

Mechanisms of Growth of Nanocrystalline Silicon Deposited by Hot-Wire Chemical Vapor Deposition

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MECHANISMS OF GROWTH OF NANOCRYSTALLINE SILICON DEPOSITED BY HOT-WIRE CHEMICAL VAPOR DEPOSITION

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ABSTRACT

We have studied the growth of silicon thin films by hot-wire chemical vapor deposition under different conditions of filament temperature (T_f) and hydrogen dilution ratio (R). We found that these two parameters have a similar effect on the properties of the deposited films and show how they interact to control the growth dynamics. For relatively low values of T_f and/or R, the films are amorphous. An increase in the value of these parameters results in the appearance of a new phase, characterized by heavily faulted (220)-oriented columnar grains; for even higher values, a randomly oriented nanocrystalline phase appears. In general, there is more than one phase present in the film, and the microstructure varies as we go from the bottom to the top of the film. Although T_f and R have similar effects on the physical properties, they affect the deposition rate in a different way.

INTRODUCTION

Nanocrystalline silicon (nc-Si) is cheaper to produce than crystalline silicon (c-Si), and thinner layers can be used to produce solar cells. In addition, it is a stable material and does not show degradation with light soaking [1], as observed with amorphous silicon (a-Si). Moreover, due to the differences in their bandgaps, it can be used in tandem solar cells with a-Si [2]. For this reason, the research on nc-Si has been increasing over the last several years. A convenient method to grow nc-Si is by using hot-wire chemical vapor deposition (HWCVD) [3]. This technique is able to produce high-quality films and provides higher deposition rates than plasma-enhanced chemical vapor deposition (PECVD) because of the efficient decomposition of silane (SiH_4) into atomic species at the filament [4]. Nevertheless, at present, much work is still needed to correlate the several growth parameters with the quality of the produced films, and to create a unified model on the mechanisms of film growth.

This work complements previous research [5], in which we studied the effects of R on the structural properties of nc-Si films. Now we correlate the evolution of the microstructure, morphology, and crystalline properties of Si films with changes in the temperature of the filament used for film growth. We also study the interdependence of T_f with R, and explain how the film growth, and consequent film structure, is determined by these parameters.

EXPERIMENTAL PROCEDURE

The films were deposited using a double W filament, with the following values for the current in each filament: 12 A ($\approx 1780^\circ\text{C}$), 13 A ($\approx 1880^\circ\text{C}$), 14 A ($\approx 1980^\circ\text{C}$) and 15 A ($\approx 2080^\circ\text{C}$). For currents below 12 A there was no deposition of film on the substrate, probably a result of the formation of silicides on the filament surface at these relatively low temperatures, which prevented the decomposition of silane [6]. We also produced films with the following values of R: 14, 25, and 50. These values are the ratio between the H_2 and SiH_4 flow rates. In our experiment, we keep the H_2 flow rate at 252 sccm, and vary the flow of silane. The implication for this procedure is that, as we vary the silane flow rate, the relative number of silicon and hydrogen atoms produced at the filament changes. We used three kinds of substrates: glass, c-Si, and SnO_2 , for comparison purposes, and because certain analyses require a specific type of substrate.

The crystalline structure of the films was investigated using X-ray diffraction (XRD), in a Scintag X1 system, using the Bragg-Brentano configuration. The relative amounts of amorphous and crystalline phases were investigated using Raman spectroscopy, with a single-grating Spex 270M spectrometer, using both 532 (green) and 633 nm (red) lasers to obtain information from different depths of the material. We studied the microstructure of the films with transmission electron microscopy (TEM) in a Philips CM30 TEM. To study the surface topography, we used atomic force microscopy (AFM), with Si tips, in a Digital Instruments Dimension 3100 scanning probe microscope (SPM). Finally, to investigate the electrical properties of the films, we used conductive-AFM (C-AFM), also in a Dimension 3100 SPM, using conductive diamond tips.

RESULTS

We did not notice any major differences in the results of AFM and XRD analyses performed in films deposited on different substrates but with the same deposition parameters. For the other analyses, we used films deposited on specific substrates: Si substrate, for Raman and TEM, and conductive SnO_2 , for C-AFM.

