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Correlation between the UV-reflectance spectra and the structure of poly-Si films obtained by Aluminium Induced Crystallization[♣]

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The structural properties of poly-Si films prepared by the method of Aluminium Induced Crystallization (AIC) of amorphous Si films (a-Si:H) deposited on glass substrates covered with Al layers were studied. Raman and XRD (X-Ray Diffraction) spectroscopy were used for characterization of their short and long range order, respectively. The UV (Ultra-Violet) reflectance spectra of poly-Si films were measured, as well. The surface morphology was revealed by optical microscopy. The dependence of the structural and optical properties of the obtained poly-Si films on the hydrogen pressure during the deposition of the a-Si:H precursor was studied. A correlation between the short and long range ordering in poly-Si films, their surface morphology and the UV optical reflectance spectra was identified. Poly-Si films with better structural properties are obtained by AIC, using a-Si:H precursor layers with moderate concentrations of hydrogen.

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1. Introduction

The method of aluminium induced crystallization (AIC) has been widely used in recent years to obtain poly-Si films, mainly because of the lower thermal budget of this technology and the generation of grains that are larger than the film thickness in the obtained poly-Si films [1,2]. Additionally, it has to be pointed out that a low cost substrate such as glass could be used for deposition of the films. For solar cell applications, the poly-Si films are used as seeding layers for epitaxial thickening [3]. This is why the qualities of their surface and crystalline structure are important.

In this work, the influence of the temperature of deposition ($T_s^{a\text{-}Si}$) of unhydrogenated (a-Si) and hydrogenated (a-Si:H) amorphous silicon layers, prepared by magnetron sputtering, on the structural properties of poly-Si films obtained by AIC of glass/Al/a-Si(a-Si:H) configurations is reported. The influence of the hydrogen pressure during the magnetron sputtering of the a-Si:H precursor films is also reported. XRD (X-Ray Diffraction) and Raman spectroscopy were applied for characterization of their structural properties. UV (Ultra Violet) reflectance spectroscopy was used to study the surface quality of the poly-Si films.

A correlation between the long range ordering in the poly-Si films, their surface morphology and the UV optical reflectance spectra was examined.

2. Experimental

Poly-Si films were obtained by AIC of the structures glass/Al/a-Si:H(or a-Si). The precursor layers of Al were deposited at a substrate temperature T_s^{Al} = 300 ^{0}C, and were kept for 24 hours in air before the deposition of the a-Si:H (or a-Si) films. Precursor Al films prepared under these conditions result in better structural properties of the obtained poly-Si films, as described earlier [4]. Unhydrogenated (a-Si) and hydrogenated (a-Si:H) films were deposited on top of the Al by magnetron sputtering with 130 W rf power at different substrate temperatures: RT (without heating of the substrates), 250, 300, 350 and 400^{0}C. Four different sets of samples were prepared with a-Si:H precursors deposited without hydrogen (a-Si) and with 0.05, 0.1Pa and 0.2 Pa of H_2 partial pressure in the Ar+H_2 sputtering gas mixture. These conditions resulted in a hydrogen concentration in the deposited precursor amorphous Si layers between 4 and 25% (measured by Elastic Recoil Detection Analyses (ERDA) [5]), and it increased with increasing H_2 partial pressure and reduction of the substrate deposition temperature [6]. The thicknesses of both precursors, Al and a-Si:H (or a-Si)

