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a-Si:H crystallization from isothermal annealing and its dependence on the substrate used

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ABSTRACT

We present hydrogenated amorphous silicon (a-Si:H) films which were deposited on two different substrates (glass and mono-crystalline silicon) after an isothermal annealing treatment at 250 °C for up to 14 h. The annealed amorphous films were analyzed using atomic force microscopy, Raman and FTIR spectroscopy. Films deposited on glass substrate experienced an amorphous–crystalline phase transition after annealing because of the metal-induced crystallization effect, reaching approximately 70% conversion after 14 h of annealing. An absorption frequency of the TO-phonon mode that varies systematically with the substoichiometry of the silicon oxide in the 1046–1170 cm^{-1} region was observed, revealing the reactivity of the film with the annealing time. For similar annealing time, films deposited on mono-crystalline silicon substrate remained mainly amorphous with minimal Si-crystalline formation. Therefore, the crystalline formations and the shape of the films surfaces depends on the annealing time as well as on the substrate employed during the deposition process of the a-Si:H film.
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1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) is a material used in the electronic industry and in solar cells manufacturing technology as top contact layer in hydrogenated amorphous silicon (a-Si:H) [1,2]. However, the tendency towards cost reduction in the photovoltaic industry has led to the development of the so-called thin film silicon technology. Among the different possible morphologies, a material that presents very promising features is nanocrystalline silicon (nc-Si:H), which consists in an aggregate of crystallites with sizes in the order of few tens of nanometers embedded in an amorphous matrix [3]. One of the most commonly used techniques to prepare μc-Si:H films has been plasma enhanced chemical vapor deposition (PECVD) [4]. Nevertheless, metal-induced crystallization (MIC) effect has also been used to crystallize a-Si:H films at relatively low temperature [5]. It is known that the solid phase crystallization (SPC) temperature of a-Si:H can be lowered adding metals such as aluminum, nickel or palladium [6]. When these metals are used, crystalline silicon grains formation of micrometric size has been observed with considerable grain growth. In these grains the internal structure changes from the amorphous to crystalline structure resulting in a metal-induced phase transition. This transformation has been investigated using aluminum among other metals [7–10]. In this work we have studied the effect of the substrate used to grow the films, particularly glass or c-Si, on the morphological and vibrational properties of a-Si:H films processed by MIC.

2. Film growth and characterization

The a-Si:H films were grown using conventional radio frequency PECVD at 13.56 MHz in an AMP 3300 PECVD system, on glass and mono-crystalline silicon substrates, at 270 °C. The source gases used are SiH_4 electronic grade and PH_3 1% diluted in H_2. All samples were cleaned by standard techniques previous to the deposition. The glasses were introduced in the system when the pressure in the chamber was pumped down to a base pressure of 5×10^2 Pa. The $R_P = PH_3/SiH_4$ flow ratio was maintained constant at the pressure of 6×10^4 Pa and 60 sccm total flow. The power density was 45 mW/cm^2. Later the a-Si:H films were subjected to MIC process by aluminum evaporation on the amorphous surface and then applying an isothermal heating during few hours. After annealing, the aluminum was removed from the samples employing a chemical solution. Growth and preparation of the samples can be found in detail elsewhere [8]. Atomic force microscopy (AFM) was used to observe superficial morphology of the crystallized sam-

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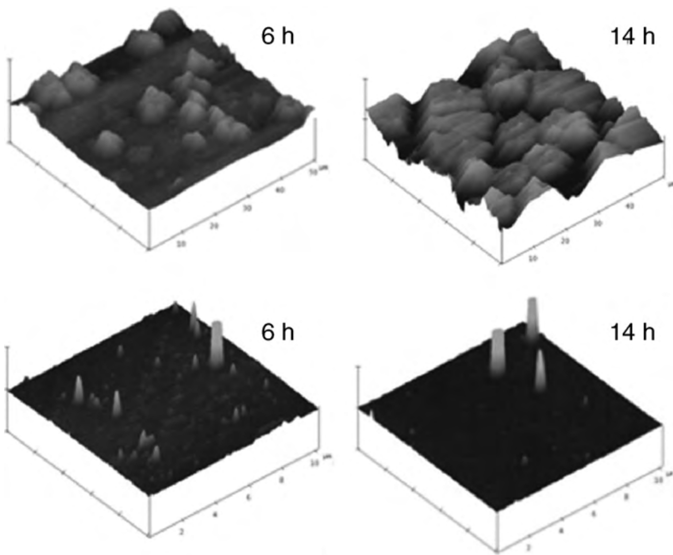

Fig. 1. Atomic force microscopy images of a-Si:H films deposited on glass substrates (upper), and mono-crystalline Si substrates (lower). The films were isothermally annealed with Al on the surface at 250 °C during the time labeled. The Al layer was removed after annealing. The images were taken on a 50 μm × 50 μm area for samples deposited on glass substrates, and 10 μm × 10 μm area for samples deposited on mono-crystalline silicon.

ples after annealing and after the aluminum was removed. Raman scattering spectra were obtained using a triple spectrometer with micro-sampling mode and a CCD detection system. Infrared absorption measurements were performed by the incidence of infrared radiation on the surface of the annealed samples using a Fourier Transform Infrared (FTIR) spectrometer Bruker Vertex 70, with especular reflectance sampling mode.