Deposition Rate

High deposition rate is a feature that distinguishes HWCVD from other techniques, such as PECVD, in the growth of Si thin films. The reason for this is the efficient dissociation of the silane and hydrogen molecules on the

heated filament. For instance, it has been reported that, for filament temperatures above 1500°C, every silane molecule that reacts with the filament is completely dissociated [4,7]. Filament temperature and dilution ratio are probably the two most important parameters controlling the deposition rate. The influence of these parameters is shown in Fig. 1. It is clear that their effect on deposition rate is opposite, which is explained by the fact that an increase in T_f increases the amount of atomic silicon available for film growth, consequently increasing the deposition rate. On the contrary, an increase in the dilution ratio, obtained by decreasing the flow rate of silane, results in fewer Si atoms and, consequently, in a decrease of the deposition rate. As we will see below, an independent increase in both T_f and R increases the amount of the nanocrystalline phase in the film. This will impose a compromise on the best value for R, but not on the value for T_f . An upper limit on the value of T_f may come from the fact that the nc-Si films grown at higher temperatures (above 1930°C) have been observed to have a porous microstructure, and minimal photoresponse [8].

X-Ray Diffraction

The diffraction peaks for all the samples corresponded to the cubic structure of silicon (JCPDS card number 27-1402). The only exception was a peak located at 26.9°, observed for most samples. We have observed this peak in the XRD data presented by other authors [6,9] and, to our knowledge, it has not been positively identified yet. Because the results were the same for films deposited in different substrates, including the relative peak intensity, for simplicity we present the results for films deposited on glass, because this substrate does not produce peaks in the diffraction pattern.

The XRD analysis showed that there is a close relationship between filament temperature and dilution ratio. Furthermore, an increase in each of these parameters separately has the same effect on the films.

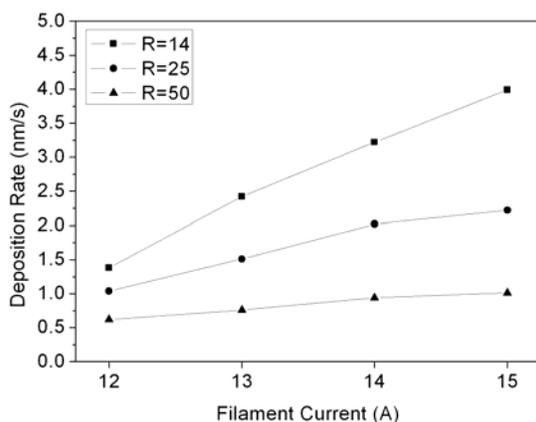


Fig. 1. Deposition rate as a function of filament current (directly related to T_f) and dilution ratio.

In Fig. 2a, we show the evolution of the crystallinity with T_f for a value of R equal to 14. A low value of T_f results in mostly amorphous films. As T_f increases, a new (220)-oriented phase appears. For higher values of T_f , a randomly oriented phase appears. This phase has been shown to be nanocrystalline [5]. The relative amount of each phase also varies as T_f is increased, with films deposited with higher filament temperatures being more nanocrystalline. For the conditions used in this work, most films were composed of more than one phase. The evolution of this process is also a function of R, as shown in Fig. 2. It is clear that the effect of varying T_f is strongly affected by the value of R. Similarly, the effect of varying R depends on the value of T_f , as can be observed if we compare curves from Figs. 2a and 2b with the same value of T_f . Because of this interrelationship, there is not a unique value of R or T_f separately that will guarantee that the film has a given crystalline structure.

Raman Spectroscopy

In Fig. 3a and 3b we show the Raman spectra of the same samples analyzed by XRD (Fig. 2), using a 633 nm laser beam. Raman provides a measure of the relative

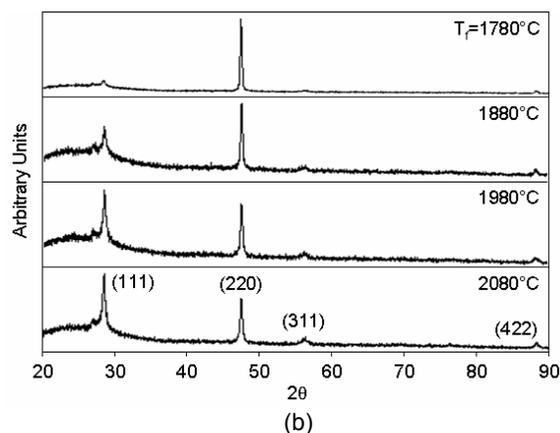
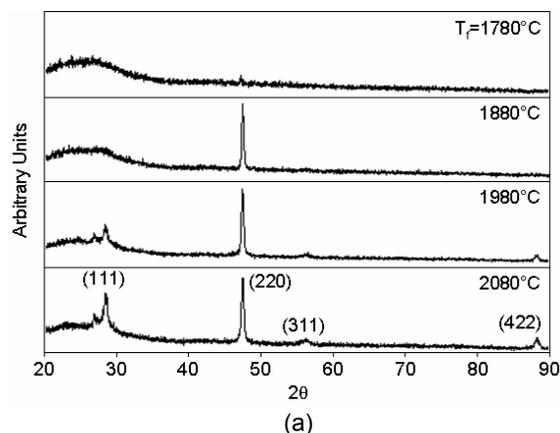


