

Polycrystalline silicon thin film prepared by aluminum-induced crystallization with native silicon oxide at the aluminum and silicon interface

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Polycrystalline Si (poly-Si) thin films with the largest grain size of about 100 nm were prepared by aluminum-induced crystallization with native SiO₂ at the Al and Si interface. The Al and amorphous (a-Si) were deposited by radio frequency magnetron sputtering. The surface of the poly-Si thin film is smooth. The poly-Si thin film has double layers and the upper layer has better crystalline quality. Both the smooth surface and the high crystalline quality of the upper layer make the poly-Si thin film from a-Si/Al structure more suitable for further epitaxy.

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1. Introduction

Polycrystalline silicon (poly-Si) thin films prepared by aluminum-induced crystallization (AIC) on low cost substrates such as glass sheets are of great interest for solar cells. Now, 8 % efficient poly-Si solar cell has been fabricated based on AIC [1]. Although the AIC poly-Si is not fit for the absorber layer of solar cell due to the high aluminum content, it can be used as a seed layer for preparing large-grained poly-Si absorber layer using its excellent structural material quality. It is well known that a native oxide at the interface between the Si and the Al layers plays an important role in the mechanism of AIC [2-4]. Both native Al₂O₃ and SiO₂ can act as the native oxide and they have the similar mechanism, namely part of Al₂O₃ or SiO₂ is transformed by Al into an Al_xSi phase which provides a diffusion channel for the Si and Al atoms [2,5,6]. So far, most of study on AIC is based on native Al₂O₃ as a diffusion channel and that based on native SiO₂ is relatively much less. In our previous work, we prepared preferential (111) orientation poly-Si thin film by AIC with a native aluminum oxide at the Al/Si interface [7] and later we found that the film had double layers and the lower layer had high crystalline quality [8]. But the high quality layer is covered by the upper layer with bad quality and the latter is not easy to be removed. Considering the fact that native SiO₂ has a similar effect on AIC process as native Al₂O₃ and a-Si /native SiO₂/Al is the inverse structure to Al/native Al₂O₃/a-Si one, the poly-Si prepared by AIC with native SiO₂ should have double layer and the upper layer is of high crystalline quality. So we prepared AIC poly-Si

using a-Si /native SiO₂/Al structure and consequently we did gain poly-Si thin film with double layer and the upper layer was of high quality. The crystalline structure, morphology and crystalline quality of the poly-Si thin films were characterized and were compared with the poly-Si prepared by Al/native Al₂O₃/a-Si structure.

2. Experimental

Corning Eagle 2000 glass was used as substrate. It was sequentially cleaned with acetone, ethanol and deionized water. Al (40 nm or 60nm)/native Al₂O₃/a-Si (240 or 360 nm) and a-Si (240 nm)/native SiO₂/Al (40 nm) structures were prepared by radio frequency magnetron sputtering. After a base pressure of 4.0×10⁻⁴ Pa was reached, Al layer was deposited by direct current magnetron sputtering in argon atmosphere of 0.05 Pa at 70 W and a-Si layer was deposited by radio frequency magnetron sputtering in argon atmosphere of 0.05 Pa at 100 W. A native Al₂O₃ thin film at the Al /a-Si interface was formed by exposing Al layer to air for 30 hours before the a-Si layer deposition and a native SiO₂ thin film was formed by exposing a-Si layer to air for 47 hours before the Al layer deposition. Isothermal anneal of the structures was performed in Ar atmosphere at temperatures of 350 °C - 500 °C. The furnace temperature rose from room temperature to set temperature at a rate of 10 °C/min and kept at set temperature for certain time, following which the system was cooled down to room temperature naturally. For the following discussion we use "Al/a-Si structure" and "poly-Si (Al/a-Si)" to

denote the Al/native Al_2O_3 /a-Si structure and poly-Si prepared from it, and the “a-Si/Al structure” and poly-Si (a-Si/Al) to denote the a-Si/native SiO_2 /Al structure and poly-Si prepared from it, respectively. After annealing, Both poly-Si (Al/a-Si) and poly-Si (a-Si/Al) thin films were etched in a standard Al etching solution (80 parts phosphoric acid, five parts nitric acid, five parts acetic acid and ten parts deionized water at 55 °C for 20 min). After the poly-Si (a-Si/Al) film was dipped in diluted HF solution (1:200) further, one layer was stripped off and was transferred to a piece of glass for characterization.