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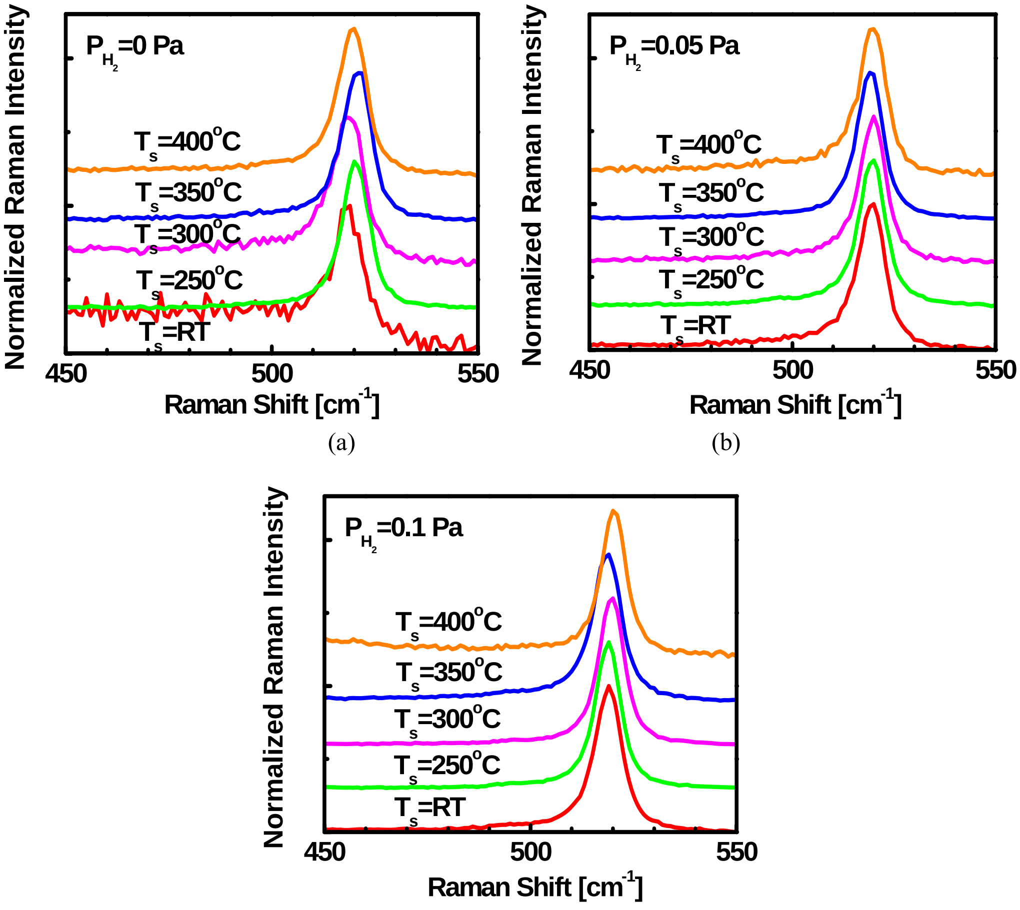
The UV hemispherical reflectance spectra in the range 250 - 400 nm were measured by Perkin-Elmer UV/VIS/NIR Lambda 900 spectrometer. The surface morphology was observed by optical light microscopy [7]. The degree of crystallization of the poly-Si films was studied by XRD and Raman spectroscopy. The XRD spectra of the samples were obtained using a Brucker D8 Advance spectrophotometer with CuKα radiation: λ $CuK_{\alpha 1}$= 1.540560 Å and λ $CuK_{\alpha 2}$ = 1.544426 Å (intensity half that of λ $CuK_{\alpha 1}$). The instrumental broadening was 0.04^0 in a 2Θ geometry. Raman spectra were excited by the 488 nm line of an Ar^+ laser, and all of them were measured under the same conditions. The peak positions and the Full Width at Half Maximum (FWHM) of the Raman bands were measured with a mean error of 0.5 cm^{-1}.

3. Results and discussion

Raman spectroscopy was used to study the influence of the deposition temperature and the hydrogen partial pressure during the sputtering of the a-Si (a-Si:H) precursor layers on the quality of the structure of the resulting poly-Si films. The Raman spectra of films obtained from a-Si or a-Si:H precursors deposited at different $T_s^{a\text{-}Si}$ and three different hydrogen partial pressures are shown in Fig. 1. All of the samples display Raman spectra typical of the crystalline Si structure - a Si-Si TO band, centered between 518.5 and 520.5 cm^{-1}. The Si-Si TO peak for crystalline silicon, measured under the same conditions, is at 521 cm^{-1} and has a Full Width at Half Maximum (FWHM) of 4.5 cm^{-1}. The dependence of the Si-Si TO peak position and its FWHM (estimated from a Lorentzian fit) on the a-Si (a-Si:H) substrate temperature and the H_2 partial pressure are presented in Fig. 2a and Fig 2b, respectively. The accuracy of the values is indicated by the error bars.