Fig. 2. X-ray diffraction patterns from silicon thin films deposited on glass and grown with different filament temperatures. (a) R=14; (b) R=25.

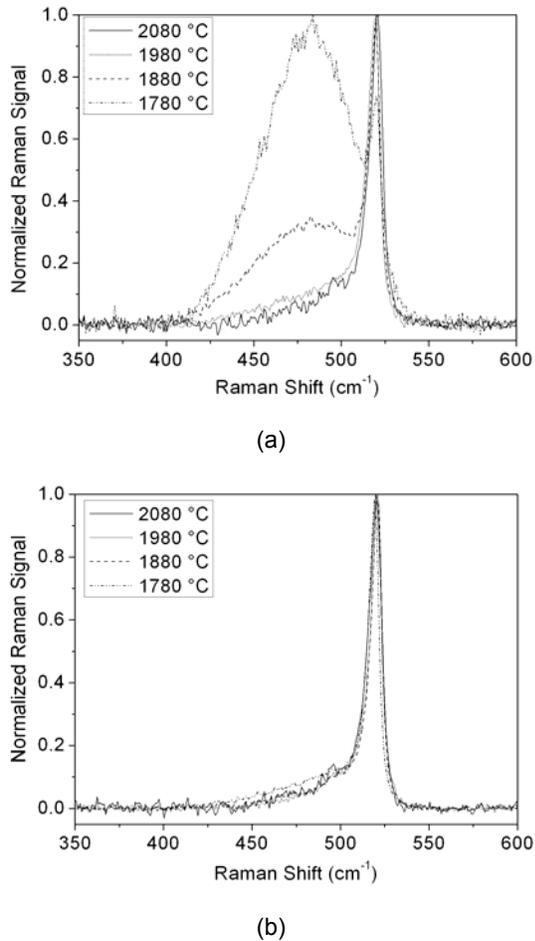


Fig. 3. Raman spectra of silicon thin films grown at different filament temperatures. (a) R=14; (b) R=25.

amounts of crystalline and amorphous phases in the films, but cannot distinguish between the different crystalline phases. Crystalline material shows a sharp Raman peak at 520 cm^{-1} , while amorphous material has a broader peak at lower wavenumber. The Raman data is consistent with the XRD results in that both increasing T_f and increasing R result in more crystalline films (Fig. 3). In Fig. 3b, we see that R is large enough to produce mostly crystalline films, even at the lowest filament temperature. Raman spectra acquired with a 532 nm laser beam show a similar trend as the data in Fig. 3, but the amorphous peaks are generally smaller in comparison to the crystalline peaks. Because the optical penetration depth in Si at 532 nm is smaller than at 633 nm, this suggests that the films are more crystalline near to the surface and more amorphous at the film/substrate interface.

Transmission Electron Microscopy

Four phases were identified in the TEM analysis: epitaxial Si, amorphous and nanocrystalline phases, and (220)-oriented columnar grains. The relative amounts of these phases depend on the values of T_f and R, and more than one phase is present in most films. Because of

sample preparation issues, we could not precisely follow the evolution of film microstructure with T_f and R. Nevertheless, the TEM results fit the Raman and XRD results. For T_f equal to 1880°C and R equal to 14, the film is composed of columnar grains, forming close to the interface with the substrate and growing all the way to the film surface, surrounded by an amorphous phase. These grains are heavily faulted, and electron diffraction showed that they are the (220) grains observed in XRD. For higher values of T_f and R, the amount of the amorphous phase decreases, and the films are mostly formed by columnar grains surrounded by nc-Si. In the conditions used in this work, even for the higher values of T_f and R, the columnar grains are still present. Nevertheless, in films grown previously, with R equal to 100 and T_f equal to 1880°C , we produced films with some epitaxial growth and nanocrystalline phase only [5]. Figure 4 shows the microstructure of a film with R equal to 14 and T_f equal to 2080°C . Few columnar grains are visible. Nevertheless, for these grains to be visible, the sample has to be positioned on the right diffraction condition; so not all the columnar grains are visible at once. An electron diffraction pattern of this film is seen in the inset of Fig. 4, where the presence of both phases is clear. The rings are characteristics of an area with small randomly oriented grains, whereas the spots are typical of the oriented material.

