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Short communication

Strong preferential (111) orientation of large-grained polycrystalline silicon thin films prepared by AIC

ZHENGXIA TANG, HONGLIE SHEN*, LINFENG LU, SHUGUANG SONG,, YUGANG YIN, DAN LI,
HAIBIN HUANG

College of Materials Science & Technology, Nanjing University of Aeronautics & Astronautics, Nanjing, China

Strong preferential (111) orientation polycrystalline silicon thin films were prepared on glass and quartz substrates by AIC process. Al and amorphous silicon layers were deposited by vacuum evaporation and r.f. magnetron sputtering respectively. The samples were annealed at 500□ for several hours. The mechanism of preferential (111) orientation is suggested to be the integrative effect of naturally oxidization alumina membrane, high annealing temperature and quartz or glass substrates. The poly-Si is of large grains about 30-40 μm and high crystalline quality according to OTM and Raman spectra. The films are high p-type conduction with a resistivity of 6.9×10^{-2} Ω•cm.

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1. Introduction

Polycrystalline silicon thin films prepared by AIC (aluminum-induced crystallization) on low cost substrates such as glass are of great interest for solar cells [1,2]. Although the AIC poly-Si is not fit for the absorber layer of solar cell due to the high aluminum content of about 10^{19} cm^{-3}, it can be used as a seed layer for preparing large-grained poly-Si absorber layer using its excellent structural material quality [3]. In order to use the AIC poly-Si as crystallization template, a benefit orientation is needed [4]. The first step to obtain a benefit orientation is to understand the mechanism behind the process inducing different preferential orientation. So far the research about the mechanism of AIC poly-Si preferential orientation is not sufficient. J. Schneider et al. [5] and M. Stöger-Pollach et al. [6] studied the mechanism of preferential (100) orientation. They mainly discussed the effect of temperature and the interlayer alumina membrane. Their conclusions were not completely consistent with each other, especially concerning the effect of the interlayer alumina membrane. J. Schneider et al. suggested that crystallineγ-Al_2O_3 increases the nucleation attempts close to the (111) orientation and M. Stöger-Pollach et al. suggested that the (111) lattice planes of γ-Al_2O_3 lead to a (100) orientation of the growing Si nucleus. In our work, AIC poly-Si films with strong preferential (111) orientation were prepared and the structural properties were analyzed by XRD. The optical transmission and reflectance microscopy and Raman measurements were performed to characterize the surface morphology and optical properties. The mechanism of preferential (111) orientation is proposed.

2. Experimental

Glass (Corning Eagle 2000) and quartz were used as substrates. The substrates were cleaned with acetone, ethanol and distilled water. Al layers (about 100nm) were deposited by vacuum evaporation at a pressure of 2.0×10^{-3}Pa and Al pellets (4 N) were used as evaporation sources. Al films were exposed to air for several hours to form an alumina membrane. Amorphous silicon layers (300-600nm) were deposited by r.f. magnetron sputtering (power 100 W, Ar pressure 1.5Pa). An isothermal anneal of the substrate/Al/a-Si bi-layer structures was performed in Ar or N_2 atmosphere. The samples were put into the furnace at room temperature first. The furnace temperature rose to 500 °C with the rate of 10□/min and kept at 500□ for several hours, and finally cooled to room temperature naturally.

Surface Profilermeter (ABIOS XP-1) was used to measure the thickness of the films. X-ray diffraction (XRD, Bruker D8 Advance) measurements were performed using Cu Kα (λ = 1.5406 Å) radiation in a regular θ-2θ scan. Raman microprobe spectroscopy (RMS, T64000) using an Ar^+ laser (wavelength 514.5 nm) with a 5 μm laser spot, equipped with an optical reflectance microscopy, was used to evaluate the crystalline quality of the samples. Optical transmission and reflectance microscopy (OTM/ORM; CMM-50) was used to characterize the surface morphology of the poly-Si films. Four-point probe (KDY-1) measurements were employed to study the electrical properties of the poly-Si films. The conduction type was measured by thermal probe method.

