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Structural properties of hydrogenated microcrystalline silicon–carbon alloys deposited by Radio Frequency Plasma Enhanced Chemical Vapor Deposition: Effect of microcrystalline silicon seed layer and methane flow rate

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ABSTRACT

Hydrogenated silicon–carbon thin films were deposited by Radio Frequency Plasma Enhanced Chemical Vapor Deposition using silane–methane gas mixtures highly diluted in hydrogen. The effects of the presence of a microcrystalline silicon seed layer and of the methane flow rate during deposition were investigated in order to find the optimal conditions for microcrystalline growth. The presence of a seed layer promotes the amorphous to microcrystalline transition at the interface with the substrate, reducing the incubation layer to a 5–10 nm thickness. At the same time, an excessive increase in the CH_4 flow rate suppresses crystalline growth, leading to extremely flat amorphous samples (root-mean-square surface roughness ρ_{RMS} ~ 0.5 nm), even with a seed layer. The total carbon content was measured by Radio Frequency Glow Discharge Optical Emission Spectroscopy. It was found that carbon is only incorporated in the amorphous tissue, and not in the crystalline phase. Thus, the increase of the crystalline fraction, directly linked to the increase of the seed layer deposition time, leads to a decrease of the carbon incorporation in the subsequent layer.

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1. Introduction

A material stable to light soaking with an electronic band-gap similar to that of hydrogenated amorphous silicon (a-Si:H) holds great potential gains for thin film silicon-based photovoltaics [1].

Hydrogenated microcrystalline silicon–carbon alloys (μc - $Si_{1-x}C_x$:H) are potential candidates but possess complicated growth dynamics and material properties. Indeed, μc - $Si_{1-x}C_x$:H samples deposited by conventional Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD), exhibit (i) a higher conductivity than their amorphous counterparts because of the presence of submicron-size silicon crystallites embedded in an amorphous silicon–carbon matrix [2,3], and (ii) a larger energy gap than that of microcrystalline silicon [4,5] due to carbon incorporation.

It is well known that the introduction of gasses containing carbon into the silane discharge can be detrimental to microcrystalline growth [6]; however, it is possible, by using a microcrystalline silicon seed layer (μc-Si:H), to eliminate the problem of carbon incorporation in the amorphous incubation layer (typical of all microcrystalline growth [7]), and to obtain thin micro-crystalline films of $Si_{1-x}C_x$:H(~50 nm).

In this paper, both the effects of the μc-Si:H seed layer and of the variation of the CH_4 flow during the subsequent growth were studied.

2. Experimental details

Hydrogenated silicon–carbon films were deposited by RF-PECVD at a substrate temperature of 275 °C. Films were grown from a mixture of silane (SiH_4) and methane (CH_4) highly diluted in hydrogen (H_2). The pressure and the inter-electrode distance were fixed at 240 Pa and 1.2 cm, respectively. All samples were deposited using a combination of a μc-Si:H seed layer, followed by a 30 minute deposition, with the addition of CH_4. Two sets of samples were deposited: in the first set (RF1) the effect of a μc-Si:H seed layer was investigated by varying its deposition time from 0 to 16 min (H_2, SiH_4 and CH_4 flow rates for the μc - $Si_{1-x}C_x$:H layer were kept constant at 500 sccm, 5 sccm, and 1 sccm, respectively). In the second set (RF2) the effect of the variation of the CH_4 flow rate (from 1 sccm to 2.5 sccm) during the μc - $Si_{1-x}C_x$:H layer deposition was studied. For both series, the H_2 flow rate was

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kept constant at 500 sccm. The SiH_4 flow rate was kept at 6 sccm during the μc-Si:H seed layer deposition and decreased to 5 sccm during the main layer deposition. Finally, the RF power was kept at 16 W during the seed layer deposition and increased to 40 W during the main layer deposition. The conditions used for the seed layer are known to result in highly microcrystalline samples when used to grow thicker films. Each sample was deposited simultaneously on two different substrates: <100> float zone silicon to perform infrared (IR) spectroscopy measurements and Corning "Eagle" glass to perform ellipsometry and Raman spectroscopy measurements as well as Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) analyses.

Ellipsometry measurements were performed using a UVISEL spectroscopic ellipsometer from HORIBA Jobin Yvon in the spectral range 1–4.7 eV. To analyze these spectra, a two Tauc–Lorentz [8] dispersion formula for microcrystalline materials and a single Tauc–Lorentz dispersion formula for the amorphous ones were used to parametrize the dielectric function $\epsilon(E) = \epsilon_r(E) + i\epsilon_i(E)$ as a function of the photon energy E, where $\epsilon_r(E)$ and $\epsilon_i(E)$ are the real and imaginary parts respectively. The thickness of the samples was then determined using a single-layer with roughness model. Raman spectra were obtained in the 200–1500 cm^{-1} range using a LABRAM Aramis system, Confocal Raman Microscope by HORIBA Jobin Yvon, equipped with a 473 nm laser. IR absorption measurements between 400 and 4000 cm^{-1} were carried out using a Brüker Equinox 55 Fourier transform infrared spectrometer. Surface roughness was studied by means of a Dimension 5000 Atomic Force Microscope by Digital Instruments Inc. in air, operated in tapping mode. TEM and Energy Filtered-TEM (EF-TEM) analyses were performed using a JEOL TEM 2010 F electron microscope operating at an accelerating voltage of 200 kV and equipped with a Gatan electron energy loss image filtering. Plasmonic images were acquired using plasmonic excitation at 16 eV (Si – Si bond) and 24 eV (Si – C bond is at 22 eV). In both cases the energy slit used had a 4 eV width. Electron transparent samples were prepared by conventional mechanical polishing and argon-ion thinning. Finally, the elemental contents and the depth profiles of carbon and silicon were determined by Radio Frequency Glow Discharge Optical Emission Spectroscopy (RF-GD-OES) using a HORIBA Jobin Yvon GD-Profiler 2.

