Structural properties of poly-Si thin films grown on ZnO:Al coated glass substrates by aluminium induced crystallisation

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The structural properties of poly-Si thin films on ZnO:Al coated glass substrates obtained by Aluminium-Induced Crystallisation (AIC) in different annealing atmospheres – air, N_2, and N_2 + H_2, have been studied by Raman microprobe spectroscopy, optical microscopy , and X-ray diffraction . The Al, ZnO:Al and a-Si films were deposited by r.f. magnetron sputtering. Annealing in forming gas led to a better structural quality of the poly-Si films, compared to annealing in air or nitrogen. The investigation of different annealing conditions in forming gas led to the conclusion that the two-step annealing technique provided AIC poly-Si films with better crystalline properties. The results indicated that the process of AIC is suitable for the preparation of poly-Si films on ZnO:Al coated glass substrates, for solar cell applications.

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1. Introduction

The formation of polycrystalline silicon (poly-Si) on low cost substrates by Aluminium Induced Crystallisation (AIC) has important applications in the development of thin film solar cells, transistors, image sensors, etc. [1,2]. Aluminium doped zinc oxide (ZnO:Al) is a transparent conducting oxide that can be prepared with high conductivity and with high transmissivity over the visible range. It can furthermore offer optical index matching, lattice constant matching and stability against a hydrogen plasma. The preparation of poly-Si thin films on ZnO:Al coated glass substrates is one of the steps that must be accomplished for their successful application in thin film silicon solar cells. Usually, AIC of bilayered structures Al/a-Si is performed in air, vacuum or nitrogen [3-7]. The properties of the resulting films have been investigated by Scanning Electron Microscopy, Transmission Electron Microscopy, Raman scattering, electrical resistivity, Hall effect measurements, etc. This has mainly been in order to study the process of crystallisation and the influence of the metal layer structure [2-7]. No attention has been focussed on the influence of the atmosphere in which the crystallization is performed.

In this paper, we report the influence of different annealing atmospheres on the structural properties of AIC poly-Si films on ZnO:Al coated glass substrates.

2. Experimental

Aluminium doped zinc oxide films were deposited on cleaned glass substrates by r.f. magnetron sputtering of a ceramic target, in an Ar atmosphere. The target was a sintered disc (4”) made from a mixture of powdered ZnO and Al_2O_3 (Al_2O_3 content 2 wt. %). The ZnO:Al films were deposited at a substrate temperature of 200 ºC and 0.5 Pa Ar pressure. For the preparation of polycrystalline silicon films, glass/ZnO:Al/Al/a-Si and glass/ZnO:Al/a-Si/Al structures were deposited. The films of Al were deposited by r.f. magnetron sputtering at a substrate temperature of T_s = 250 ºC in an Ar atmosphere, at 0.5 Pa. The first set of samples were kept for 24 hours in air, before the deposition of a-Si films, to allow native aluminum oxide formation. Un-hydrogenated a-Si layers were deposited by r.f. magnetron sputtering of a Cz c-Si target (Wacker, 9-12 Ω.cm) at T_s = 250 ºC in an Ar atmosphere, at 0.5 Pa. The thicknesses of both layers, Al and a-Si, were 150 nm.

The prepared glass/ZnO:Al/Al/a-Si and lass/ZnO:Al/a-Si/Al samples were isothermally annealed at temperatures ranging from 480 to 530 ºC, for different durations from 2 to 7 hours. Different annealing atmospheres were used: air, N_2, and forming gas (N_2+H_2). Annealing in different gas atmospheres under atmospheric pressure was performed in a horizontal tube furnace. The remaining Al surface layer was removed with a standard etch, before the structural investigations of the films. These were studied by Microprobe Raman scattering, Optical microscopy (OM) and X-ray diffraction (XRD). Microprobe Raman spectra were excited by the 514 nm line of an Ar^+ laser with a 1 μm laser spot, using a Renishaw Ramascope. XRD measurements were performed on a TUR-M-62 diffractometer using Cu Kα (λ = 1.5406 Å) radiation in a regular θ-2θ scan.

3. Results and discussion

The XRD spectra (Fig. 1) show that the films obtained by AIC are polycrystalline, with a preferential (111) crystallographic orientation of the Si crystallites which form polycrystalline grains.

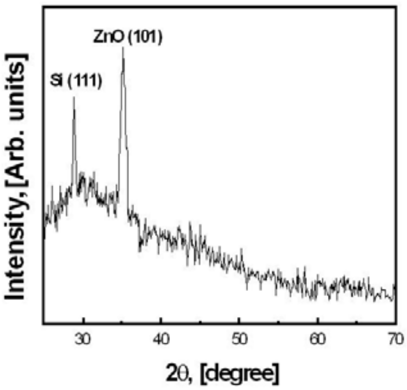


Fig. 1. X-ray diffraction spectrum of a poly-Si film on a ZnO:Al/Al coated glass substrate prepared by AIC of glass/ZnO:Al/Al/a-Si in forming gas.