3. Results and discussion

3.1 Structural properties

X-ray diffraction measurement provides information on the structural properties and crystalline quality. XRD is also possible to determine the dominant crystal grain orientation in a polycrystalline material [7]. The XRD measurements were performed on samples (a) and (b). The bi-layer structures of samples (a) and (b) were glass/Al(100 nm)/a-Si(300 nm) and quartz/Al(100nm)/a-Si(600 nm) respectively. After annealing, the Al matrix got to the top of the sample and was removed prior to XRD by wet-chemical etching with standard Al etching solution. The XRD results of the sample are shown in Fig. 1. The films on glass and quartz are both with strong preferential (111) orientation of silicon crystalline. Similar result was reported on poly-Si thin films grown on ZnO:Al coated glass substrates by AIC[8], and our result is better than theirs. It is evident that the (111) peak of poly-Si on quartz is much stronger than that on glass. Although the a-Si films on quartz are only twice as thick as that on glass, the (111) peak of the poly-Si on quartz is about six times as strong as that on glass. This demonstrates that the much stronger (111) peak of the poly-Si on quarts can not only be attributed to the a-Si thickness but also to the quartz substrate itself and so quartz is more benefit for AIC process than glass. It is most probably that the expansion coefficient of quartz is lower than that of glass and during the annealing progress quartz is more stable and induces less stress which is detrimental to the growing of poly-Si.

The interlayer alumina membrane between Al and a-Si influences the orientation of AIC poly-Si. When heated to 500 ^{o}C, the naturally oxidized alumina film changes to porous crystalline γ-Al_2O_3 with grain boundaries and cracks which are the advantage position for aligning the Si nucleus in (111) orientation [6]. The work of E. Pihan et al [9] showed that glass and SiO_2 substrates are easier to induce (111) oriented AIC poly-Si. It could be suggested that the strong preferential (111) orientation here is the integrative effect of naturally oxidized alumina membrane, high annealing temperature and quartz or glass substrates.

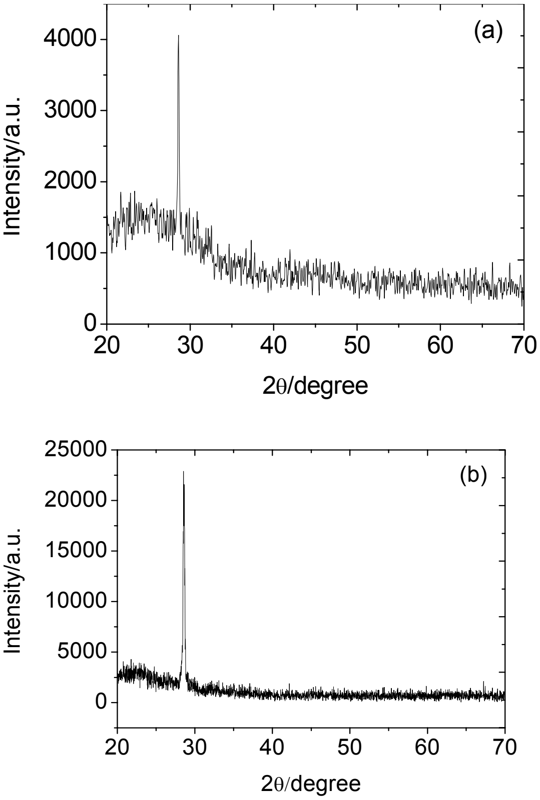

Fig. 1. XRD spectra of the films on glass and quartz substrates treated by AIC process. The Al matrix was removed prior to XRD by means of a wet - chemical etching. (a) glass substrate; (b) quartz substrate.

