Influence of film thickness on the crystallization of Ni-doped amorphous silicon samples

http://producao.usp.br/handle/BDPI/16616

Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo
Influence of film thickness on the crystallization of Ni-doped amorphous silicon samples

F. A. Ferri and A. R. Zanatta
Instituto de Física de São Carlos—USP, São Carlos 13560-250, São Paulo, Brazil

(Received 19 March 2008; accepted 5 May 2008; published online 15 July 2008)

This work reports on the crystallization of amorphous silicon (a-Si) films doped with 1 at. % of nickel. The films, with thicknesses ranging from 10 to 3000 nm, were deposited using the cosputtering method onto crystalline quartz substrates. In order to investigate the crystallization mechanism in detail, a series of undoped a-Si films prepared under the same deposition conditions were also studied. After deposition, all a-Si films were submitted to isochronal thermal annealing treatments up to 1000 °C and analyzed by Raman scattering spectroscopy. Based on the present experimental results, it is possible to state that (a) when compared to the undoped a-Si films, those containing 1 at. % of Ni crystallize at temperatures ~100 °C lower, and that (b) the film thickness influences the temperature of crystallization that, in principle, tends to be lower in films thinner than 1000 nm. The possible reasons associated to these experimental observations are presented and discussed in view of some experimental and thermodynamic aspects involved in the formation of ordered Si–Si bonds and in the development of Ni-silicide phases. © 2008 American Institute of Physics. [DOI: 10.1063/1.2955457]

I. INTRODUCTION

For a long time, amorphous silicon (a-Si) films and their alloys have attracted considerable attention because of technological applications, such as thin film transistors, solar cells, image sensors, and radiation detectors. In certain cases, however, microcrystalline materials are required and several experimental methods have been succeeded in producing them from a-Si films. Within these approaches the solid-phase crystallization is the preferred one due to its simplicity and convenience. The effective conversion of a-Si by solid-phase crystallization, however, usually involves temperatures that are incompatible with certain substrates and/or with large areas. This drawback can be partially circumvented by inserting metallic species into a-Si films or by putting them in contact with metallic surfaces in a process known as metal-induced crystallization (MIC). Actually, the MIC of a-Si was achieved with Au, Al, Cu, Ag, Pd, and Ni, where, for example, the temperature of crystallization could be as low as ~200 °C in contrast to the 800 °C required to crystallize plain a-Si films.

Despite its relative technical simplicity, the microscopic aspects involved in the MIC phenomenon depend very much on various experimental details (annealing conditions, preparation method, metal characteristics, etc.) and are still under debate. At present, it is possible to distinguish two main crystallization mechanisms: (1) those driven by the diffusion of atomic (Si and/or metal) species, typically found in a-Si/metal multilayered films and (2) those that depend on the presence of crystallization seeds (either metal atoms under a specific coordination or related to the presence of metal silicides) that take place in amorphous semiconductors doped or implanted with certain metallic species.

Specifically related to the influence of sample thickness on the MIC of a-Si, the literature presents different approaches: (a) multilayered structures, where only the thickness of the metal film is varied, and (b) multilayered structures where the thickness of both a-Si and metal films are varied and the crystallization is induced by laser radiation. According to these reports it is natural that the crystallization mechanism depends not only on chemical-energetic aspects but, to a large extent, on the energy and time required to promote the diffusion of Si and/or metal species. In this respect, the investigation of a-Si films with thicknesses in the range of ~10–300 nm and doped with a fixed amount of Ni, as in the present case, can provide original and valuable information related to the MIC of a-Si thin films. Moreover, the doping of a-Si films with metal provides a system free of uncontrollable-undesirable effects, such as the presence of contaminants, the surface barrier between the a-Si/metal layers, and the amount of (un)reacted metallic precursors.

II. EXPERIMENTAL

The present a-Si films were prepared by radio frequency (13.56 MHz) sputtering a silicon target in an atmosphere of pure argon. The films were deposited onto crystalline quartz substrates at 200 °C. The thicknesses of the films (10, 30, 100, 300, 1000, and 3000 nm) were determined by the sputtering rate and time and checked with the help of a quartz crystal monitor during deposition. Two series of a-Si films were prepared: one undoped and one doped with 1.0 at. % of Ni. Ni doping was achieved by partially covering the silicon samples with metal targets with small pieces of metallic nickel, and the film composition was confirmed through x-ray energy dispersive spectroscopy.

