

Effect of annealing time on aluminum-induced crystallization of silicon suboxide thin films

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Abstract. Polycrystalline silicon (poly-Si) thin films were obtained by aluminium induced crystallisation of amorphous silicon suboxide ($a\text{-SiO}_x$, $x = 0.22$) via annealing of $a\text{-SiO}_{0.22}/\text{Al}$ bilayer structures at 550 °C for 4 - 30 h. The $a\text{-SiO}_{0.22}/\text{Al}$ thickness ratio was approximately 1. According optical microscopy measurements, the crystallized fraction reached the saturation value of 85% after annealing for 20 h. The further increase in the annealing time didn't lead to an increase in this value. X-ray diffraction measurements revealed that the formed poly-Si had a strong Si (111) preferred orientation.

1 Introduction

The fabrication of large-grained polycrystalline silicon (poly-Si) thin films with large grains on foreign cheap substrates (e.g. glass) is of considerable interest for thin-film transistors and silicon solar cells technologies [1]. The preparation of poly-Si thin films on glass substrates is carried out in two stages. The first stage involves the synthesis of the amorphous silicon (a-Si) layers and then, in a second stage, a-Si is subjected to conventional solid phase crystallization (SPC), metal-induced crystallization (MIC) or liquid-phase crystallization (LIC) [2]. By the present time, having quite important advantages over other techniques, aluminium-induced crystallization (AIC), the particular case of MIC, seems the most prospective way of thin poly-Si films fabrication on glass [3]. The crystallization of a-Si by AIC implies thermal annealing of a-Si/Al layers below the eutectic temperature of the Si-Al system (577 °C) as a result of which aluminium-induced layer exchange mechanism (ALILE) takes a place [4]. Aluminum oxide (AlO_x) interfacial layer plays an important role in ALILE [5]. Acting as a permeable membrane, this layer controls the flux of Si atoms into the Al film, determining the kinetics of AIC. The AlO_x layer is intentionally prepared before the deposition of a-Si film by holding the deposited Al layer for several tens of hours in air ambient [1].

In this paper, amorphous silicon suboxide ($a\text{-SiO}_x$, $0 < x < 2$) is used instead of a-Si as a silicon source in AIC which allows eliminating the technological step associated with the formation of AlO_x layer [5]. The impact of annealing time on the AIC of $a\text{-SiO}_x$ is analyzed.

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2 Experimental details

At first, Corning Eagle XG glass substrates were ultrasonicated in an aqueous solution of sodium dodecyl sulfate surfactant, acetone, DI water, and dried using a nitrogen gun. Then, the initial Al layers ~ 220 nm thick were deposited at room temperature using sputtering with Ar plasma. Subsequently, without Al sample exposure to air, Al-coated substrates were transferred into vacuum chamber for a-SiO_x thin films deposition by the gas-jet electron beam plasma chemical vapor deposition method [6]. The thickness of a-SiO_x thin films coated onto the Al layers was ~ 220 nm. Thus, the a-SiO_{0.22}/Al thickness ratio was approximately 1. Thicknesses of Al and a-SiO_x were measured by transmission electron microscopy using a JEOL 4000 EX microscope operated at 400 kV [7]. Fourier transform infrared (FTIR) spectrometry was used for the investigation of the composition (bonded oxygen and hydrogen atomic concentration) and the bond structure of as-deposited film obtained on crystalline silicon wafer. Bruker IFS-113V Fourier spectrometer was used for the recording of FTIR spectra in the wavenumber range of 400-4000 cm⁻¹ with a 1 cm⁻¹ resolution. The procedure used for obtaining of the concentration of bonded hydrogen and oxygen is described in [8]. After the Al and a-SiO_x layers deposition, the layer structure was annealed in furnace (Nabertherm RHTC 80-710/15) at 550 °C in vacuum for duration of 2-30 hours. During the heating process, the heating rate was kept constant – 5 °C/min. Also during the heating, the samples were annealed at 400 °C for 30 min for slow and non-destructive effusion of bonded hydrogen from the a-SiO_x thin films. Optical microscope (OM) OLYMPUS BX51M was used for the investigation of the surface morphology of the samples including the continuity of formed poly-Si thin films. X-ray diffraction (XRD) was used to characterization of the crystalline properties of the samples. XRD patterns were obtained using time resolved diffractometry station (channel 5b, VEPP-3) of the Siberian Synchrotron and Terahertz Radiation Center [9]. An OD-3M position-sensitive detector was used in the conventional experimental setup with a wavelength 1.516 Å. The detector was positioned at an angle of 25°–56° to record the main silicon peaks. The acquisition time was 20 min. After intensity normalization, the signal of the empty substrate was eliminated from the signal of the sample. After annealing, the formed Al-matrix was etched by a standard etching solution (80% of phosphoric acid + 5% of nitric acid + 5% of acetic acid + 10% of DI water) at 50 °C for 20 min [3].