3.2 Surface morphology

The optical microscope image provides a quick estimate of the film's surface morphology and crystalline quality and is therefore a very useful diagnostic tool in c-Si thin-film work [9]. Before annealing, the glass/Al(100nm)/a-Si (420 nm) samples are opaque and no image can be seen in OTM. After annealing at 500 ^{o}C for 7 hours, the film exhibits the large grains of about 30-40 μm with dendrites in it in OTM (Fig. 2(a)). The dendrites are rounded by a lots of grey clusters. After wet-chemical etching by standard Al etching solution for 20 minutes, the film also exhibits dendrites (Fig. 2(b)) in OTM. But there are no clusters around the dendrites any more. According to these phenomena, it can be considered that the clusters around the dendrites are aluminum. The resistivity of the as annealed samples (see section 3.4) can also support this assignment. The phenomena reveal that the layer positions of aluminum and silicon exchanged during the annealing, which is the main process of AIC [10]. Fig. 2(c) is the ORM image of the same sample of Fig. 2(b). From this image we can obviously see that the film is continuous with dendrites in it.

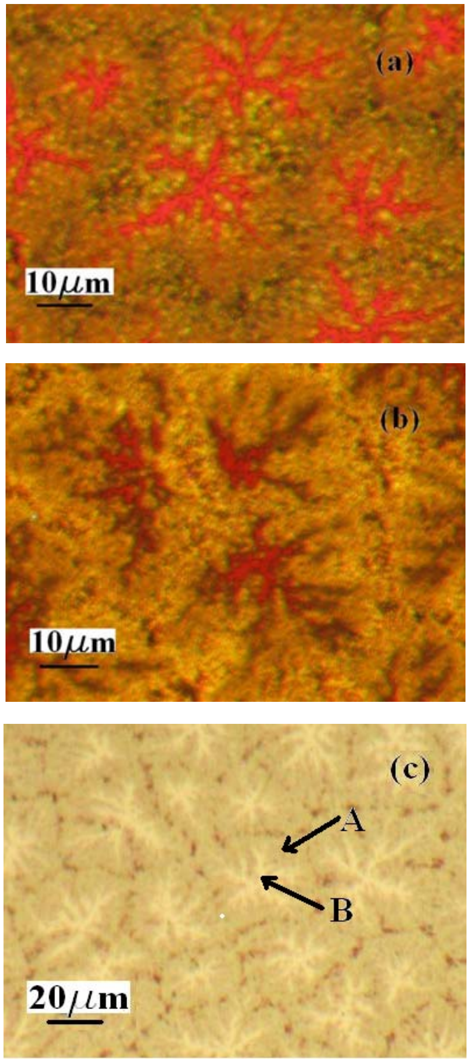

Fig. 2. The OTM/ORM micrographs of the AIC samples. The bi-layer structure was Glass /Al (100nm) / a-Si (420nm). (a) The OTM micrographs of the sample annealed at 500 for 7 hours; (b) The OTM micrographs of the sample annealed at 500 for 7 hours and the surface Al matrix were removed by wet-chemical etching; (c) The ORM micrographs of the sample annealed at 500 for 7 hours and the surface Al matrix were removed by wet-chemical etching.

3.3 Optical properties

As section 3.2 shows, for large-grained poly-Si thin-films, the grain structure of the samples is visible in optical microscopy. It is therefore possible to select specific grains with particular material quality with an optical microscope and then perform Raman measurements on these selected grains [7]. A focused green laser beam (λ =514.5 nm) was used for these Raman measurements. Such a light has a penetration depth about 1 μm in c-Si [7]. For comparison, the result obtained on a c-Si wafer is also shown in Fig. 3(a). The glass/Al(100 nm)/a-Si(420 nm) samples were annealed at 500 ºC for 7h and the Al matrix was removed prior to measurement. The Raman peak of a c-Si wafer is typically at 521 cm^{-1}. And the Raman peak of point A between dendrites (Fig. 2(c)) appears at near 519.7 cm^{-1} (Fig. 3(a)), showing the presence of poly crystalline phase in the Si film. The poly-Si peak here exhibits a decrease in frequency and a broadening comparing to the c-Si peak. In reference [11], Fernando Cerdeira et al. reported that as the carrier concentration of p-type crystalline silicon increased, the Raman spectra peaks exhibited a remarkable decrease in frequency and a considerable broadening. Similar result was reported on heavily B-doped and P-doped polycrystalline silicon thin films [12]. The decrease of Raman peak wave number and broadening of peak in poly-Si prepared by AIC is likely due to the p-type doping of aluminum. The Raman spectra (Fig. 3(b)) of point B in Fig. 2(c) exhibit two peaks: a broad peak near 480 cm^{-1} and a sharp peak near 519 cm^{-1}, which are usually attributed to amorphous and crystalline silicon phases, respectively [13,14]. It is likely that the material in point B (dendrite) is with amorphous and poly crystalline silicon phases. More specific and detail explanation will be presented in our coming paper.

