Influence of the hydrogen content in a-Si:H layers on the structural properties of poly-Si films obtained by AIC of glass/Al/a-Si:H structures

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Abstract. Polycrystalline silicon films were fabricated by aluminium-induced crystallization of glass/Al/a-Si(a-Si:H) structures. The Al, unhydrogenated (a-Si) and hydrogenated (a-Si:H) precursor layers were deposited by RF magnetron sputtering. The structures prepared were annealed in forming gas (N\textsubscript{2}+5% H\textsubscript{2}) at atmospheric pressure for 6 h at 530° C. The structural properties of the poly-Si films were studied by Raman and X-ray diffraction spectroscopy and optical microscopy. Studies were performed of the influence of the substrate temperature of the a-Si:H precursor layers, T\textsubscript{s}\textsubscript{a-Si}, and H\textsubscript{2} pressure during the sputtering, \eta, on the structure of the poly-Si films obtained. It was shown that the grain size in the poly-Si films increases with T\textsubscript{s}\textsubscript{a-Si} and \eta. The value of the tensile stress in the poly-Si films decreases with the increase of the substrate temperature of the a-Si (a-Si:H) precursor and the decrease of the H\textsubscript{2} partial pressure.

1. Introduction
The preparation of poly-Si films by using the aluminium-induced crystallization (AIC) technique has attracted the attention of the scientific community because of the advantages that it offers, namely, a lower thermal budget than other crystallization methods, the possibility to use low-cost substrates and the generation of grains that are larger in size than the thickness of the poly-Si films obtained [1, 2]. It has been reported that the parameters of the AIC process and the preparation of the precursor layers are of great importance for providing good properties of the resulting poly-Si layers [1-6].

In this work, the influence is studied of the deposition temperature (T\textsubscript{s} of the 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) structures. The influence is also investigated of the hydrogen partial pressure, \eta, during the magnetron sputtering of the a-Si:H precursor films.

2. Experimental details
Glass/Al/a-Si and glass/Al/a-Si:H structures were prepared to obtain poly-Si thin films by AIC. Precursor Al layers were deposited on glass substrates by RF (13.56 MHz) magnetron sputtering with...
120 W RF power at 0.5 Pa Ar pressure and a substrate temperature of 300 °C. Before the a-Si (a-Si:H) layer deposition, the Al precursor layer was kept in air for 24 h to form a native oxide. It has been reported [6] that precursor Al films prepared under these conditions result in better structural properties of the poly-Si films. Unhydrogenated (a-Si) and hydrogenated (a-Si:H) amorphous Si films were deposited on top of the Al layer by RF magnetron sputtering from a c-Si target in Ar (0.5 Pa) and Ar (0.5 Pa) + H₂ (0.05 Pa or 0.1 Pa), respectively, with 130 W RF power. The base pressure in the chamber before sputtering was 10⁻⁴ Pa. The a-Si and a-Si:H precursors were deposited at various temperatures – without heating and with heating up to 400 °C. The thicknesses of the Al and a-Si (a-Si:H) precursors were equal - 100 nm. The resulting glass/Al/a-Si(a-Si:H) structures were annealed in forming gas (N₂ + 5%H₂) under atmospheric pressure at 530 °C for 6 h. During the annealing, crystalline silicon grains were formed in the bottom layer, while Al atoms moved to the top surface, resulting in a layer exchange. After annealing, the aluminium was removed from the surface of the poly-Si films by etching in a chemical solution based on phosphoric acid. X-ray Diffraction (XRD) spectra were obtained using a Brucker D8 Advance spectrophotometer with CuKα radiation. The Raman scattering was registered in photon counting mode using a SPEX 1403 spectrometer. The Raman spectra were excited by the 488 nm line of an Ar⁺ laser. The spectral bandpass of the instrument for these measurements was 3.3 cm⁻¹. The error in determining the position and the full width at half maximum (FWHM) was 0.5 cm⁻¹. The total concentration of hydrogen in the a-Si:H films was determined by elastic recoil detection analysis (ERDA) [7]. The concentration of hydrogen bonded to Si was calculated from the IR absorption spectra.