3 Results and discussion

According to FTIR spectroscopy, as-deposited a-SiO_x films contain ~ 18 at.% (stoichiometric coefficient $x = 0.22$) and ~ 4 at.% bonded oxygen and hydrogen, respectively.

Fig. 1 shows OM images of the glass/Al interface after annealing at 550 °C for 4 h (a), 8h (b), and 30 h (c).

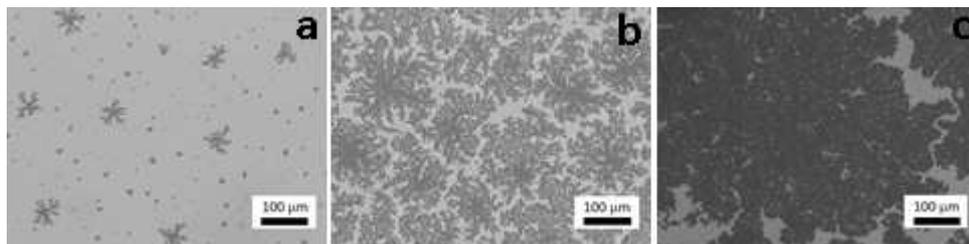


Fig. 1. Optical micrographs of samples after annealing at 550 °C for (a) 4 h , (b) 8 h, (c) 30 h.

At the images obtained from the backside of the samples, dark and white areas corresponding to poly-Si and Al, respectively, due to the lower reflectivity of Si in comparison with Al. During the annealing process, as a result of the interdiffusion of Si and Al atoms through the barrier layer, which is probably formed at the initial deposition of a-SiO_x [5] a supersaturation of Si in Al and the formation of Si nuclei occurs. Fig. 1 (a) demonstrates isolated poly-Si regions, which have conventional dendritic structure [4]. With increasing of the annealing time, these poly-Si regions increase in size in all directions in the observed plane and begin to close (Fig. 1 (b)). During the subsequent annealing, poly-Si regions form continuous sections as a result of coalescence (Fig. 1 (c)). However, the formation of a continuous poly-Si film does not occur. Thus, according to the OM images (Fig. 1a-c), one can conclude that during the aluminium-induced annealing of the a-SiO_x thin films, the conventional ALILE process proceeds with its characteristic growth morphology and the evolutionary features of the emerging poly-Si regions [10]. The macroscopic layer exchange as a result of ALILE was confirmed by scanning and transmission electron microscopy investigations of annealed samples cross sections [7].

Crystallized fraction (percentage of the surface covered by poly-Si) versus annealing time of the samples obtained on the basis of OM images is shown in Fig. 2 (a). The Si crystallites first appear on OM photos for the annealing time of 4 h. The curve has a S-shape which is typical for a phase transformation process [10]. As can be seen from Fig. 2 (a), saturation regime of crystallization process begins at 20 h and the further increase in the annealing time doesn't lead to an increase in the crystallized fraction. Apparently, the formation of a continuous poly-Si film (the saturation value of crystallized fraction equals to 85%) doesn't occur due to a lack of the sufficient Si content in an as-deposited a-SiO_{0.22} film [4, 7 10]. Thus, an increase in the crystallized fraction and, as a consequence, the fabrication of a continuous poly-Si film is possible by increasing the initial a-SiO_{0.22}/Al thickness ratio and/or by increasing Si content in as-deposited silicon suboxide thin film. But even in the case of a-Si AIC the thickness ratio should not be less than 1 [4].