After deposition, the films were submitted to cumulative
isochronal (15 min each) thermal annealing treatments at 200, 300, 400, 500, 600, 700, 800, 900, and 1000 °C under a continuous flow of argon.

The films were investigated using Raman scattering spectroscopy under 632.8 nm photon excitation in a commercial setup (Renishaw RM 2000). Given the high sensitivity of amorphous semiconductors to laser radiation, great care was taken during the Raman measurements to avoid unintentional crystallization. In the present investigation, a laser power of \( \sim 200 \ \mu \text{W} \ \mu \text{m}^{-2} \) was adopted.

Since most of our analyses are based on the thicknesses of the films, in addition to the data provided by the quartz crystal monitor during deposition, they were also determined by profilometry and optical transmission measurements.

### III. RESULTS

Figure 1 shows the sample thickness as obtained by profilometry and optical transmission measurements as a function of the estimated thickness during deposition. The data correspond to (a) undoped and (b) Ni-doped \( \alpha \)-Si films. The dashed straight lines represent a one-to-one slope.

![FIG. 1. Sample thickness as obtained by profilometry and optical transmission measurements as a function of the thickness indicated by the quartz crystal monitor during deposition. The data correspond to (a) undoped and (b) Ni-doped \( \alpha \)-Si films. The dashed straight lines represent a one-to-one slope.](image)

The films were investigated using Raman scattering spectroscopy under 632.8 nm photon excitation in a commercial setup (Renishaw RM 2000). Given the high sensitivity of amorphous semiconductors to laser radiation, great care was taken during the Raman measurements to avoid unintentional crystallization. In the present investigation, a laser power of \( \sim 200 \ \mu \text{W} \ \mu \text{m}^{-2} \) was adopted.

![FIG. 2. Raman spectra of Si films (a) undoped and (b) doped with 1.0 at. % of Ni. The spectra correspond to films deposited onto quartz substrates and thermally annealed up to 700 °C. The thickness of each sample is indicated in the figure. The Raman signal at \(-470 \ \text{cm}^{-1} \) (\(-520 \ \text{cm}^{-1} \)) indicates the presence of distorted Si–Si bonds (Si crystallites). The spectra have been normalized and vertically shifted for comparison purposes. The contributions at approximately 298 and 405 \( \text{cm}^{-1} \) (enlarged for the 1000 nm thick film) denote the formation of nickel disilicide (NiSi\(_2\)) after thermal annealing.](image)
result, the first-order Raman scattering signal of crystallites are shown in Fig. 3. The crystalline characteristics of the films and have been measured and postdeposition treatments. Besides, the crystallization process is determined not only by the bulk material lower, but that the formation of NiSi2 occurs before the Si films. For clarity reasons, the figure only displays the crystalline fraction of films with thickness equal to 30, 100, and 3000 nm. The lines joining the data points are just guides to the eyes.

FIG. 3. Crystalline fraction (as obtained from the Gaussian fitting of the Raman spectra) as a function of the annealing temperature of (a) undoped and (b) Ni-doped a-Si films. For clarity reasons, the figure only displays the crystalline fraction of films with thickness equal to 30, 100, and 3000 nm. The lines joining the data points are just guides to the eyes.

IV. DISCUSSION

In a-Si, the conservation of momentum for the lattice vibration is relaxed by the structural randomness, with all of the lattice vibrational modes becoming Raman active. As a result, the first-order Raman scattering signal of a-Si films mirrors the spectrum of a vibrational density of states (DOS) weighted by transition matrix elements, and the spectral information is mainly concerned with the short-range order (SRO) or with the vibrational properties of the a-Si network. In practical terms, the Raman peak (or the vibrational DOS) of a-Si can be fitted with three Gaussian functions that are usually attributed to an amorphous contribution (centered at ~470 cm⁻¹), to the presence of Si crystallites (at ~520 cm⁻¹), and to the amorphous-crystalline interface modes (typically in the ~480–500 cm⁻¹ range). Actually, the ratio between the integrated areas of these contributions provides a good estimate of the crystalline characteristics of the films and have been considered in our analyses. The main results of this estimation are shown in Fig. 3.