3. Results and discussion

3.1. Role of the seed layer

Initial attempts at growing thin μc - $Si_{1-x}C_x$:H layers (50–100 nm) by RF-PECVD for this study had resulted in fully amorphous samples. This was attributed to the presence of CH_4 at the beginning of the deposition interfering with nucleation. It was therefore decided to investigate the effect of a μc-Si:H seed layer, for which the deposition time was varied from 0 to 16 min.

Ellipsometry (only the imaginary part $<\epsilon_i>$ of the pseudodielectric function) and Raman spectra of the samples are presented in Fig. 1, while thickness and crystalline fraction, deduced from those measurements, are listed in Table 1. A transition from an amorphous to a crystalline phase can be observed as soon as a μc-Si:H seed layer is added. In the case of no seed layer, the ellipsometry spectrum results in a broad peak in the imaginary part $<\epsilon_i>$ of the pseudo-dielectric function, typical of an amorphous sample. The introduction of a seed layer, on the other hand, induces the presence of two structures, typical of μc-Si:H, at about 3.5 eV and 4.2 eV, meaning that a phase transition has taken place. Regarding the Raman spectra, the absence of the seed layer leads to a broad component located around 480 cm^{-1} which is characteristic of amorphous silicon. With an increase in the seed layer deposition time, the Si–Si Transversal Optical (TO) mode located at 520 cm^{-1} appears and grows with increasing the seed layer deposition time. Considering that no SiC-related mode can be detected in the Raman spectra, one can accept the dominant presence of silicon crystallites embedded in an amorphous $Si_{1-x}C_x$ matrix [9,10].

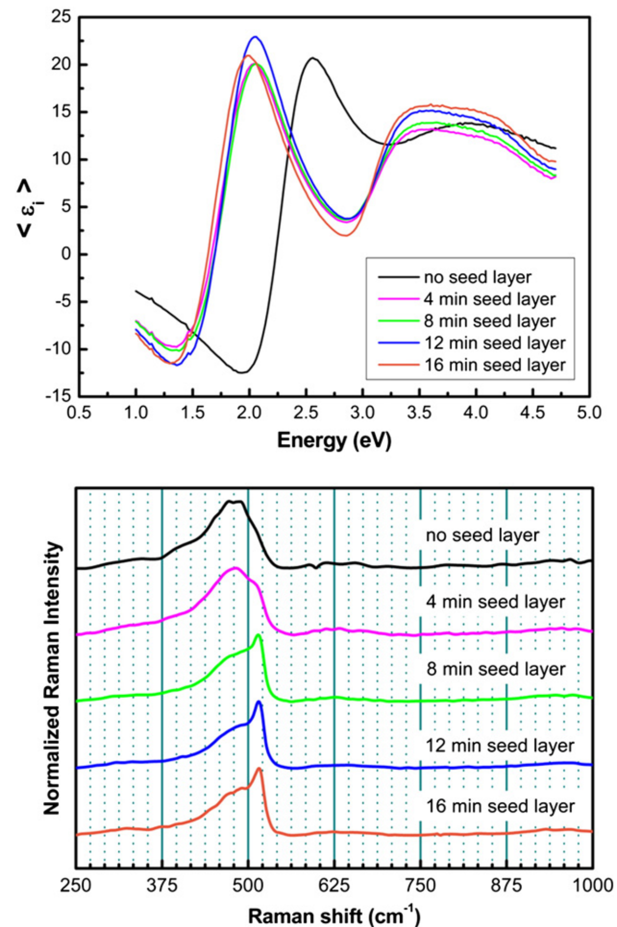

Fig. 1. Experimental ellipsometry spectra and Raman spectra of samples deposited varying the seed layer deposition time.

An estimation of the crystalline volume fraction, f_c, was obtained according to the relation

$$f_c = \frac{I_{510} + I_{520}}{I_{480} + I_{510} + I_{520}} \quad (1)$$

where I_{480}, I_{510} and I_{520} are the areas of the peaks located at 480 cm^{-1}, 510 cm^{-1} and 520 cm^{-1}, respectively [11]. So, while samples deposited without seed layer are completely amorphous ($f_c = 0\%$), with the introduction of such a layer it is possible to induce a phase transition. Moreover, increasing the seed layer deposition time leads to an increase of the crystalline content, up to 35%.

The importance of the seed layer can also be underlined by the surface structure, as shown in the topographic images obtained from AFM measurements in Fig. 2a) and b). When no seed layer is deposited, the sample exhibits an extremely flat surface; in contrast, the introduction of a thin μc-Si:H seed layer induces the presence of protrusions emerging from the surface, that are even more evident in Fig. 2c).

Table 1
Thickness and crystalline volume fraction f_c calculated from ellipsometry modeling and Raman spectroscopy fitting, respectively.

Sample	Seed layer time (min)	Thickness (nm)	f_c (%)
RF1(1)	0	40	0
RF1(2)	4	59	11
RF1(3)	8	58	29
RF1(4)	12	56	34
RF1(5)	16	59	35

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