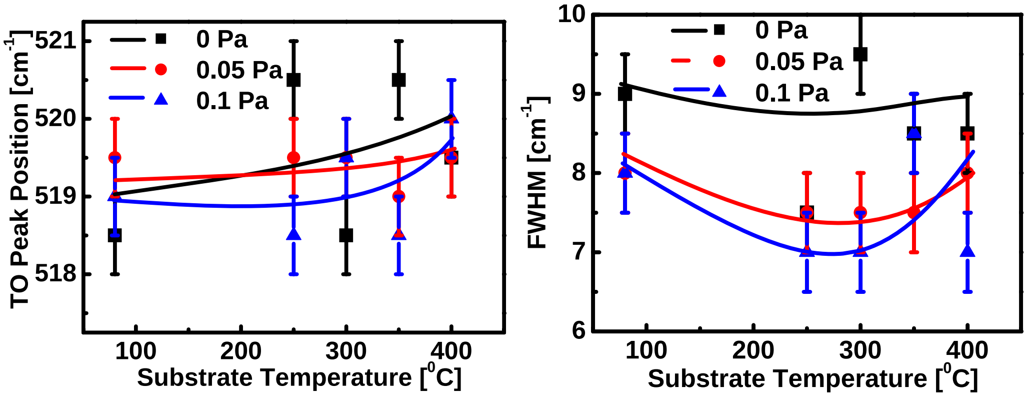
An estimate of the grain size can be deduced from both the downshift and the FWHM of the



(a) (b)

(c)

Fig.1. Raman spectra of poly-Si films obtained from a-Si and a-Si:H precursors deposited at different $T_s^{a\text{-}Si}$ and different H_2 pressures: 0 Pa (a), 0.05 Pa (b) and 0.1 Pa (c).



(a) (b)

Fig. 2. Si-Si TO-like peak position (a) and FWHM (b) taken from Raman spectra of the samples presented in Fig 1. The lines are guides to the eye.

Raman peak [8]. Although accurate values cannot be determined from the relationships described previously in the literature, comparisons between the spectra obtained from similar materials are valid [8, 9]. The grain size is inversely proportional to the FWHM of the peak [9]. On the other hand, a shift in the Si-Si TO peak position, ω_{TO}, to a lower wave number could be related to an increase in the value of the tensile stress [10]. The following tendencies can be seen. The Si-Si TO peak position shifts slightly to a higher wave number with increasing T_s^{a-Si}. This is an indication of a reduction in the tensile stress in the poly-Si samples with increasing T_s^{a-Si} [11]. A weak tendency for increased stress in the poly-Si films, when a-Si:H precursors were used, could be noticed, and could be explained by the effusion of H during the AIC. This could leave pinholes and microvoids in the poly-Si films, resulting in higher tensile stresses.

The FWHM of the Si-Si TO peak passed through a minimum for poly-Si films obtained from hydrogenated precursor layers deposited at T_s^{a-Si} between 250 and 350° C - in this case, larger grains were obtained in the poly-Si films. It should be noted that we observed similar results for the AIC of glass/a-Si(a-Si:H)/Al structures [12]. During the annealing, effusion of H from the a-Si:H films takes place. It is possible to suppose that this will enhance the disorder in the a-Si:H precursor during the annealing. This stimulates the dissolution of Si atoms into the Al and the consequent re-arrangement into a Si crystalline structure, resulting in a higher growth rate and larger grains in the poly-Si films. The suggestion is based on the fact that the higher degree of disorder creates energetically more favourable conditions for the transformation of the a-Si:H film into a poly-Si one. It is known that the H concentration in a-Si:H films decreases with increasing substrate temperature, so that the precursors deposited at RT (without heating) should have a higher H content [13]. In this case, the higher effusing quantity of hydrogen probably creates conditions for an increased diffusion rate of Al and Si. Thus, intermixing of Al and Si would take place within the bulk of the resulting poly-Si film, which would inhibit the exchange between Al and Si and would lead to a lower rate of crystallite growth and a smaller grain size. The deposition of the precursor layers, at temperatures > 350° C, would result in a reduced H content and in better short range order of the a-Si:H films [10], which would slow down the re-arrangement into the crystalline structure – the poly-Si films would again have grains of a smaller size.