The crystalline quality of the formed poly-Si was characterized by XRD. Before the XRD analysis of the annealed samples, the top layer (a mixture of aluminum, silicon, and oxygen) [7] was etched off. Etching of the upper layer made it possible to obtain a more intense signal of crystalline silicon in XRD patterns. The XRD pattern of the sample annealed for 30 h (Fig. 2 (b)) demonstrates a narrow peak centered on $2\theta = 28.4^\circ$ (θ is the angle of incidence-reflection), which corresponds to crystalline silicon with the (111) plane [11]. Peaks corresponding to other orientations were not observed in the pattern. This picture is typical of all samples annealed for 4 h and more.

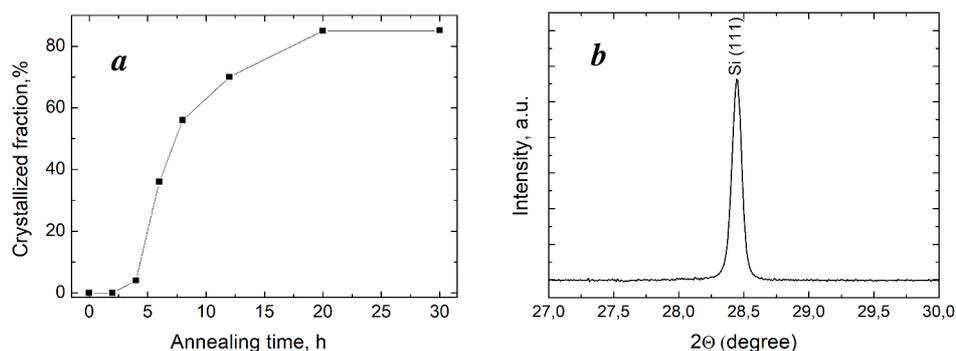


Fig. 2. (a) Crystallized fraction versus annealing time of the samples. (b) XRD pattern of the sample annealed at 550 °C for 30 h.

4 Conclusions

Poly-Si thin films were obtained by annealing of a-SiO_{0.22}/Al bilayer samples with a thickness ratio of ~ 1 at 550 °C for 4 - 30 h. According optical microscopy measurements, the crystallized fraction reached the saturation value of 85% after annealing for 20 h. Further increase in the value is possible due to an increase of an initial thicknesses ratio and/or a decrease in stoichiometry of a-SiO_x thin film. XRD measurements revealed that the formed poly-Si had a strong Si (111) preferred orientation.

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References

1. M. Jung, A. Okada, T. Saito, T. Suemasu, and N. Usami, *Appl. Phys. Exp.* **3**, 095803, (2010).
2. J. Haschke, D. Amkreutz, and B. Rech, *Jpn. J. Appl. Phys.* **55**, 04EA04 (2016).
3. J. Chen, J. Suwardy, T. Subramani, W. Jevasuwan, T. Takei, K. Toko, T. Suemasu and N. Fukata, *Cryst. Eng. Comm.* **19**, 2305, (2017).
4. O. Nast, S.R. Wenham, *J. Appl. Phys.* **88**, 124 (2000).
5. J.-H. Yoon, *Phys. Status Solidi RRL* **10**, 668 (2016).
6. E. Baranov, S. Khmel, A. Zamchiy, M. Buyko, *Phys. Status Solidi A*, **213**, 1783 (2016).
7. A.O. Zamchiy, E.A. Baranov, S.Ya. Khmel, V.A. Volodin, V.I. Vdovin, A.K. Gutakovskii, *Appl. Phys. A* **124**, 646 (2018).
8. E. Baranov, A. Zamchiy, and S. Khmel, *Tech. Phys. Lett.* **41**, 1013 (2015).
9. O.V. Evdokov, V.M. Titov, B.P. Tolochko, M.R. Sharafutdinov, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **603**, 194 (2009).
10. S. Tutashkonko, N. Usami, *Thin Solid Films* **616**, 213 (2016).
11. A.O. Zamchiy, E.A. Baranov, I.E. Merkulova, V.A. Volodin, M.R. Sharafutdinov, S.Y. Khmel, *Vac.* **152**, 319 (2018).