3. Results and discussion

XRD and Raman spectroscopy were 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 structure of the resulting poly-Si films. XRD spectra obtained for 20 scans between 20° and 80° after subtracting the XRD background from the glass substrate are shown in figure 1. All samples are polycrystalline and exhibit a (111) preferential crystalline orientation. Similar results have been reported in [8, 9]. The average grain size D (calculated by applying the Scherrer equation) and the stress σ in the poly-Si films, calculated from the (111) peaks to an accuracy of about 10%, are presented in table 1.

The Raman spectra of films obtained from a-Si or a-Si:H precursors deposited at different T_a-Si and different hydrogen partial pressures are shown in figure 2. All samples display Raman spectra which are typical for crystalline Si structures - a Si-Si TO-like band centered between 518.5 and 520.0 cm⁻¹. The Si-Si TO-like peak for crystalline silicon, measured under the same conditions, is at 521.0 cm⁻¹.

Figure 1. XRD spectra of poly-Si films obtained from a-Si:H deposited at different T_a-Si and 0.1 Pa H₂ partial pressure (a) and with different H₂ partial pressures at T_a-Si = 250°C (b).
Table 1. Deposition conditions of the precursor layers. H concentration is calculated from FTIR absorption spectra; $\phi$ - from ERDA, $\xi$ and 2$\theta$ - from (111) XRD peak and its FWHM; $\Delta 2\theta$ and average grain size in the poly-Si films D - from the XRD data. The values of the position of the Si-Si TO-like peak, $\omega_{TO}$, and its FWHM are given as well.

| $T_s^{a-Si}$, $^\circ C$ | $T_s^{Al}$, $^\circ C$ | $P_{H2}$, Pa | $\phi$, at % | $\xi$, at % | 2$\theta$, deg. | $\Delta 2\theta$, deg. | D, Å | $\sigma$, MPa | $\omega_{TO}$, cm$^{-1}$ | FWHM, cm$^{-1}$ |
|-------------------------|----------------------|-------------|-------------|-------------|---------------|-----------------|-----|-------------|----------------|----------------|
| Without heating         | 300                   | 0.10        | 19          | 25          | 28.44         | 0.13            | 630     | -           | 680            | 519                                 | 8               |
|                         | 250                   | 0.10        | 15          | 19          | 28.49         | 0.13            | 630     | -           | 700            | 518.5                                | 7               |
|                         | 300                   | 0.10        | -           | -           | -             | -               | -       | -           | -              | 519.5                                 | 7               |
|                         | 400                   | 0.10        | 11          | 16          | 28.40         | 0.15            | 546     | -           | 393            | 520                                    | 7               |
|                         | 250                   | 0.00        | 0           | 4           | 28.50         | 0.21            | 431     | -           | 629            | 520                                    | 7.7              |
|                         | 250                   | 0.05        | 9           | 14          | 28.48         | 0.23            | 372     | -           | 661            | 519.5                                 | 7.5              |

Figure 2. Raman spectra of the poly-Si films obtained from a-Si:H deposited at different $T_s^{a-Si}$ and $P_{H2} = 0.1$ Pa (a) and with different $H_2$ partial pressures at $T_s^{a-Si} = 250^{\circ}C$ (b).

and has FWHM of 4.5 cm$^{-1}$. An estimate of the grain size can be deduced from both the downshift and the FWHM of the Raman peak [10,11]. Although accurate values cannot be determined from the relationships described previously in the literature, comparisons between the spectra obtained from similar materials are valid [10]. The grain size is inversely proportional to the FWHM of the peak [11]. On the other hand, a shift of the Si-Si TO-like peak position, $\omega_{TO}$, to a lower wavenumber could be related to an increase in the value of the tensile stress [12]. The following tendencies can be pointed out. The Si-Si TO-like peak position shifts slightly to a higher wavenumber with increasing the $T_s^{a-Si}$. This is an indication for a reduction in the tensile stress in the poly-Si samples with increasing $T_s^{a-Si}$. A similar tendency can be seen for the stress $\sigma$ calculated from XRD data (see table 1). A weak tendency for increasing the tensile 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-like peak decreases with increasing the $H_2$ partial pressure and the deposition temperature of a-Si:H precursors (figure 2 and table 1), which is evidence for an increase of the grain size in the poly-Si films. This tendency is clearly expressed with the increase of $H_2$ partial pressure form 0.05 to 0.10 Pa, according to the XRD data (table 1).