3. Results and discussion

To analyze the effect of the annealing process on the surface morphology of the samples atomic force measurements were realized. Important differences among the layers deposited on different substrates and by the annealing process were observed. For case of the a-Si:H layers deposited on glass substrates the surface morphology after annealing (from 0 to 14 h at 250 °C) can be observed in Fig. 1 (top). The 3-dimensional images ranges an area of 50 μm × 50 μm of the samples. In this case the grain formation is observed and the effect of the annealing process on the surface morphology is therefore observed by the formation of micrometric size grains, which increase with the annealing time [9]. This state of silicon is known as microcrystalline silicon (μc-Si:H). For the layers deposited on mono-crystalline silicon substrates (Fig. 1 bottom) the surface is uniform with columnar growth and also not suffers changes with the annealing process. The 3-dimensional images ranges an area of 10 μm × 10 μm.

Due to the dependency of the surface morphology of the layers with the type of used substrate and also with annealing time, it was necessary to investigate the crystalline nature or amorphous nature of these layers. Vibrational techniques as FTIR and Raman spectroscopies were used to analyze the mentioned properties. In the first case (glass substrate films) the spectra is dominated by a band associated to the Si–Si vibration from μc-Si:H which shift from 490 to 527 cm^{-1} with the annealing time, as depicted in Fig. 2. This shift represents a change from low microcrystallized state to a high-crystallized state. It is important to point out that on the analyzed area the FTIR spectra contains the absorption of both μc-Si:H and a-Si:H phases, although the amorphous absorption seems to have a negligible contribution. In these films the MIC process starts

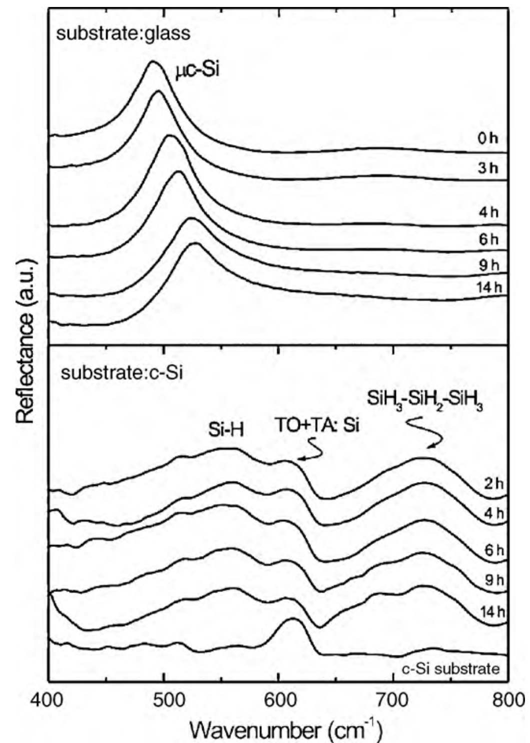

Fig. 2. FTIR spectra of a-Si:H films deposited over (upper) glass and (lower) on mono-crystalline silicon substrates.

with the local formation of Si nuclei during the annealing process, increasing in diameter with the annealing time at the given temperature of 250 °C. In this process Si nuclei grows into the Al layer, forming μc-Si and Al grains. During the annealing process the Al grains rearrange themselves, which leads an extensive intermixing of these Al and μc-Si grains. However, Si diffusion in Al is quite rapid at temperatures above 200 °C [5]. Thus, the Si can diffuse into the Al grain and form solid Si nuclei. These nuclei can grow by continuous diffusion of Si through the Al. Hence, Al acts as a solid phase medium for the nucleation and μc-Si:H growth. For the layers deposited on mono-crystalline silicon substrates, the FTIR spectra suggest that the film is mainly amorphous due to the presence of two broad bands associated to the Si–H and SiH_3–SiH_2–SiH_3 vibrations at 560 and 720 cm^{-1}, respectively [11], although a band at 612 cm^{-1} is observed too which is associated to the transversal optical plus transversal acoustic TO + TA vibrational modes of Si–Si bond in c-Si [12]. The mono-crystalline silicon substrate spectrum confirms the formation of crystalline Si regions immersed in the amorphous matrix. The strength of the Si–Si bond at 612 cm^{-1} (c-Si) remains unaltered with annealing time and the main features of the rest of the spectra are similar. This last suggest a stable and low reactive film with no evidence of oxidation in comparison to the glass substrates films where the oxidation increases with annealing time.