The data in Fig. 3 are illustrative of all samples considered in this work and clearly indicate that both the crystalline fraction and the minimum temperature to start crystallization of the Si samples are influenced by the film thickness and by the presence of nickel.

Moreover, the crystalline fraction values displayed in Fig. 3 could be related to some (or to a combination) of the following factors: to the method we adopted to estimate the crystalline fraction, to the thermal annealing conditions (isochronal and cumulative up to 1000 °C), to small density variations due to the unavoidable presence of microvoids in amorphous films, and to intrinsic stress effects. Nevertheless, it is common sense that, in amorphous networks of a small coordination number, crystallites can only exist when immersed in a disordered tissue. The argument is very intuitive, and in addition to thermodynamic considerations, it is claimed that the disordered regions (which include the presence of microvoids) help in relaxing and absorbing the random orientation of the crystallites. As a consequence, it is suggested that most of the features present in Fig. 3 result from different degrees of disorder (see below) in association with the presence of Ni species. A detailed investigation concerning the influence of mechanical stress on the crystallization of similar Si films was considered in a previous report. According to this study, carried out on 2000 nm thick a-Si films, the presence of 1 and 10 at. % of Ni limits the crystalline fraction in the ~600–800 °C temperature range because of a compressive stress on the order of ~1 GPa. Thermal annealing at increasing temperatures promotes the development of Si- and Ni-based (essentially NiSi₂) microstructures that diffuse to the surface of the films. As a result, the stress present in the films is released and their crystalline fraction is slightly improved.

As far as the present authors are aware, there is no unique theoretical model that satisfactorily predicts (or explains) the crystallization of amorphous thin films. Part of the difficulty in describing these systems arises from their nonequilibrium state as well as from their high susceptibility to experimental details, such as preparation method and conditions, nature of the substrate materials, film-substrate adherence, film thickness and geometry, atomic composition, and postdeposition treatments. Besides, the crystallization process is determined not only by the bulk (volume) free energy, but also by the surface and/or interfacial free energies—not always possible to measure or estimate in thin films.

Hitherto, there is a relative consensus that the MIC of a-Si/Ni systems is driven by the diffusion of Si and/or Ni atoms that react in the form of some Ni-silicide (Ni₅Si₃) compound. According to this reasoning, the production of Ni silicide acts as nucleation sites that assist the subsequent crystallization of a-Si. Just to illustrate the preceding discussion, let us consider the activation energies Ea found by Her et al. in a-Si/Ni systems prepared by ion beam assisted deposition and investigated by transient reflectivity measurements and transmission electron microscopy: The activation energy involved in the crystallization of a 200 nm thick layer of pure a-Si (a-Si₂0 nm) is approximately 4.2 eV. Such a value is reduced to ~3.5 eV when the a-Si₂0 nm/ Ni₃0 nm structure is considered instead. Furthermore, in a-Si₂0 nm/Ni₃0 nm structures the activation energy for NiSi₂ phase formation stayed around 1.12 eV, while the activation energy to crystallize pure a-Si₂0 nm was determined to be ~2.19 eV. These figures clearly indicate that not only is the energy required to crystallize a smaller volume of material lower, but that the formation of NiSi₂ occurs before (or during) the crystallization of a-Si—in perfect agreement with
the idea that NiSi$_2$ acts as nucleation sites for the crystallization of Ni-containing $\alpha$-Si films. Actually, and based on the experimental data in Fig. 3, it is possible to establish the crystallization onset ($T_{\text{onset}}$) of the present Si samples, which are displayed in Fig. 4.

