STRUCTURE AND PROPERTIES OF POLYMORPHOUS SILICON THIN FILMS DEPOSITED BY RF DUSTY PLASMAS.

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Abstract

In this work, we present a detailed structural characterization by transmission electron microscopy (TEM) and Raman spectroscopy of polymorphous silicon (pm-Si:H) thin films deposited in a pulsed plasma enhanced chemical vapor deposition (PECVD) process using an argon- silane gas mixture in dust-forming conditions. Square- wave modulation (T_D) of the plasma and gas temperature (T_G) were varied to obtain films with different nanostructures, which are related to different growth stages of Si nanoparticles formed in the plasma gas phase. TEM analysis and electron diffraction have revealed the presence of Si crystallites in the as-deposited pm-Si:H film. The role of the film nanostructure in the crystallization process induced by laser heating is emphasized by Raman scattering analysis. Atomic force microscopy (AFM) and film density measurements, are performed and discussed versus film morphology.

1. Introduction

For several years, amorphous silicon films (a-Si:H) produced by PECVD have stimulated great interest in the photovoltaic and microelectronic industry. The use of dusty plasma conditions allows to enhance the deposition rate and leads to the growth of several kinds of medium-ordered silicon-based materials. Recently, silicon thin films grown in nanoparticles-containing plasmas have revealed new interesting opto-electronic properties, in particular better transport properties compared to standard a-Si:H [1,2]. This new type of silicon thin films, referred as polymorphous (pm-Si:H) or nanostructured silicon (ns-Si:H) [3] has been deposited using a wide range of plasma conditions close to the formation of dust particles. They are found to be constituted by a silicon amorphous matrix in which silicon ordered domains with nanometer sizes (2-3 nm) are embedded. In this contribution, structural analysis using transmission electron microscopy (TEM) and electron diffraction are reported. The presence of Si crystallites in the as-deposited films, as revealed by high resolution transmission electron microscopy (HRTEM), is found to make easier the crystallization process by laser annealing, as studied in-situ by Raman scattering at gradually increasing laser
intensities on the sample. The threshold energy allowing the laser-induced amorphous-to-crystalline transition of these films, the crystal size, the crystalline volume fraction and the surface temperature reached by the sample during laser irradiation, were determined carefully from the Raman analysis. Atomic force microscopy (AFM) and film density measurements, are performed and discussed versus film nanostructure. The results obtained are correlated with the deposition plasma properties.

2. Experimental procedures

Film preparation

The experimental configuration used in this work has been previously described in detail [4,5]. Silicon thin films were grown by PECVD using square-wave modulated RF (13.56 MHz) glow discharges of SiH₄-Ar. The square-wave modulation of the discharge is composed of two alternate periods: a plasma-on period (T_{ON}), in which the RF discharge is switched on and so Si film and particles grow up, and a plasma-off period (T_{OFF}), in which the discharge is turned off and particles can abandon the plasma bulk and so contribute to the growing film. The experimental conditions are the following: 30 sccm of Ar, 1.2 sccm of SiH₄, total pressure of 12 Pa, and RF power density of 60 mW/cm². The T_{ON} was varied from 0.1 to 5 s in order to produce films with different particle size and concentration [6]. In this paper, nanostructured films deposited with different T_{ON} (0.1 s < T_{ON} < 5 s) and deposition temperatures (T_{D}= 25, 100, 150 °C) have been considered.

Film characterization

High resolution and conventional transmission electron microscopy (HRTEM and TEM) images and electron diffraction patterns were obtained using a microscope Philips CM30 operating at 300kV.

Raman spectroscopy was used to investigate the film nanostructure and to study “in situ” the crystallization of the films. Raman spectra were measured with a laser confocal micro-Raman spectrometer DILOR XY. The excitation was done by means of the 488 nm blue line of an Ar⁺ laser. Then the irradiated area can be varied from 1 up to 100 μm² and the laser power density can be controlled from 0.35 up to 2000 kW/cm². In the beginning, the Raman measurements were performed at the lowest power in order to avoid any thermal or crystallization effects on the samples. Then, we increase gradually the laser power density in order to determine the crystallization threshold (Pₜ). From the accurate measurements of Raman shift and of peak broadness, crystal size, crystalline volume fraction and surface temperature were deduced. The surface roughness of the films in their as-deposited state was determined by AFM. The AFM measurements were performed on a Park Scientific Instrument microscope operating in air in the contact mode.
3. Results

TEM measurements

TEM observations were performed on as-deposited thin films obtained under different experimental conditions. From dark-field micrographs, a treatment software allowed us to quantify the number and the size of crystalline domains in the films. Figure 1 shows histograms of particles sizes. The majority of crystallites exhibits dimensions inferior to 2 nm, with decreasing populations for larger grain sizes. In histograms are also reported the crystalline density $d_c$, which increases when the gas temperature decreases, and even more when plasma duration increases. We have to notice here that $d_c$ is the ratio of the surface of the crystallites present on the micrograph to the total surface of the image.