X-ray diffraction (XRD, Bruker D8 Advance) measurements were performed using $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation in a regular θ - 2θ scan. Surface Profilermeter (ABIOS XP-1) was used to measure the thickness of the film. Raman microprobe spectroscopy (RMS, T64000) using an Ar^+ laser (wavelength 514.5 nm) with a 1 μm laser spot, equipped with an optical reflectance microscopy, was used to evaluate crystalline quality. Optical transmission/reflection microscopy (OTM/ORM, Shanghai Changfang Optical Instrument Co., LTD. CMM-50) and scanning electron microscopy (SEM, LEO 1530VP) with operating voltage of 5 kV were used to characterize morphology.

3. Results and discussion

3.1 Structural property

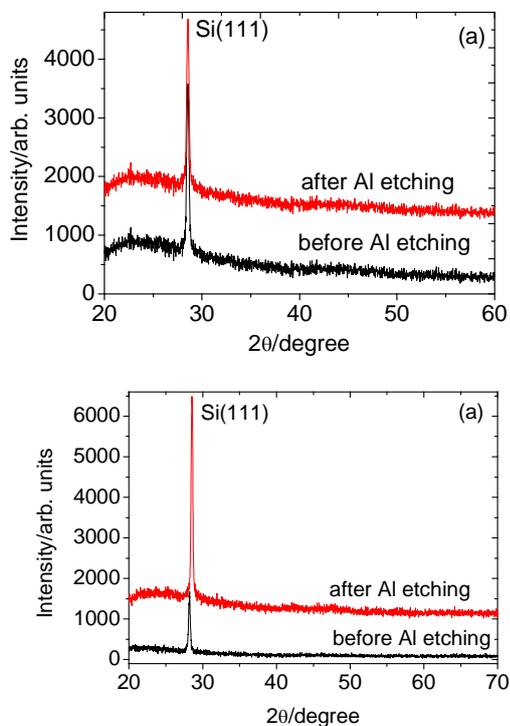


Fig. 1. XRD spectra of (a) poly-Si (a-Si/Al) and (b) poly-Si (Al/a-Si) thin films.

Fig. 1 is the XRD spectra of the a-Si(240nm)/Al(40nm) (Fig. 1 (a)) and Al(40nm)/a-Si(240nm) (Fig.1 (b))

structures annealed at 500 °C for 5 h. The results show that all the films are poly-Si with strong preferential (111) orientation. Our previous research on the AIC of Al/a-Si structure when the Al layer was deposited by vacuum thermal evaporation revealed similar result [7]. Before Al etching, the XRD spectra show that 2θ angles of poly-Si (a-Si/Al) and poly-Si (Al/a-Si) are 28.5 ° and 28.2 °, respectively. The standard Si(111) 2θ angle is 28.5 °. The main process of AIC is the exchange of aluminum and silicon [2]. So after annealing, a-Si/Al and Al/a-Si structures changed to Al+(Si)/poly-Si and poly-Si/Al+(Si) structures, respectively. After Al on the poly-Si surface was removed, neither the XRD intensity nor the 2θ angle of the poly-Si (a-Si/Al) obviously changed, while the intensity of the poly-Si (Al/a-Si) thin film became much higher and 2θ angle was shifted from 28.2 ° to 28.5 °. It indicates that aluminum on the poly-Si (Al/a-Si) thin film induces stress in the film and after Al removal the stress is released. While on the other hand, though some Al remains on the surface of poly-Si (a-Si/Al) thin film, most of Al moved to where under poly-Si thin film by the exchange mechanism and it seems that the aluminum between poly-Si film and glass substrate does not induce stress in poly-Si (a-Si/Al) thin film.

3.2 Morphology

OTM and ORM images of a-Si(360 nm)/Al(60 nm) structure on the backside of the poly-Si through glass are shown in Fig. 2. The stack was annealed at 425 °C for 5 h. Comparing with the poly-Si (Al/a-Si), the OTM image of the poly-Si (a-Si/Al) thin film shows similar large grain with orange dendritic formations in the center. The largest grain is about 100 μm which is the largest created by AIC technique ever reported. Zou et al. [9] reported the largest grain about 93 μm but the annealing time was about 20 h and it is too long. The annealing time is 5 h here and it is acceptable.

