of a seed layer for films with large amounts of the amorphous phase, in which the seed layer increases the amount of crystalline phase in the film. No significant differences were found in Raman spectra of seeded and unseeded films for R equal or larger than 20.

Atomic force microscopy and transmission electron microscopy

The AFM images of the α-Si phase show structures that resemble grains. For this reason, it is very difficult to unmistakably assign grain-like structures to crystalline material in AFM images without the aid of other kinds of analysis.

From the AFM and TEM data, we observed that the structure and morphology of the samples vary with changes in R, independently of the substrate temperature. For low values of R, the film is completely amorphous. As R increases, some (220)-oriented grains start to grow at the interface with the substrate. These grains grow as columns while the film is being deposited, also growing laterally. They appear as elongated grains in AFM images. In this way, the amount of the crystalline phase increases as the film grows. For larger values of R, the density of these grains increases, increasing the amount of the crystalline phase. At this point, there is also the appearance of a randomly oriented phase, observed in the XRD analysis. For further increase in R, the film nucleates preferably as nc-Si, and the number of columnar grains decreases, until they almost disappear for large values of R. As the substrate temperature increases, the amount of crystalline material in the film increases, for the same values of R. This is more evident for lower values of R (up to 25), where the number of elongated grains increases with temperature, as observed in Fig. 4. For large values of R, when the density of elongated grains decreases, it is difficult to distinguish between the amorphous and the nanocrystalline phase in AFM images. It is important to notice that, for intermediate conditions of R and T_{sub}, three distinct phases are present in the films: α-Si, nc-Si, and the columnar grains, which are large crystals, extending over the whole thickness of the film.

In general, the morphology of the films does not change for seeded and unseeded films. As observed before, the seeded layer makes a difference, increasing the amount of the crystallinity, only for samples with large amounts of the amorphous phase. Finally, we did not notice any major effect of the substrate on the morphology of the films.

CONCLUSIONS

The dilution ratio is the major parameter for controlling the structural properties of silicon thin films. As the value of this parameter increases, the film goes from completely amorphous, to a mixture of amorphous and crystalline, to nanocrystalline. We have also seen a temperature dependence, where increasing the substrate temperature increases the crystallinity of the films. The use of a seed layer is only effective in improving the crystallinity of films grown with a high concentration of the amorphous phase.

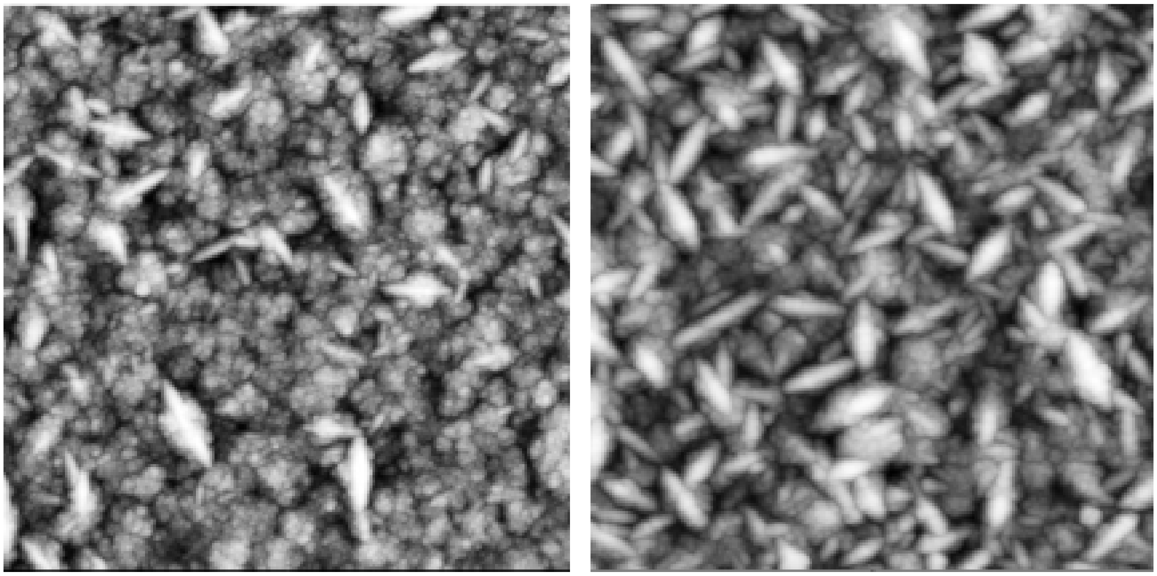

Figure 4. AFM images of Si film grown with R equal to 25 and substrate temperature equal to 200°C (left) and 400°C (right). The images have a 2μm x 2μm scale.

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