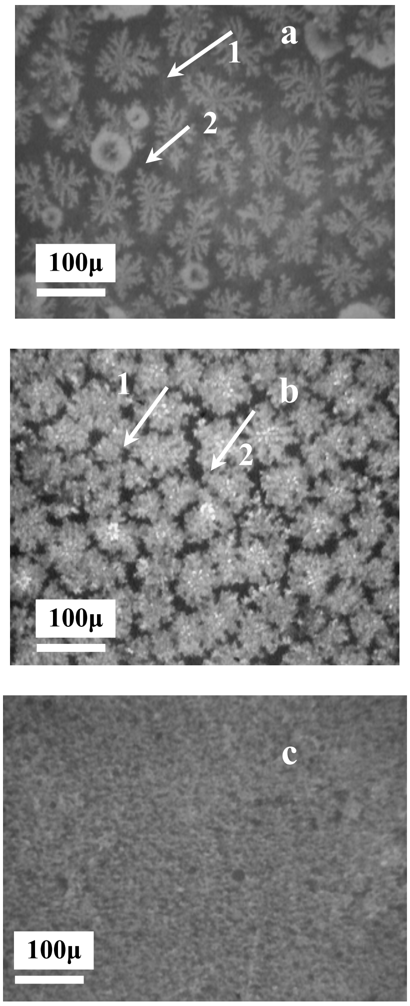
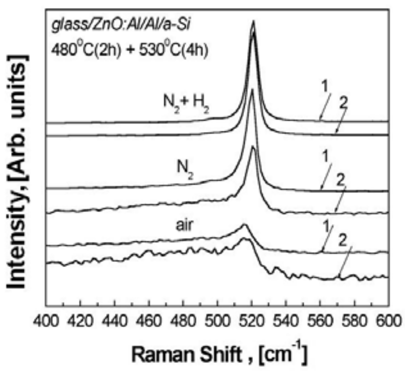


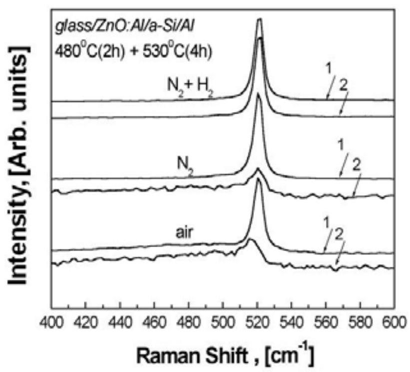
Fig. 2. Optical images of poly-Si films on ZnO:Al/Al coated glass substrates annealed at 480 (2h) and 530 ºC (4h) in different atmospheres: air (a), N_2 (b); N_2+H_2 (c).

Optical images of poly-Si thin films on ZnO:Al/Al coated glass substrates prepared by two-step annealing in different atmospheres are shown in Fig. 2. Films obtained by annealing in air and N_2 (Fig. 1a, b) exhibit large grains (dendrites) of 20-30 µm size (Fig. 2a, b, arrow 1), separated by inter-grain spaces of about 10-20 µm (Fig. 1a, b, arrow 2). When annealing is performed in an atmosphere containing H_2 (Fig. 1c) the surface of the resulting poly-Si is very smooth. The grains are very closely packed, and continuous poly-Si films are formed. The inter-grain spacing decreases to about 2-3µm.

The crystallinity of the samples after annealing was investigated by Raman microprobe spectroscopy. The Si-Si TO-like peak of a c-Si reference wafer occurs at 521.3 cm^{-1}. Microprobe Raman spectra of poly-Si films on ZnO:Al coated glass substrates, prepared by isothermal two step annealing of glass/ZnO:Al/Al/a-Si and glass/ZnO:Al/a-Si/Al stacks in different atmospheres at 480 ºC for 2h + 530 ºC for 4h are shown in Fig. 3a and 3b, respectively. Two spectra were measured for each sample - on the grain surface (spectrum 1) and between the grains (spectrum 2). All of these spectra (except those annealed in air) have a Si-Si TO-like phonon band centered in the range 520.4 to 521.3 cm^{-1}, showing the presence of only the Si crystalline phase.