Previous studies [6,7] have shown that the particle formation evolves as a function of the plasma duration $T_{on}$ and of gas temperature $T_0$. Three growth phases in the particle formation have been defined: the nucleation, the coagulation and the growth by molecular sticking on particle surface. The characteristic times for the onset of particle nucleation ($t_1$), of coagulation ($t_2$) and of molecular sticking ($t_3$) for the three temperatures $T_0$ are the following: a) at $T_0=25^\circ$C, $t_1=0.001-0.01$ s, $t_2=0.15$ s and $t_3=4$ s; at $T_0=100^\circ$C, $t_1=0.35$ s, $t_2=2$ s and $t_3=13$ s; while at $T_0=150^\circ$C, $t_1=1$ s, $t_2=10$ s and $t_3=20$ s.

In view of these results, the sample deposited at 150°C and $T_{on}=5$ s, as well as the sample grown at 100°C and $T_{on}=1$ s, could contain mainly crystallites of few nanometers coming from the first nucleation stage, as demonstrated from figure 1. It is important to remark that, for the sample deposited at 100°C and $T_{on}=1$ s, the plasma duration used is smaller than the $t_2$-2 s. Therefore, a higher density of nanocrystallites is expected for the corresponding film obtained during particle coagulation, and this is consistent with the higher crystalline density of the sample deposited at 100°C and $T_{on}=5$ s (figure 1c).

HRTEM of the as-deposited thin film deposited at $T_{on}=5$ s but at higher temperature $T_0 = 150^\circ$C (not shown here) showed a highly amorphous structure. On the other hand, HRTEM of the as-deposited thin film deposited at the same $T_{on}=5$ s and at lowest temperature $T_0=100^\circ$C confirmed the presence of small ordered domains embedded in an amorphous matrix. The nanocrystalline domains were closed to three or four crystalline planes of Si atoms, and corroborated an average crystallite size inferior to 2 nm as found from dark-field images. Direct measurements on these small ordered domains reveals that the interplanar distance is 3-3.3 Å.
Figure 2 shows the Raman spectra of a pm-Si:H and of an a-Si:H thin films after the onset of the laser-induced crystallization. The four Raman spectra for each sample were recorded on the same point of the sample: a) Raman spectrum recorded at the threshold laser power density for crystallization; b) after some time and on the same point, at very low laser power; c) at higher laser power; and d) again at low laser power. All these spectra were dissolved into two parts, one associated to the crystalline component and another to the amorphous one. Table 1 shows peak downshift $\Delta \omega$, FWHM and Lorentzian percentage of the crystalline-like Raman peak. Assuming that no crystallization is induced when the laser is changed from high to very low power, the calculated crystalline volume fraction $X_c$ can be used as a merit parameter during the fit of the corresponding Raman peaks. Table 1 shows that, indeed, $X_c$ is almost invariable at high laser power and afterward at low power.

