Aluminum-induced crystallization of silicon suboxide thin films

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Abstract
Polycrystalline silicon (poly-Si) thin films are fabricated by aluminum-induced crystallization (AIC) of amorphous silicon suboxide (a-SiO_x, x = 0.22) at 550 °C for 20 h. AIC of a-SiO_{0.22} via thermal annealing of a-SiO_{0.22}/Al bilayer structures leads to layer exchange with the formation of poly-Si films with (111) preferential orientation and high-crystalline quality-coated with a layer of a mixture of Al, Si, and O atoms with inclusions of silicon nanocrystallites. The initial a-SiO_{0.22}/Al thickness ratio approximately equal to 1 provides the formation of a discontinuous poly-Si film with a crystallized fraction of 85%, as shown by optical microscopy.

1 Introduction
Polycrystalline silicon (poly-Si) thin films on inexpensive substrates (e.g., glass) are of great interest for thin-film transistor technology and solar cell fabrication [1]. Various methods are used to transform amorphous silicon (a-Si) to poly-Si on glass, such as: solid-phase crystallization (SPC) [2], laser-induced crystallization (LIC) [3], and metal-induced crystallization (MIC) [4]. Among these techniques, MIC, particularly aluminum-induced crystallization (AIC), is considered as one of the most promising approaches to obtaining poly-Si thin films on glass. AIC allows to reduce the temperature and time of crystal grain formation in comparison with SPC, while providing a much larger size of grains (> 10 µm) and their high quality and predetermined orientation [5].

Unlike the complex LIC technique, AIC allows one to obtain large-area poly-Si films, and seems to be a more economical approach. AIC involves thermal annealing of adjacent a-Si and Al layers at temperatures below the eutectic point of the Al-Si system (577 °C). Si atoms formed due to the weakening of Si–Si bonds diffuse through the Al oxide layer into the Al layer, and then nucleation of Si grains within the Al layer occurs. Growing Si grains displace the bottom Al layer [6, 7]. The mechanism was called the aluminum-induced layer exchange (ALILE) [1]. The Al oxide interfacial layer between a-Si and Al acts as a diffusion barrier and has an important influence on the ALILE mechanism, in particular, by promoting the growth of large Si grains [7].

The possibility of using amorphous silicon suboxide (a-SiO_x, 0 < x < 2), instead of a-Si, as a silicon-containing precursor in AIC was first demonstrated in [8]. The use of a-SiO_{1.4} instead of a-Si in AIC has several advantages, such as reducing the cost of the process and eliminating the time-consuming air-exposure process after Al layer deposition for the formation of the interfacial layer of Al oxide [9].

In this letter, we investigate the possibility of AIC of a-SiO_x thin films obtained by gas-jet electron beam plasma chemical vapor deposition (GJ EBP CVD). The method is a variation of the plasma-enhanced chemical vapor deposition and based on the expansion of gaseous reactants in the form of a supersonic jet with its subsequent activation by electron-beam plasma. GJ EBP CVD method allows to obtain SiOx thin films and nanowires with high growth rates at low energy consumption and low vacuum conditions [10, 11]. The morphology and crystalline properties of layers formed by AIC were studied.
2 Experimental details

A 220-nm-thick Al layer was sputtered at a room temperature on cleaned Corning Eagle XG glass substrates and n-type (100) Czochralski (Cz) monocrystalline silicon (c-Si) wafers with a SiO₂ thermal oxide layer 80 nm thick (c-Si/SiO₂ substrate). Next, without exposure of the Al layer to air, an a-SiOₓ layer 240 nm thick was deposited by the GJE BP CVD method using a mixture of H₂, O₂ and argon-diluted 5% SiH₄ at a substrate temperature of 260 °C. Finally, to provide the ALILE mechanism, the as-deposited layer structure was annealed at 550 °C for 20 h in vacuum at ~10⁻⁷ mbar. The heating rate was kept constant at 5°C/min. After annealing, the system was cooled to a temperature below 100 °C naturally.

Fourier transform infrared (FTIR) spectrometry (Bruker IFS-113V Fourier spectrometer) was used to investigate the composition of the as-deposited a-SiOₓ film. The crystalline properties of the material were evaluated by X-ray diffraction (XRD) (the resolved diffractometry station of the Siberian Synchrotron and Terahertz Radiation Center) and Raman spectroscopy (T64000 Horiba Jobin–Yvon, λ = 514.5 nm). An optical microscope (OM) integrated with a Raman spectrometer was used to investigate the surface morphology of the sample. The structure of the layers was studied by transmission electron microscopy (TEM) of (110) cross-section specimens using a JEOL 4000 EX microscope operated at 400 kV. Visualization of the chemical elements distribution (elemental mapping) was performed by energy-dispersive X-ray spectroscopy (EDAX) using a Hitachi SU8220 scanning electron microscope (SEM).