According to Fig. 4, the minimum temperature necessary to induce the crystallization of the undoped Si films is $\sim 775 \, ^\circ C$ for the thicker sample ($t = 3000 \, \text{nm}$) and stays in the 675–700 °C temperature range for the thinner ones ($10 \leq t \leq 1000 \, \text{nm}$). In the case of the Ni-doped samples, the thicker film crystallizes at $\sim 675 \, ^\circ C$, whereas the thinner ones ($10 \leq t \leq 1000 \, \text{nm}$) crystallize in the 530–560 °C temperature range. Based on these facts and taking into account our experimental resolution ($\pm 10 \, ^\circ C$), it is possible to distinguish two clear crystallization regimes:

(a) typical of the thicker films ($t = 3000 \, \text{nm}$), where the crystallization temperature tends to be $\sim 100 \, ^\circ C$ higher than that verified in (both undoped and Ni-doped) $\alpha$-Si with $t \leq 1000 \, \text{nm}$ and

(b) influenced by the presence of nickel in the sense that there is a systematic decrease in the crystallization temperature (on the order of $\sim 100 \, ^\circ C$) for films of comparable thickness when 1 at. % of Ni is present in the $\alpha$-Si matrix.

The formal aspect of every crystallization process predicts that during an amorphous-to-crystalline transition heat will be produced.$^{14,18}$ This heat flows into the surroundings of the reaction front and will raise the temperature. Contrary to bulk materials, however, thin films have a total surface energy that cannot be neglected in calculating the free energy of these different phases. Therefore, it is natural to expect that the temperature rise in the region of the reaction front depends on the thickness of the film. Once more, this picture is consistent with the fact that the thicker the film (higher amount of disordered Si atoms to be crystallized), the higher the thermal energy required to induce crystallization (Figs. 3 and 4). Moreover, the presence of nickel species (mainly in the form of NiSi$_2$, as indicated by our Raman analysis) acts, reducing the energy barrier that leads to Si crystallization.$^{3,4}$

The previous phenomenological discussion can be improved with some structural characteristics of the present Si samples. Experimentally, the SRO of $\alpha$-Si can be investigated by different spectroscopic techniques, such as x-ray or neutron diffraction experiments, extended x-ray absorption fine structure, and Raman scattering. Since the vibrational properties of an amorphous network are highly influenced by small variations in their SRO, the transverse-optical-(TO)-like Raman signal at $\sim 470 \, \text{cm}^{-1}$ is the most sensitive probe to variations in the dihedral bond angle between Si atoms.$^{14}$ Accordingly, the peak position ($\omega_0$), as well as the full width at half maximum height ($\Delta \omega$) of the TO-like mode, provides a good description of the structural (dis)order present in amorphous or partially crystallized Si films. Figure 5 shows the $\omega_0$ and $\Delta \omega$ values for undoped Si samples as deposited and annealed at 500 and 900 °C. Except for slightly higher $\Delta \omega$ values, it is important to mention that the Ni-doped Si films present similar results to those exhibited in Fig. 5.

As can be seen from Fig. 5(a) and within our experimental spectral resolution, the peak position due to the amorphous contribution (TO-like mode) does not appreciably change with the sample thickness. As the thermal annealing advances, however, its frequency is shifted from $\sim 460$ to $\sim 480 \, \text{cm}^{-1}$ as a clear indication that the Si films are becoming less disordered.$^{14,21}$ Such behavior is consistent with the variations that take place in $\Delta \omega$ [Fig. 5(b)], which is known to be proportional to changes in the dihedral Si–Si bond angle$^{14}$ and with the development of Si crystallites (Fig. 3) at

**FIG. 4.** Minimum temperature at which crystallization takes place or crystallization onset ($T_{\text{onset}}$) as a function of the thickness of Si films undoped and doped with 1 at. % of Ni. According to the experimental data, there are two main crystallization regimes: characteristic of the thicker films (thickness $\sim 3000 \, \text{nm}$) and that associated to the presence of Ni. The lines joining the data points are just guides for the eyes.

**FIG. 5.** (a) Raman peak position $\omega_0$ and (b) Raman linewidth $\Delta \omega$ corresponding to the TO-like vibrational mode of the present Si samples. The data are represented as a function of the sample thickness and after different annealing conditions (as indicated in the figure). The error associated to the experimental determination of $\omega_0$ and $\Delta \omega$ is almost the size of the symbols. AD stands for as-deposited, and the lines joining the data points are just guides for the eyes.
higher annealing temperatures. Furthermore, \( \Delta \omega \) is systematically larger for films thinner than \( \sim 300 \) nm, which can be attributed to their high susceptibility to interfacial effects and/or to crystal size effects.