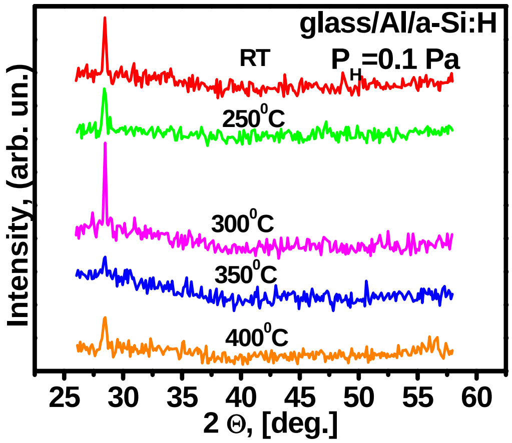
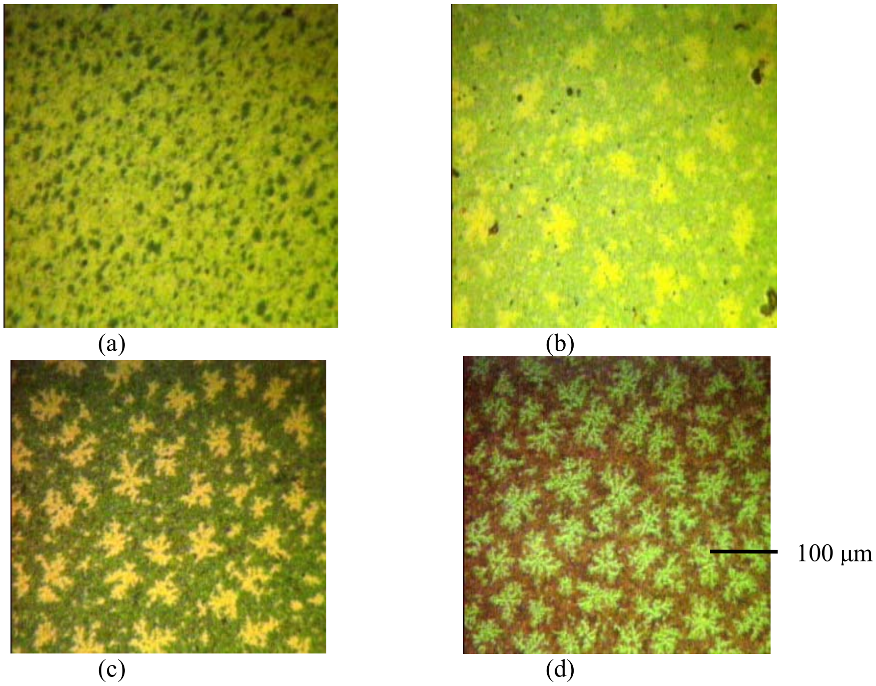


Fig.3. XRD spectra of the set of poly-Si samples deposited at different T_s^{a-Si} and P_{H2} = 0.1 Pa.