It is needed to point out that the Al/a-Si structure prepared here was more difficult to crystalline than the a-Si/Al structure with the same film thickness. The a-Si(240nm)/Al(40nm) can be completely crystallized by annealing at 400 °C for 5h. While the Al(40nm)/a-Si(240nm) structure can not be completely crystallized under temperature below 500 °C for 5 h. And when both the above mentioned structures were annealed at 500 °C for 5 h, the grains of poly-Si(Al/a-Si) were smaller than that of poly-Si(a-Si/Al). That is because that Al is easier to oxidize naturally than Si and although the Si was oxidized a little longer than Al, the native SiO_2 membrane was thinner than the native Al_2O_3 membrane. Even though the native SiO_2 membrane is as thick as native Al_2O_3 membrane, when annealed at 500 °C, it will change into Al oxide and an Al_xSi phase [5] or $\text{SiO}_x/\text{AlO}_y$ and the membrane became thinner [6]. So the Si oxide in a-Si/Al structure is equivalent to a thinner Al oxide of Al/a-Si structure. So the a-Si of a-Si/Al structure here has a higher crystallization rate. As we all know AIC with lower crystallization rate

will induce larger grain size. It is the same reason for the a-Si/Al structure to be easier crystallize at lower temperature than the Al/a-Si structure.

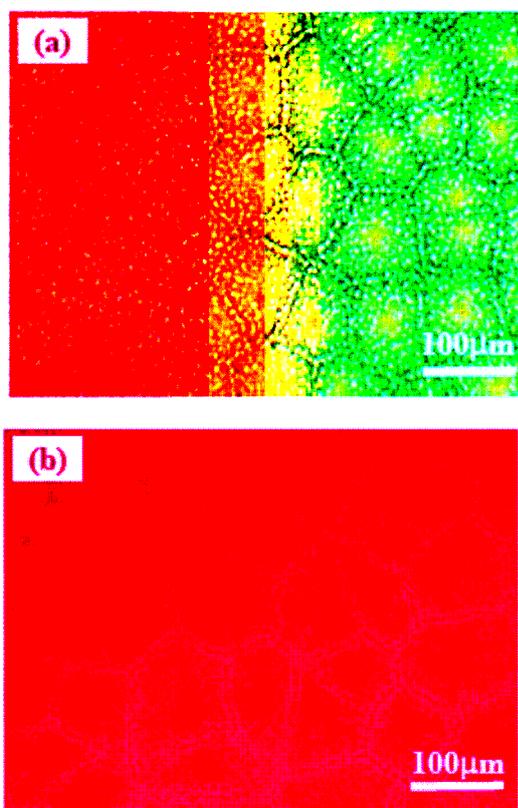


Fig. 2. (a) OTM and (b) ORM images of a-Si(360 nm)/Al(60 nm) on the backside through glass. It was annealed at 425 °C for 5 h.

The ORM image on the backside of the poly-Si through glass side shows obvious dendritic formations too. It is opposite to the Al/a-Si structure which has dendrite formation on the poly-Si surface but no dendritic formations in ORM image on the backside of the poly-Si through glass side. The orange dendrite formations are amorphous silicon [7,8]. It is easy to understand that it is because a-Si/Al and Al/a-Si are inverse structures and after the aluminum-induced layer exchange process (ALILE) the poly-Si and Si(Al) layers are inverse too. And in Al/a-Si structure amorphous silicon is on the upper layer, so in a-Si/Al structure it should be opposite. The difference is that ORM image of Al/a-Si on the backside of the poly-Si through glass side shows obviously grain boundaries [7,8], while the ORM image (not showed here) on the poly-Si surface shows no dendritic formations or grain boundaries but a smooth uniform appearance.

In the experiment, occasionally we found an interesting unclosed wheatear formations not ever reported for the poly-Si thin film prepared by AIC. We prepared a-Si/Al structure leaving some region with only Al layer but no a-Si under it. The Al and silicon layers are 40 nm and 240 nm, respectively. After the sample was annealed at 350 °C for 5 h, a row of wheatears like grains were found between the region with and without a-Si layer in ORM