An interesting outcome of Figs. 4 and 5 is the relative insensitivity of the crystallization onset \( T_{\text{onset}} \) to the structural (dis)order present in the Si films, as measured by Raman scattering spectroscopy. This is in contrast to a previous study on the crystallization of a-Ge films (10–1000 nm thickness range) in a-Ge/a-GeN multilayers,\(^{22}\) which shows that thinner (more disordered) a-Ge layers require higher temperatures to crystallize. According to the authors it happens because of an increase in the interfacial (amorphous-crystal) energy as the crystallization takes place. Honma \textit{et al.}\(^{22}\) also commented on the crystallization of a-Ge layers, of various thicknesses, when in contact with crystalline Pb films.\(^{23}\) In this case, interestingly, the thinner the a-Ge layer, the lower the crystallization temperature. In addition to thermodynamic considerations, Honma \textit{et al.}\(^{22}\) claimed that both the periodicity and the nature of the Ge heterointerfaces are fundamental in determining the crystallization temperature of the a-Ge layers.

It is clear from the preceding discussion that the fine details concerning the crystallization of amorphous thin films depend exclusively on the experimental conditions, particularly on the characteristics of each investigated system, on the presence of metallic species, as well as on the annealing conditions. The method employed to decide or to quantify the crystalline condition of the samples is also crucial and, ideally, should not interfere on the structural characteristics of the samples.

\section*{V. CONCLUDING REMARKS}

The influence of sample thickness on the crystallization of amorphous silicon (a-Si) thin films has been investigated. The effect of the annealing temperature and the presence of Ni species (in the low 1 at. %) have also been considered in detail. All samples were prepared by cosputtering, and the films, with thicknesses in the range of 10–3000 nm, were investigated mainly by Raman scattering spectroscopy. An accurate analysis of the experimental data allowed us to conclude that:

\begin{itemize}
  \item[(a)] when compared to undoped a-Si samples, the Ni-doped films (regardless of their thickness) crystallize at temperatures that are \( \sim 100 \) \(^{\circ} \text{C} \) lower;
  \item[(b)] the minimum temperature to crystallize the thicker (3000 nm) films, both undoped and Ni-doped, is \( \sim 100 \) \(^{\circ} \text{C} \) higher than that required to crystallize the thinner ones;
  \item[(c)] under the present experimental conditions (a-Si films doped with 1 at. \% of Ni, followed by cumulative isochronal thermal annealing up to 1000 \(^{\circ} \text{C} \)), there is no apparent connection between the structural (dis)order and the minimum temperature required to induce crystallization; and
  \item[(d)] our experimental results are consistent with the fact that NiSi\(_2\) mediates the development of Si crystallites either by acting as crystallization seeds or by reducing the energy barrier that leads to Si crystallization.
\end{itemize}

Because of its nonequilibrium nature, the crystallization mechanism of amorphous semiconductor thin films is not unique and depends very much on several experimental details (multilayered or doped systems, the presence of foreign atomic species, annealing conditions, characterization method, etc.). Notwithstanding these limitations, it is the author’s belief that the present contribution adds relevant and original information to further understand the MIC of a-Si thin films.

\section*{ACKNOWLEDGMENTS}

This work was financially supported by the Brazilian agencies FAPESP and CNPq. Dr. C. T. M. Ribeiro (IFSC-USP) is acknowledged for a critical reading of the manuscript.

\(^{14}\)K. A. Tanaka, E. Maruyama, T. Shimada, and H. Okamoto, \textit{Amorphous Silicon} (Wiley, Chichester, UK, 1999), and references therein.
\(^{15}\)C. Smit, R. van Swaaij, H. Donker, A. Petit, W. Kessels, and M. van de Sanden, \textit{J. Appl. Phys.} \textbf{94}, 3582 (2003);