It is well known that hydrogen creates Si-H bonds in a-Si:H and is present in the microvoids of the films as well. The H concentration in a-Si:H films decreases with increasing the substrate temperature.
and with decreasing the hydrogen partial pressure, $\eta$ [13]. The concentration of hydrogen $\varphi$ bonded to Si in the a-Si:H precursors was evaluated from FTIR absorption spectra (with accuracy of 10%) and the total concentration of hydrogen $\xi$ from ERDA analyses (with accuracy of 1%) (table 1). According to the ERDA data the hydrogen is homogeneously distributed in the depth of the a-Si:H films; only at the surface region and close to the substrate its concentration decreases due to the effusion during the film deposition [14]. In the poly-Si films the total hydrogen concentration measured by ERDA is about 5 at.% and increases slightly at the surface region (up to 7 – 8 at.%) probably due to the absorption from the ambience, as it is the case of a-Si film sputtered without H$_2$, and/or during the annealing in the forming gas.

Considering the thermodynamics of the Si-H and Si-Si bonds, one should expect that the disorder in the a-Si:H precursor during the annealing increases via breaking of the Si-H bonds [8]. The increased disorder and the outward diffusion of the hydrogen from the broken bonds and voids stimulate the diffusion of Si atoms in the Al and the subsequent re-arrangement into a Si crystalline structure, resulting in a higher growth rate and larger grains in the poly-Si films. This suggestion is based on the fact that the higher degree of disorder is energetically more favourable for the transformation of the a-Si:H film into a poly-Si one. Thus, it is reasonable to assume that a precursor layer with higher hydrogen content will result in a higher rate of the crystallization process and formation of larger grains in the poly-Si layer.

4. Conclusions
A 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 and XRD spectroscopy. The results show that the grain sizes in the poly-Si films increase with increasing the deposition temperature of the a-Si:H precursor and with increasing the H$_2$ partial pressure in the sputtering chamber from 0.05 to 0.10 Pa. The tensile stress in the poly-Si films decreases with increasing the deposition temperature of the amorphous silicon precursor and increases with the H$_2$ partial pressure. The results are discussed considering the influence of hydrogen in the precursor layer on the process of AIC.

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5. References
[1] Nast O, Brehme S, Pritchard S, Aberle A and Wenham 2001 Solar Energy Material & Solar Cells 65 358
[2] Hwang J D, Chi T Y, Liu J C, Kung C Y and Husein I C 2006 Japan. J. Appl. Phys. 45 7675
[3] Grigorov V, Angelov O, Sendova-Vassileva M and Dimova-Malinovska D 2006 Thin Solid Films 511-512 381
[4] Pihan E, Slaoui A, Roca i Cabarrocas R and Focsa A 2004 Thin Solid Films 451-452 328
[5] Nast O and Wenham S 2000 J. Appl. Phys. 88 124
[6] Dimova-Malinovska D, Nichev H, Grigorov V, Angelov O, Sendova-Vassileva M, Sendova M and Mikli V 2007 J. Optoelectr. Adv. Mater. 9 359
[7] Cottereau P, Camplan J, Chaumonts J, Meunier R, and Bernas H 1990 NIM B 45 293
[8] Ornaghi C, Beaucarne G, Poortmans J, Nijs J and Mertens R 2004 Thin Solid Films 451-452 476
[9] Matsumoto Y and Yu Z 2001 Japan J. Appl. Phys. 40 2110
[10] Fauchet F M and Campbell I H 1988 Crit. Rev. Solid State Mater. Sci. 14 S79
[11] Igbal Z and Veprek S 1982 J. Phys. C 15 377
[12] Langsfeld P and Nickel N 2002 *J. Non-Cryst. Solids* **299-302** 778
[13] Tzenov N, Tzolov M and Dimova-Malinovska D 1994 *Renewable Energy* vol 5, part III (Elsevier Science Ltd, Pergamon, UK) p 1685
[14] Nedialkova L, Dimova-Malinovska D and Kudojarova V 1992 *Solar Energy Materials and Solar Cells* **27** 37