(Fig. 3). The right lower part was without Si layer and the left upper part was with Si layer. The region with Si layer was not completely crystallized and only parts of aluminum and silicon changed their positions. Grains of about 20-40 μm size and grain interface can be seen, while after it is completely crystallized at 500 °C for 5 h, ORM image shows no grains and grain boundaries any more. Nast et al. [2] elucidated the nucleation and growth mechanism of AIC of Al/a-Si structure and they proposed a diffusion-controlled model. With that model, they discussed that there is an effective diffusion distance of adjacent grains, and when it begins to overlap, the competition for the available Si atoms dissolved in the Al layer occurs and till at last the adjacent grains grow overlap and the crystallization process completes. Schneider et al. verified the theory with experiments [10]. The mechanism of nucleation and growth process in AIC of a-Si/Al structure is similar. In the left upper region of Fig. 3, Si grains are rounded by adjacent grains and there exists the competition for the available Si atoms, so the Si grains form closed polygon formations. While there is no Si grain in the Al layer without Si under layer and so there are no competitions at the direction to the region without Si layer for the grains at the border with and without Si layer. So the grains grow up and become unclosed wheatear formations.

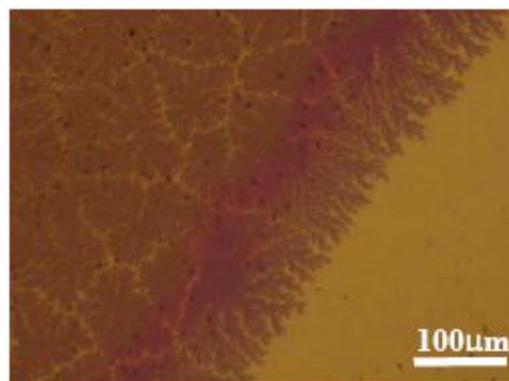


Fig. 3. ORM image of a-Si/Al structure annealed at 350 °C for 5 h.

3.3 Poly-Si(a-Si/Al) thin film after etching

The a-Si(240nm)/Al(40nm) structure annealed at 500 °C for 5 h was etched with Al etching solution for 20 min and the ORM image is shown in Fig. 4 (a). Different from the ORM image before Al etching, obviously grain interfaces can be seen in the ORM image after Al etching. Comparing with the poly-Si(Al/a-Si) thin film, the surface of the poly-Si(a-Si/Al) thin film is smooth and without Si island. This makes poly-Si(a-Si/Al) thin film more suitable for epitaxy than poly-Si(Al/a-Si).

Double layers of poly-Si (Al/a-Si) thin film were discussed in our previous work [8]. Here it was found that poly-Si (a-Si/Al) thin film has double layers too. After the sample was annealed at 400 °C for 5 h and etched by Al etching solution for 20 min, it was further etched by HF

solution (1:200) for 5 min. Then the upper layer of the film stripper off and was transferred onto a piece of glass and the lower one was still slicked on the origin glass substrate.

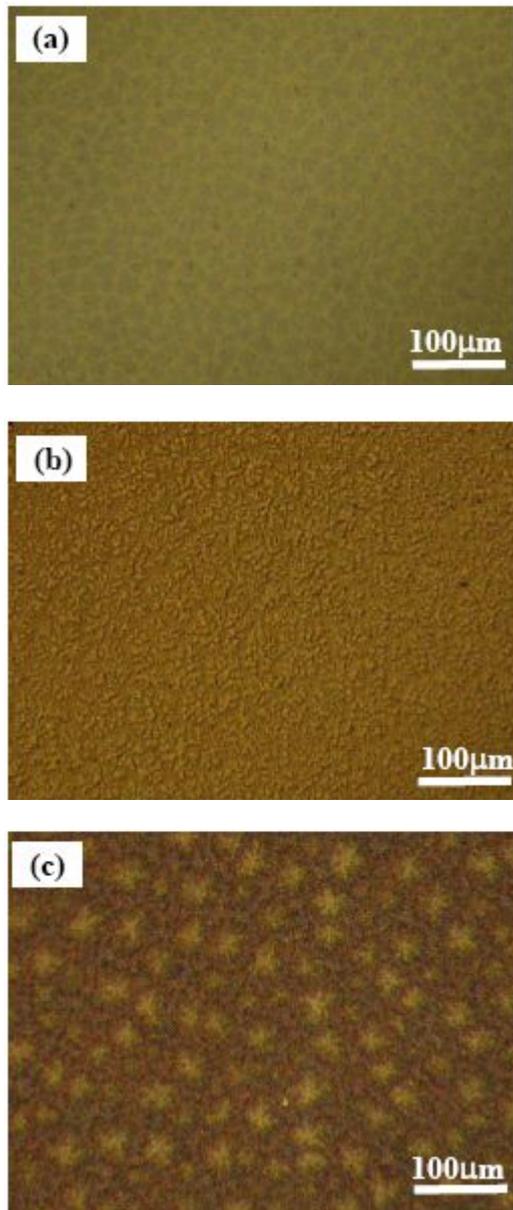


Fig. 4. (a) ORM image of the a-Si/Al structure after annealing at 500 °C for 5 h and Al etching, ORM of (b) upper layer and (c) lower layer of the a-Si/Al structure after annealed at 400 °C for 5 h and etched by diluted HF solution (1:200) for 5 min.