The crystallization fraction (X_c) for samples deposited on glass substrate can be observed in Fig. 3, where the Si–Si vibration mode of the microcrystalline phase in the FTIR spectra (450–550 cm^{-1}) was identified. The frequency shift is associated to the crystallized fraction determined in reference [9], using the Avrami equation

$$X_c(t) = 1 - \exp(-kt^n)$$

where $X_c(t)$ is the crystallized fraction at time t, k is a kinetic parameter (or rate constant) and n is the Avrami exponent [13,14]. The Avrami equation provides a reasonably approximation for the growth behavior during the amorphous–crystalline phase transfor-

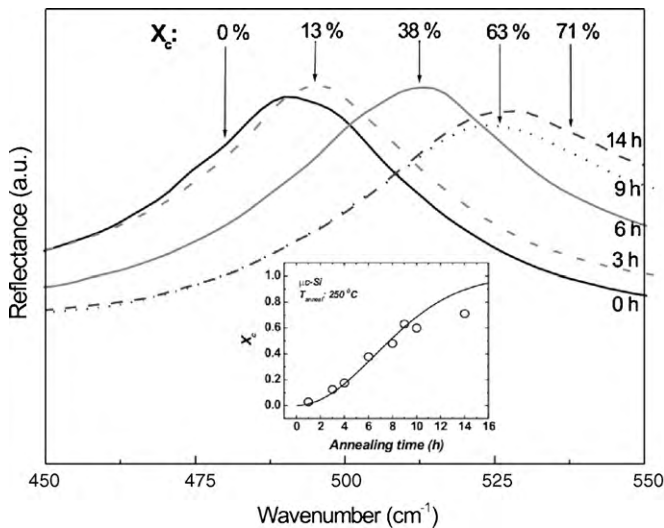

Fig. 3. FTIR spectra of the annealed a-Si:H films deposited over glass substrates on the 450–550 cm^{-1} interval. The frequency shift to high energies of the Si–Si mode of the microcrystalline state with annealing time is associated with the crystallized fraction X_c.

mation as shown on the inset in Fig. 3. A maximum X_c = 71% was obtained after 14 h of annealing.

To investigate more on the vibrational properties in the region of the silicon oxides, were recorded and analyzed the FTIR spectra of the annealed a-Si:H films deposited over the two types of substrates in the 800–1400 cm^{-1} interval, as is shown in Fig. 4. The transversal acoustic TO Si–O$_x$ vibration mode found in the 1046–1170 cm^{-1} region is observed for the films deposited on glass substrates revealing the reactivity of the film with annealing time. It has been suggested that the absorption frequency of the TO-phonon

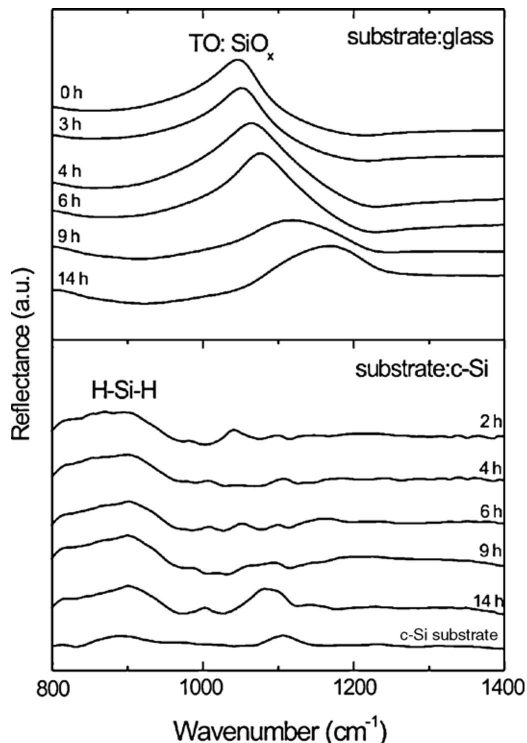

Fig. 4. FTIR spectra of a-Si:H films deposited on (upper) glass and (lower) mono-crystalline Si substrates for different annealing times for the interval 800–1400 cm^{-1}.