Atomic Force Microscopy

Due to the nature of the Si surface, even the amorphous material looks to be composed by small grains. The parameter that differentiates the amorphous phase from the nanocrystalline phase is the roughness, which is about ten times higher for the nanocrystalline phase. Also, the (220) columnar grains seemed to be formed by small grains at the surface, which makes it difficult to isolate the nanocrystalline and the (220) phases at the surface unambiguously. For R equal to 14 and T_f equal to 1780°C , the surface of the film is formed by elongated grains (the columnar grains observed in TEM), surrounded by a relatively smooth amorphous phase. As we increased R or T_f , the amorphous phase disappeared (in the Raman analysis, we observed that the material is more crystalline at the surface), the number of elongated grains increased, and a nanocrystalline structure appeared (grain size varying mostly from 30 to 80 nm). For further increase in R, the number of elongated grains decreased and the amount of the nanocrystalline phase increased. To a lesser extent, the same effect seemed to be present for further variation in T_f .

Conductive-Atomic Force Microscopy

The analysis confirmed that the crystalline phase is significantly more conductive than the amorphous phase. Nevertheless, it was not possible to make a correlation between the current and the amounts of the nanocrystalline and the (220)-oriented phases. The technique proved to be especially useful for detecting the (220) columnar grains from the amorphous phase. On the AFM images, it is difficult to distinguish the (220) grains

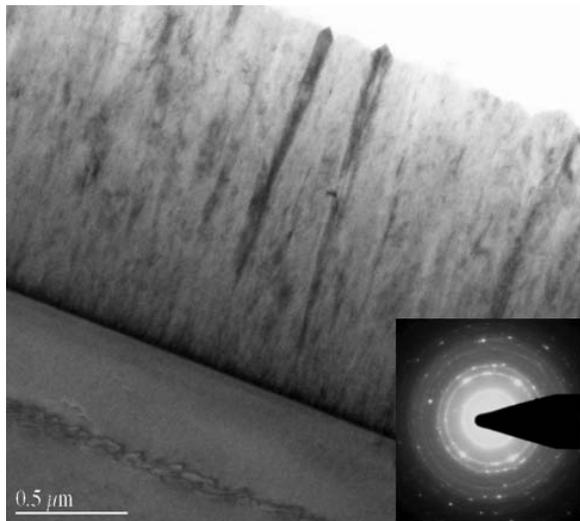


Fig. 4. Transmission electron microscopy of a Si film grown with $R=14$ and $T_f=2080^\circ\text{C}$. The inset shows an electron diffraction pattern of the same film.

from grain-like structures that we believe to be amorphous material. However, on the C-AFM image, the (220)-oriented grains produce a higher current and are easily distinguishable. Due to lack of space, these results will be presented in more detail in a future publication.

DISCUSSION

By increasing the hydrogen dilution ratio in the chamber, we increase the relative amount between atomic hydrogen and silicon. This results in more etching of weak bonds during film growth, resulting in more crystalline films. Similarly, an increase in the filament temperature also produces more atomic hydrogen, increasing the etching process. For this reason, a variation of T_f and R produces similar results, as we have observed. Our results also demonstrate that the growth process of nanocrystalline Si is very complex, and it is very difficult to produce the material with a single phase, unless we use high values of T_f and/or R . The growth of the columnar grains for relatively low concentration of H indicates that this phase grows faster than the nanocrystalline phase, but the bonds may be relatively weak. We believe that, for higher concentrations of atomic hydrogen, weak bonds in the (220) phase are etched away, resulting in the preferential growth of the nanocrystalline phase.

CONCLUSIONS

We have shown that the growth of nanocrystalline silicon films is complex, and, in general, results in a material with more than one phase. The filament temperature and the hydrogen dilution ratio have a similar effect on the properties of the films, and there is interdependence between these two parameters, which is related to the relative amounts of silicon and hydrogen atoms available during film growth. For lower values of T_f

and R , the film is mostly amorphous, with the development of a (220)-oriented columnar grain structure, and, subsequently, a nanocrystalline structure, as the values of these parameters are increased. On the contrary, although an increase in R decreases the deposition rate, an increase in T_f promotes a faster growth of the films.

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