Fig. 4 (b) and (c) show the ORM images of the upper and lower layer, respectively. Fig. 4(b) shows that the upper layer surface is rough and some silicon at the grain interfaces were etched off by HF solution (1:200). It is needed further research why HF solution (1:200) can etch the silicon at the grain interfaces. The lower layer is with yellow dendritic formations which should be a-Si. It is opposite to poly-Si (Al/a-Si) thin film, in which the a-Si is in the upper layer surface.

3.4 Crystalline quality

Fig. 5 shows the Raman spectra obtained on the upper layer (solid line) and on the lower layer (dot line) of a poly-Si(a-Si/Al) thin film. Narrow Raman peaks at 519.7 cm^{-1} and 514.4 cm^{-1} were obtained on the upper layer and the lower layer, respectively, showing the existence of poly-Si. But the latter is shifted much to the lower wave number and the spectrum is asymmetric showing the existence of a-Si phase too. In addition to that the peak position of the spectrum on the upper layer is shifted less than that on the lower layer comparing to single crystalline wafer, the intensity of the peak is stronger and the full width at half maximum is narrower too. That indicates that the crystalline quality of the upper layer poly-Si is much better than the lower layer. It is opposite to the poly-Si (Al/a-Si) thin film in which the lower layer is of better crystalline quality [8]. It is easy to be understood that the inverse poly-Si crystalline quality is because the inverse structures of a-Si/Al and Al/a-Si. Besides the good morphology mentioned in sections 3.2 and 3.3, the better crystalline quality of the upper layer also makes the poly-Si (a-Si/Al) thin film more suitable for epitaxy than poly-Si (Al/a-Si).

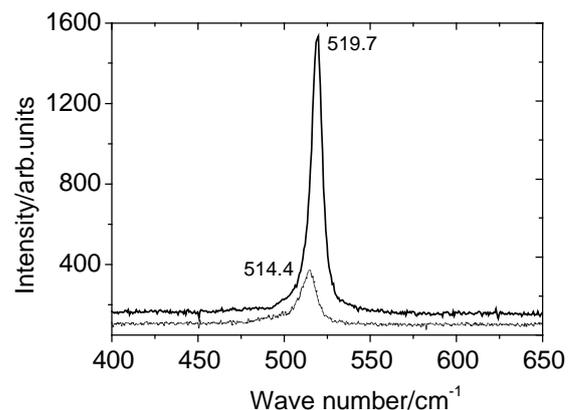


Fig. 5. Raman spectra obtained on the upper layer (solid line) and the lower layer (dot line) of a poly-Si thin film.

4. Conclusions

Poly-Si thin films were prepared by AIC with native SiO_2 at the Al and Si interface. For comparison, poly-Si thin films were prepared by AIC with native Al_2O_3 at the Al and Si interface too. The poly-Si (a-Si/Al) thin films are strongly preferential (111) orientations with large grains just like poly-Si (Al/a-Si). The largest grain size is about 100 μm and it is almost the largest ever reported. The surface of the poly-Si(a-Si/Al) thin film is smooth and without Si island. The incompletely crystallized poly-Si (a-Si/Al) thin films showed that the grains form closed polygon formations in the stack of a-Si/Al and form unclosed wheatear formations at the border of a-Si/Al stack and Al layer without Si under layer. Poly-Si (a-Si/Al) thin

film has double layers just like poly-Si (Al/a-Si), but the properties of the two layers are opposite. Namely, the crystalline quality of the upper layer is better than the lower layer for the poly-Si (a-Si/Al) thin film but the lower layer is better than the upper layer for the poly-Si (Al/a-Si). Both the smooth surface and the high crystalline quality of the upper layer make the poly-Si (a-Si/Al) thin film more suitable for further epitaxy.

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