3 Results and discussion

According to FTIR spectroscopy, the as-deposited a-SiOₓ films contain ~18 at.% bonded oxygen (stoichiometric coefficient x = 0.22) and a negligible amount of bonded hydrogen. Raman spectroscopy reveals that the material has an amorphous structure [12].

Cross-sectional TEM images of a sample on a c-Si/SiO₂ substrate before and after AIC are shown in Fig. 1a, b, respectively. The thicknesses of the Al layer on the c-Si/SiO₂ substrate and the a-SiO₀.₂₂ layer on Al in the initial sample are approximately the same and are about 220 nm. The Al/a-SiO₀.₂₂ interface and the a-SiO₀.₂₂ surface have roughness of about 30 nm. Thus, the a-SiO₀.₂₂/Al thickness ratio was approximately 1. Annealing of the structure led to the ALILE process, mediated by the Al oxide membrane formed at the initial stage of a-SiO₀.₂₂ growth [8], with the formation of a poly-Si layer on the c-Si/SiO₂ substrate (Fig. 1b). The high-resolution TEM (HR TEM) image in the left inset to Fig. 1b shows a fragment of the poly-Si layer formed as a result of the ALILE process and the interface between thermal SiO₂ and poly-Si. One can see the (111) atomic planes, the distance between which is 0.314 nm and corresponds to bulk silicon [8]. The material has a perfect crystalline structure without defects and dislocations. These results are in good agreement with XRD data (not shown) which demonstrate a strong Si (111) peak while any other peaks are absent.

The HR TEM image in the right inset to Fig. 1b confirms the formation of silicon nanocrystallites (Si-NC) with a size of about 10 nm in the top layer of the annealed sample. Apparently, during the AIC process, the formation of Si-NC is initiated by contact of a-SiOₓ remaining in the top layer with Al “plumes” [13] which are pushed up into this layer by Si grains growing within Al [7].

To obtain more information on the chemical composition of annealed samples, we performed EDAX mapping.
analysis of aluminum, silicon and oxide atoms (Fig. 2a) in a cross-sectional SEM image of an annealed sample on a c-Si/SiO2 substrate. An example of such an image is presented in Fig. 2b. EDAX analysis clearly shows each layer of the annealed stack, in particular the Si layer formed on the substrate as a result of AIC, whose structure was described above. In addition, according to the element mapping results, the poly-Si layer formed is discontinuous. During AIC of a-Si, a continuous poly-Si film forms at an initial a-Si/Al thickness ratio of not less than 1 [4]. In the case of AIC of a-SiO0.22 at an a-SiO0.22/Al ratio equal to 1, the number of silicon atoms in the initial silicon suboxide film is not sufficient for the formation of a continuous poly-Si layer. In addition, EDAX analysis confirmed that the top layer formed by the ALILE process consists of a mixture of Al, Si, and O atoms, as can be seen in Fig. 2a. In the future, we are going to investigate this layer in more detail.

Figure 3a, b shows the Raman spectra of an annealed sample on a glass substrate taken from the bottom and top of the sample, respectively. Optical microscopy (OM) pictures of the analyzed areas are shown in the insets to Fig. 3a, b. OM of the bottom side of the sample (inset to Fig. 3a) demonstrates that the obtained poly-Si film is discontinuous, the crystallized fraction is 85%, and there is a considerable number of narrow gaps (bright areas) between Si grains (dark areas). Raman spectroscopy revealed that the film formed was poly-Si, as evidenced by the presence of a symmetric sharp peak (transverse optical mode) at 519.6 cm−1 (Fig. 3a). For poly-Si, the peak position is shifted by ∼0.5 cm−1 relative to the reference Cz-Si wafer (not shown), which may indicate a slight stress in the material formed [14]. The similarity of the full width at half maximum values of the Raman peaks of the poly-Si films and the reference Cz-Si wafer suggests the high-crystalline quality of the material [6]. The Raman spectrum taken from the top of the sample (Fig. 3b) is similar to that of nc-Si. The crystallite size and crystallinity derived by the standard decomposition of the spectrum into Gaussian curves were 6.4 nm and 48%, respectively [15].
4 Conclusions

Poly-Si thin films were fabricated from a-SiO$_{0.22}$/Al stacked layers by the AIC process at 550 °C for 20 h. TEM and SEM confirmed the ALILE mechanism of the process. An a-SiO$_{0.22}$/Al thickness ratio equal to 1 provided the formation of a discontinuous poly-Si film with a crystallized fraction of 85% calculated from OM images. Raman spectroscopy revealed the high-crystalline quality of the material. TEM and XRD methods showed the (111) preferred orientation of Si grains. According to the EDAX data, the top layer formed as the result of ALILE consists of a mixture of Al, Si, and O atoms with inclusions of silicon nanocrystallites, whose presence was revealed by TEM and Raman spectroscopy. The results show that the use of a-SiO$_x$ holds promise for the development of AIC.

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