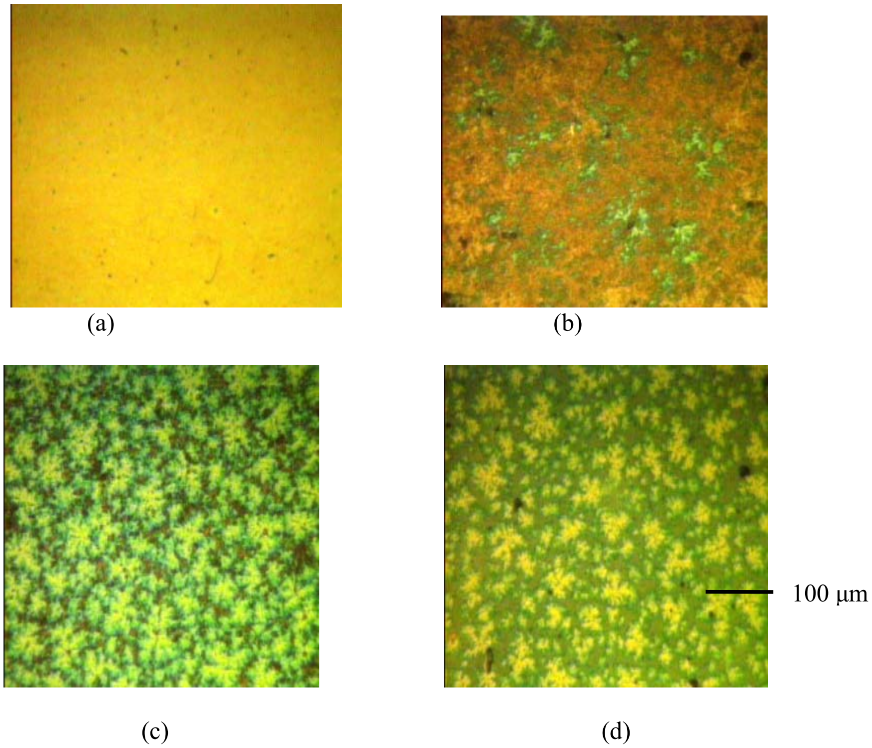
XRD spectra of the set of sample deposited at different T_s^{a-Si} and P_{H2} = 0.1 Pa are presented in Fig. 3. This set of samples was chosen because it had a relatively larger grain size (the narrowest FWHM of the Si-Si TO Raman band). Only one peak of reflection in the XRD spectra at about $2\theta = 28.39 - 28.48^0$ is observed for the poly-Si films, which correspond to the (111) preferential orientation. The position of this peak in the c-Si is at $2\theta = 28.48^0$. The intensity of the peak is higher



(a) (b)

(c) (d)

Fig 4. Optical micrograph images of poly-Si films using precursor layers of a-Si:H deposited with $P_{H2}=0$ *Pa at different* $T_s^{a\text{-}Si}$ *: RT (a), 250*^{o}*C (b), 300*^{0} *C (c) and 400*^{o}*C (d).*



(a) (b)

(c) (d)

Fig 5. Optical micrograph images of poly-Si films using precursor layers of a-Si:H deposited with $P_{H2} = 0 .05$ *Pa at different* $T_s^{a\text{-}Si}$ *: RT (a), 250*^{o}*C (b), 300*^{0} *C (c) and 400*^{o}*C (d).*