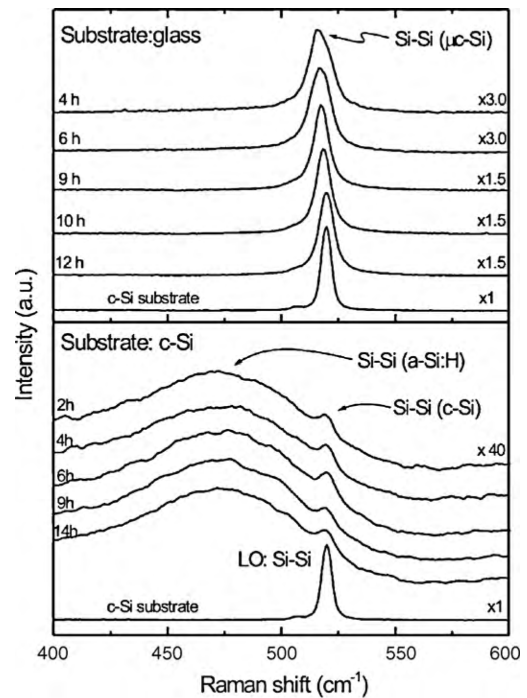

Fig. 5. Raman scattering spectra of a-Si:H films deposited on (upper) glass and (lower) mono-crystalline substrates for different annealing times.

mode varies systematically with the substoichiometry of the silicon oxide: a frequency around 1000 cm^{-1} is expected to belong to $SiO_{0.5}$, around 1030 cm^{-1} is assigned to SiO, around 1050 cm^{-1} indicates $SiO_{1.5}$, and around 1078 cm^{-1} to SiO_2 [15]. We observe a continuous range of asymmetric mode frequencies due to the large variety of possible arrangements present in the amorphous region and the influence of the isothermal annealing process. The FTIR spectra for films deposited on mono-crystalline Si substrates, shown in the inferior part of Fig. 4, presents mainly bands associated to H–Si–H vibration modes near 900 cm^{-1} [16], and a low contribution to the intensity of the Si–O$_x$ bands of the silicon oxide as in case of films deposited over glass substrate.

Raman scattering analysis gives also important information from the structural point of view about the phenomenological response of the a-Si:H layers with the annealing time and also with the type of substrate used. The Raman spectra of the annealed films deposited on glass and on mono-crystalline Si substrates are shown in Fig. 5. For films deposited over glass, the measurements were performed in micro-Raman configuration on the microstructures formed on the surface of the film which can be observed in AFM images of Fig. 1. As in the FTIR spectra, Raman measurements describe the vibrational response of the microcrystalline part of the film. It begins within the first hours of annealing with a broad band associated to the longitudinal optical LO Si–Si mode of Si (microcrystalline state). This band suffers a shift in frequency to higher energies (512–520 cm^{-1}) with annealing time. Hydrogen effusion occurs in the a-Si:H films during annealing process [17] and produces an ordering on the Si-crystalline structure which is characterized by a decreasing of the full width at half maximum (FWHM) of the Raman band approaching its frequency to bulk crystalline Si at 520 cm^{-1} [10]. In comparison, the Raman spectra of the annealed a-Si:H films deposited on mono-crystalline Si substrates, shown in the inferior part of Fig. 5, exhibits a broad and weak band associated to amorphous silicon phase (a-Si:H) at 480 cm^{-1} [18]. A weak but distinctive band at 520 cm^{-1}, typical of crystalline silicon phase (c-Si) [19], is also observed. In these Raman spectra, a mono-crystalline Si signature identifies the presence of the LO

Si–Si vibration mode (c-Si) in the films. Therefore, for the annealed a-Si:H films deposited on mono-crystalline Si the annealing time does not affect the Raman spectra and this suggests a stable and a low reactive film which is in a good agreement with FTIR results. Here the c-Si regions are immersed within the silicon amorphous matrix (a-Si:H) and the relative proportion of these phases seems to be constant with annealing time.

4. Conclusions

We have analyzed the morphological and vibrational properties of a-Si:H films deposited by PECVD over glass and mono-crystalline silicon. These a-Si:H films were treated by isothermal annealing with aluminum on the surface during several hours. Morphological analysis reveals that the films deposited on glass substrates experience an amorphous–crystalline phase transition with annealing time, reaching 71% transition after 14 h of annealing. The surface of the samples develops microcrystalline grains immersed on the amorphous matrix. FTIR and Raman studies on a-Si:H films deposited on glass substrates show Si–Si vibration bands that experience a frequency shift to high energies with annealing time as well as oxidation due the presence of the O–Si–O vibration modes. On the other hand, films deposited on mono-crystalline silicon were more uniform and flat with no apparent variations with annealing time. FTIR and Raman studies on a-Si:H films deposited on mono-crystalline silicon substrates showed Si–Si vibration bands with the frequency of the crystalline silicon and with no oxidation of the surface. This kind of studies in silicon may contribute to the design of semiconductor surfaces based on the metal-induced crystallization effect performed during the isothermal annealing processes.

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