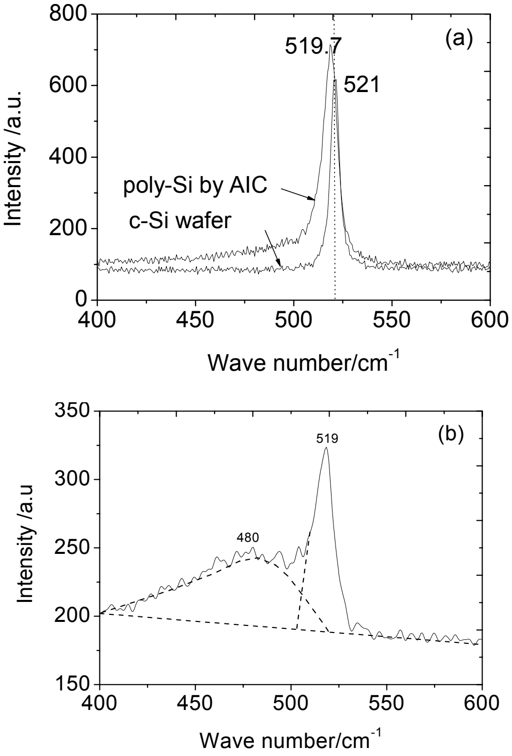

Fig. 3. Raman spectra of the film formed by AIC on glass substrate. The Al matrix was removed prior to measurement by means of a wet-chemical etching. (a) from poly-Si between dendrites and from c-Si wafer; (b) from dendrites.

3.4 Electrical properties

Table 1 shows the resistivity of sample glass/Al(100 nm)/ a-Si(300 nm) before annealing, after annealing at 500 ºC for 3h and after etching. As the film is bi-layer and the layers exchanged each other during the AIC process, the thickness of surface film is not accurate. In order to be convenient for comparison, we calculated the resistivity assuming the thickness is 300 nm for all films. Before annealing, the surface is amorphous silicon with resistivity of 5.0×10^4 Ω•cm. After annealing, Al moved to the upper surface and amorphous silicon changed to polycrystalline silicon as the underlying layer. So the resistivity of the film reduced dramatically to 4.5×10^{-4} Ω•cm. After Al layer was removed, the surface was polycrystalline silicon and the resistivity became to 6.9×10^{-2} Ω•cm. The film is high p-type conduction due to aluminum content in the silicon layer. Though it is not fit for absorber layer for solar cell [15], it can function as a built-in back surface field [4].

Table 1. The resistivity of sample glass/Al(100nm)/a-Si(300 nm).

	Before annealing	After annealing	After etching
Resistivity /Ω.cm	5.0×10^4	4.5×10^{-4}	6.9×10^{-2}

4. Conclusions

Poly-Si films with strong preferential (111) orientation were prepared by AIC process. The mechanism is suggested to be the integrative effect of naturally oxidization alumina membrane, high annealed temperature and quartz or glass substrates. The OTM/ORM micrographs show that the poly-Si is of large grains about 30-40 μm. Raman spectra demonstrate that the films are poly-Si with high crystalline quality. The resistivity of the films is 6.9×10^{-2} Ω•cm and the films are high p-type conduction due to aluminum content in the silicon layer. This kind of poly-Si film prepared by AIC process will be good for epi-growth of high quality Si layer for solar cell application.

Acknowledgements

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[*] Corresponding author: hlshen@nuaa.edu.cn