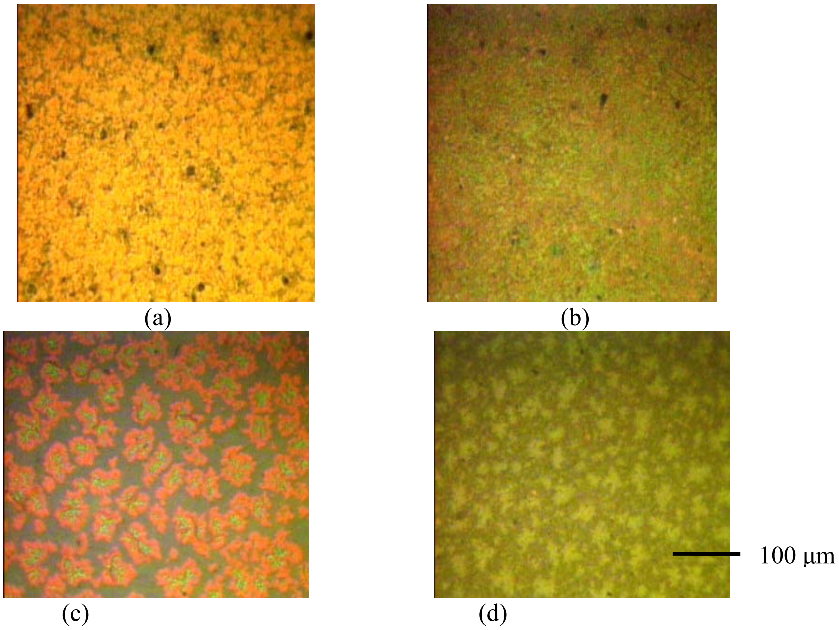


Fig 6. Optical micrograph images of poly-Si films using precursor layers of a-Si:H deposited with P_{H2}*=0.1 Pa at different* $T_s^{a\text{-}Si}$ *: RT (a), 300°C (b), 350*^{0}*C(c), and 400°C (d).*

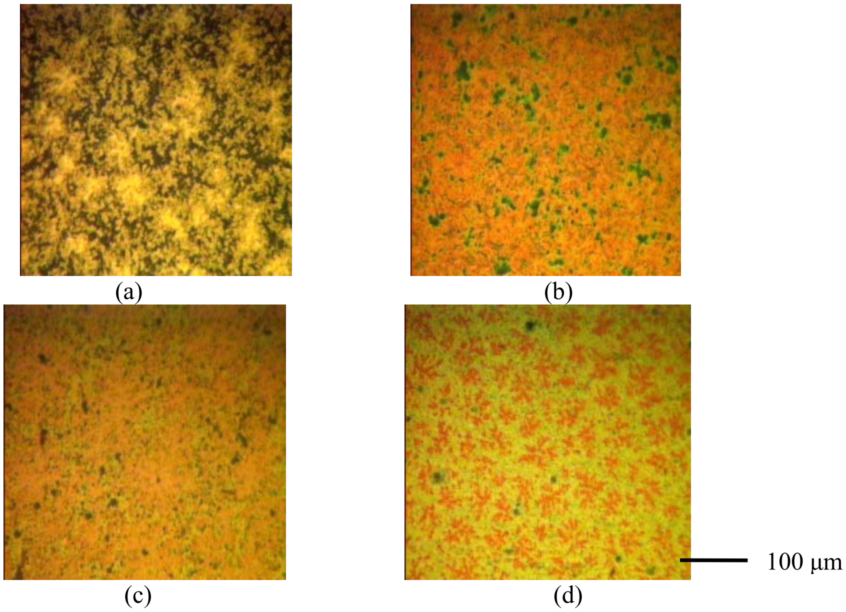
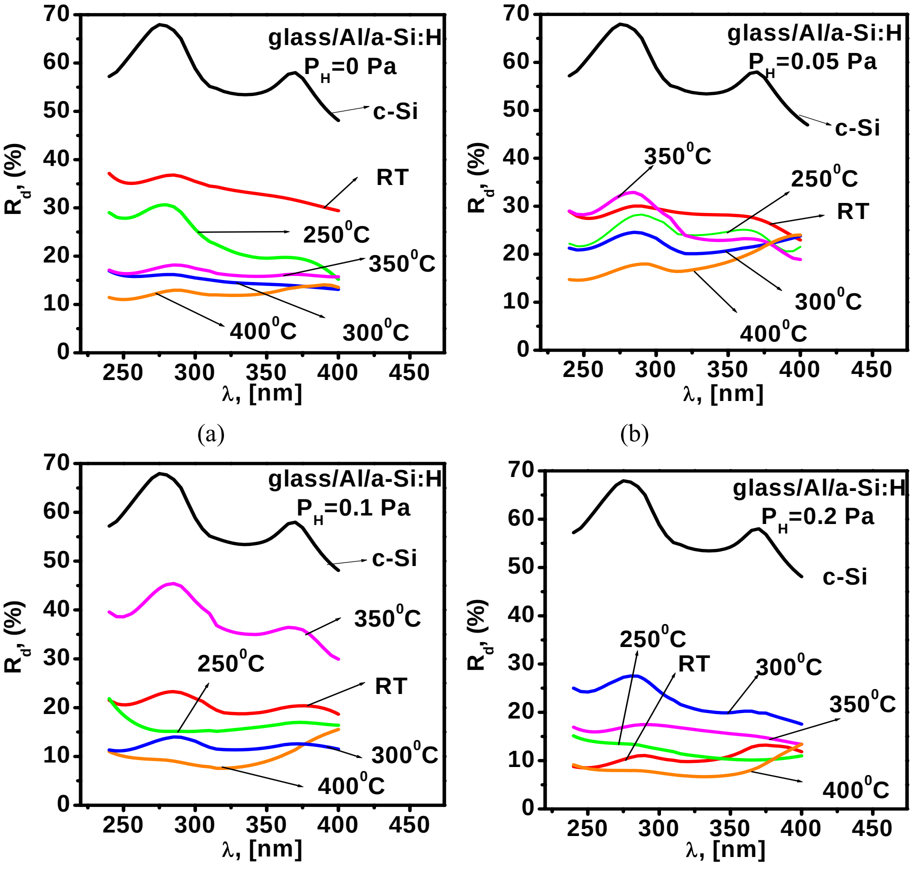