The other parameters calculated from the Raman spectra of the figure 2 (crystal size $D$ and temperature $T$) are also shown in Table 1. Both downshift and FWHM of the crystalline Raman peak are much larger for the ns-Si:H than for the a-Si:H films. This reveals a smaller crystal size in the first crystallization stages of the ns-Si:H film. The origin of the difference between nanostructured and amorphous films can perhaps be found in the particular microstructure of the nanostructured ones, because the Si-ordered particles already present in the as-deposited ns-Si:H films may cause a heterogeneous nucleation process, in which they act as seeds for crystallization. The relative increase in the crystalline Raman peak when increasing laser power (figures 2a and 2c) is evident from the deconvolution of the Raman spectra. We can notice also a faster crystallization process in the pm-Si:H thin film in comparison with the standard a-Si:H. This result has been already attributed to the presence of crystalline entities of 1-2 nm in the matrix of the pm-Si:H thin films (as revealed by HRTEM), which can act as precursors in the amorphous-to-crystalline transition, while without such nanocrystallites (typical a-Si:H films), higher energies are needed to start nucleation [8, 9].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta \omega$ (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>%L</th>
<th>$X_c$</th>
<th>$D_c$ (nm)</th>
<th>$T$ (°C)</th>
<th>$\pm T$ (°C)</th>
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<tbody>
<tr>
<td>ns-Si:H(a)</td>
<td>25.1</td>
<td>25.5</td>
<td>0.65</td>
<td>20.4</td>
<td>705</td>
<td>34</td>
<td></td>
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<tr>
<td>ns-Si:H(b)</td>
<td>8.1</td>
<td>17.8</td>
<td>0.75</td>
<td>20.1</td>
<td>1.85</td>
<td></td>
<td></td>
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<tr>
<td>ns-Si:H(c)</td>
<td>25.3</td>
<td>26.9</td>
<td>0.37</td>
<td>34.7</td>
<td>888</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>ns-Si:H(d)</td>
<td>3.8</td>
<td>15.3</td>
<td>0.92</td>
<td>34.9</td>
<td>3.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-Si:H(a)</td>
<td>17.6</td>
<td>15.1</td>
<td>1</td>
<td>5.8</td>
<td>754</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>a-Si:H(b)</td>
<td>1.2</td>
<td>5.1</td>
<td>0.22</td>
<td>4.9</td>
<td>6.8</td>
<td></td>
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</tr>
<tr>
<td>a-Si:H(c)</td>
<td>17.2</td>
<td>15.1</td>
<td>0.73</td>
<td>26.6</td>
<td>777</td>
<td>85</td>
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</tr>
<tr>
<td>a-Si:H(d)</td>
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<td>4.4</td>
<td>0.81</td>
<td>24.2</td>
<td>8.5</td>
<td></td>
<td></td>
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</table>

Table 1. Fit and calculated parameters obtained from the Raman spectra of figure 2.
a matter of fact, the sample in figure 3a that crystallizes more easily (film grown at 25°C and T_on=5s in molecular sticking growth phase) could contain a high density of crystalline domains in view of TEM results in section A and of previous studies [6,7].

In figure 3, the evolution of threshold crystallization laser power determined by Raman spectroscopy (P_c) is compared to the density and the roughness of pm-Si:H samples deposited at different gas temperature using the same plasma-on period T_on=5s. As a comparison, the value for the standard a-Si:H is also included (deposited at 250°C). It was not possible to measure the roughness of the sample deposited at room temperature due to the dusty character of this film. Figure 3a shows that P_c remains low up to 100°C and then strongly increases for T_G=150°C. The big difference in crystalline density found between the samples deposited at 150°C and 100°C (figures 2a and 2c) could explain the huge drop in the crystallization threshold as observed in figure 3a, since precursors for crystallization are less numerous at 150°C and this fact can increase the energy needed to start crystallization.

However, other reasons have been emphasized to explain this faster crystallization process. Other authors have shown that changes in film porosity and in surface roughness can also influence the crystallization kinetics [10]. For example, the roughness can induce a photon “trapping” during the Raman analysis that can increase surface heating and facilitate the crystallization process. Deposition temperature is also known to affect the film structure. Indeed, density and surface roughness evolve as a function of temperature (figures 3b and 3c), and they could also affect the film crystallization to some extent. In particular, the mobility of the species deposited on the film surface during the plasma deposition process is strongly affected by temperature. The increase in temperature enhances the structural rearrangement on the surface and this is found to improve the film microstructure. Denser films and with less surface roughness are then obtained at increasing deposition temperature. This is consistent with the results reported in figures 3b and 3c. In addition, it is important to stress that the powder formation in the plasma gas-phase, which is temperature triggered, can also modify film density and surface roughness. However, we can notice that the film density of the sample deposited at 150°C and 5s is found to be similar to that of the a-Si:H sample as shown in figure 3b, while P_c is vastly different (figure 3a). This result proves that even if the increase in temperature improves the film density, there is not a clear correlation between the crystallization process and the film density.

4. Conclusion

In the present study, TEM measurements have put in evidence the presence of crystalline domains embedded in amorphous matrix and have shown that the crystalline density increases when gas temperature T_G decreases and T_on increases. These analyses have demonstrated the correlation
between the Si crystallites embedded in the films and the nanoparticles formed in the plasma gas-phase during film deposition. The structural characterization by Raman spectroscopy has shown that the presence of Si-ordered clusters in the as-deposited ns-Si:H films facilitates the laser induced crystallization during the Raman analysis. The role of surface roughness and film density in the film crystallization has also been studied. However, results have shown that film density has not a dominant effect in the laser-induced film crystallization process.

References