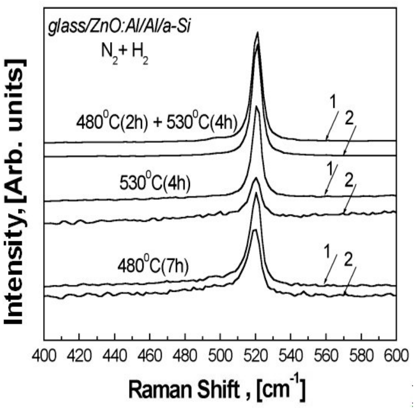
(a)



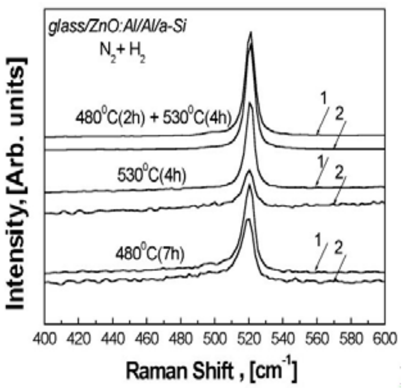
(b)

Fig. 3. Microprobe Raman spectra of samples: glass/ZnO:Al/Al/a-Si (a) and glass/ZnO:A/a-Si/Al (b), measured at grain (1) and inter-grain (2) positions, annealed in different atmospheres at 480^0C (2h) +530 ^{0}C (4h).

The microprobe Raman spectrum taken from the grains (Fig. 3a, air, spectrum 1) of the poly-Si film prepared by annealing of the structure glass/ZnO:Al/Al/a-Si in air, has a band centered at 516.2 cm^{-1}, with a Full Width at Half Maximum (FWHM) of 9.8 cm^{-1}. The Raman peak, corresponding to the inter-grain material (Fig. 3a, air, spectrum 2) has a larger FWHM – 12.8 cm^{-1}. The spectra of the samples annealed in nitrogen exhibit bands centered at 520.4 cm^{-1} and with FWHMs of 7.5 and 8 cm^{-1}, respectively. When the annealing is performed in forming gas (N_2+H_2) the positions of both Raman peaks, taken from the grain surface and from the inter-grain material, (Fig. 3a) are centered at 521.3 cm^{-1}, with a lowest value of the FWHM of 6 cm^{-1}. Similar results occur for poly-Si prepared from glass/ZnO:Al/a-Si/Al stacks. The results demonstrate that annealing in the presence of H_2 leads to an improvement in the structure of both the grains and the inter-grain material of poly-Si thin films obtained by AIC.



(a)



(b)

Fig. 4. Microprobe Raman spectra of poly-Si films prepared by AIC of glass/ZnO:Al/Al/a-Si (a) and glass/ZnO:Al/a-Si/Al (b) stacks, under different conditions, measured at grain (1), and inter-grain (2), positions.

An estimate of the grain size and the stress in the films can be deduced from the downshift and the FWHM of the Si-Si TO-like Raman peak [6-8]. It should be noted that accurate values of the grain size cannot be determined from the relationships described previously in the literature [6-8], as they depend on the structure of the grains and their boundaries. In spite of this, comparisons between spectra obtained from similar materials are valid. The grain size is inversely proportional to the FWHM of the peak, so it can be deduced that the grain size increases when annealing is performed in the presence of H_2. It is possible to suppose that H_2 stimulates the crystalline grain growth during annealing, by increasing the diffusion rates of Al and Si. The downshift of the Si-Si TO-like peak is related to the presence of stress in the polycrystalline films. From these results, it can be concluded that annealing in the presence of H_2 results in stress-free poly-Si films.

The influence of the annealing duration and temperature in an N_2+H_2 atmosphere has also been studied. Fig. 4 shows the microprobe Raman spectra of poly-Si films on ZnO:Al coated glass substrates obtained by annealing in N_2+H_2 at 480ºC for 7h, 530ºC for 4h and for two-step annealing – 480ºC for 2h followed by 530ºC for 4h, measured at grain and inter-grain positions. Both spectra of the sample annealed at the lowest temperature (480 ^{o}C) exhibit a Si-Si TO-like band centred at about 521.3 cm^{-1}, showing the presence of a crystalline phase. However, the Si-Si TO-like band is broader and asymmetric, with a shoulder at 510-515 cm^{-1} (Fig. 4b). This intermediate band can be attributed to small-grained (nano-crystalline) Si, grain boundary defects or stress. The spectra taken from the grain and inter-grain material have FWHMs of 8.8 and 10.2 cm^{-1}, respectively. Full crystallization of the structure is achieved when a two-step annealing – 480 ^{o}C for 2h +530 ^{o}C for 4h is employed. No difference in the microprobe Raman spectra is observed for the grain and the inter-grain materials in this case. The two-step annealing technique in forming gas results in poly-Si films with superior quality. Similar results were reported by us for polycrystalline Si obtained by AIC of a-Si deposited on an Al-coated glass substrate [5].

4. Conclusions

The structural properties of poly-Si films grown on ZnO:Al coated glass substrates by AIC of glass/ZnO:Al/Al/a-Si and glass/ZnO:A/a-Si/Al stacks in different atmospheres (air, N_2, and N_2+H_2) have been studied by microprobe Raman spectroscopy, optical microscopy and XRD analysis. The results indicate that the structure of the poly-Si films is improved when the annealing is performed in an atmosphere containing H_2. More significant improvement occurs for the inter-grain material. Full crystallisation after annealing in forming gas is achieved when a two-step annealing technique is employed.

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