Fig 7. Optical micrograph images of poly-Si films using precursor layers of a-Si:H deposited with P_{H2}*=0.2 Pa at different* $T_s^{a\text{-}Si}$ *: RT (a), 300°C (b), 350*^{0}*C(c), and 400°C (d).*

and is at $2\theta = 28.48^0$ in the poly-Si films obtained from a precursor deposited at $T_s^{a\text{-}Si} = 300\ ^0$C. This observation is an indication of better crystalline quality. The FWHM of the (111) peak in the XRD spectra decreases with increasing $T_s^{a\text{-}Si}$. This demonstrates an increase of the average grain size with preferential (111) orientation which is in agreement with the tendencies in Raman spectra. The position of the (111) peak of the sample deposited at $T_s^{a\text{-}Si}$=350^0 C ($2\theta = 28.48^0$) coincides with the c-Si one. The peak shifts to the lower2θ (28.39^0) for the samples deposited at the other $T_s^{a\text{-}Si}$, which could be due to the tensiel stress in the films and is in agreement with the conclusions from the Raman spectra.

Optical micrographs images of the surface of poly-Si films obtained from a-Si and a-Si:H precursors, deposited at different $T_s^{a\text{-}Si}$, are shown in Figs. 4 - 7. Images of the samples obtained from unhydrogenated amorphous Si layer precursors deposited at $T_s^{a\text{-}Si} < 250^0$C have a smooth surface. Those deposited at substrate temperatures of 250, 300 and 400°C exhibit a high density of Si precipitates (hillocks or islands) on the poly-Si surface. However, in the case of poly-Si, prepared from a hydrogenated amorphous silicon precursor, silicon islands appear on the surface only for precursors deposited at the higher temperatures, $T_s^{a\text{-}Si} = 300\ ^0$C (for $P_{H2} = 0.05$ Pa), 350^0C(for $P_{H2} = 0.01$ Pa) and $400\ ^0$C (for $P_{H2} = 0.2$ Pa). The substrate temperature of the a-Si:H precursor at which the precipitates appear on the poly-Si film surfaces increases with increasing hydrogen partial pressure. The presence of numerous Si islands on the poly-Si surface after AIC has been reported when the Al precursor is thicker than he amorphous silicon one, and in the case of precursors of a-Si:H with high short range disorder and of microcrystalline Si films deposited by PE CVD methods [1,14]. It is possible to suppose that the growth of the silicon hillocks in our case is a result of the better structural order in the a-Si:H precursors deposited at higher temperature. The influence of the hydrogen concentration in a-Si:H should be taken in account, as well, because it depends on the T_s and the hydrogen pressure during the deposition. The conditions of deposition of the precursor layers define the balance between the rate of nucleation and of the crystal growth and the circumstances for the preparation of poly-Si with a smooth surface.

The spectra of the UV hemispherical reflectance of the obtained poly-Si films are presented in Fig. 8.



(a) (b)

(c) (d)

Fig. 8. UV reflectance spectra of poly-Si films obtained by AIC from a-Si:H precursors deposited at different T_S and with different H_2 partial pressures: 0 (a), 0.05 (b*) 0.1 (c) and 0.2Pa (d) .*

The corresponding spectra of c-Si polished wafer measured inder the same conditions is shown, too. The two maxima in the spefctrum of single-crystalline Si at 280 nm and 365 nm are caused by optical interband transition at the X-poimt (band E_2) and along the Γ-L axis (band E_1) of the Brillouin zone, respectively [15,16]. The deviation from the UV-R spectrum of bulk crystalline Si is related to the long-range order deterioration or amorphisation of the material [15]. The intensity of the E_2 band (280nm) decreases and that of the E_1 (375nm) increases with long range disorder, according to the theory of long range order relaxation effects. Additionally, at short wavelengths, in particular at 280 nm, the reflectance is largely determined by the high value of the absorption coefficient ($\alpha > 10^6$ cm^{-1}) corresponding to a penetration depth of less than 10 nm. Imperfect crystallinity in the near-surface region will cause a broadening and height reduction of this maximum [15, 16]. It is seen from Fig. 8a that for the poly-Si films obtained from a-Si deposited at $T_s > 250^0$ C without hydrogen ($P_{H2} = 0$ Pa), the UV-R is very low in the whole photon range, and smeared out maxima are observed. The maximal value of the UV-reflection and the best expressed maxima of E_1 and E_2 bands are observed for the case of a a-Si:H precursor deposited at $T_s^{a\text{-}Si} = 300^0$ C and $P_{H2} = 0.05$ and 0.1 Pa. However, in the case of $P_{H2} = 0.1$ Pa, the values are the highest and closer to the reflection of the c-Si polished wafer – these samples have better long range order and better structure of the near surface region. This is in an agreement with the XRD and Raman spectra, and with the surface morphology observed from optical light microscopy images.

4. Conclusions

The study of the influence of amorphous silicon precursor layers, deposited at different substrate temperatures by magnetron sputtering, in an atmosphere with and without H_2, on the structural properties of poly-Si films obtained by AIC of glass/Al/a-Si(a-Si:H) structures has been performed by Raman spectroscopy, XRD, UV-reflectance spectra and optical light microscopy. The results showed that poly-Si with larger grain sizes were obtained using a precursor of a-Si:H deposited at a moderate $T_s^{a\text{-}Si}$ = 250-300°C and 0.05 and 0.1 Pa H_2 pressures in the sputtering chamber. The tensile stress in the poly-Si films decreased with increasing temperature of deposition of the amorphous silicon precursor. Poly-Si films with smooth surfaces were obtained from an a-Si precursor deposited at $T_s^{a\text{-}Si}$ = 300°C and from an a-Si:H one at $T_s^{a\text{-}Si}$ = 400°C. The differences in the structural properties of the poly-Si films could be explained by the different structural order and different content of hydrogen in the precursor a-Si (a-Si:H) layers deposited under different conditions.

The complex study of the structural properties, such as short and long range ordering and the quality of the structure of the surface area of poly-Si films prepared by AIC demonstrated a good correlation between the data obtained from XRD, Raman spectroscopy, optical microscopy and UV-reflectance spectra. Poly-Si films with better structural properties were obtained by AIC using a- Si:H precursor layers deposited at a moderate hydrogen partial pressure and $T_s^{a\text{-}Si}$ about 300^0 C.

The results were explained by the influence of the presence of hydrogen in the precursor a-Si:H layer on the process of AIC.

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