Large-grained poly-Si films on ZnO:Al coated glass substrates

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Abstract

Thin film polycrystalline silicon (poly-Si) films have been fabricated by the aluminium-induced layer exchange (ALILE) process on ZnO:Al coated glass. The formation of the poly-Si films was observed during the annealing process using an optical microscope. Poly-Si films formed on ZnO:Al coated glass consist of high-quality poly-Si material, as evidenced by Raman measurement. The average grain size of the poly-Si films slightly increases with decreasing annealing temperature. The formation of poly-Si films on ZnO:Al coated glass led to a preferential (001) orientation at all annealing temperatures (425 ^{o}C ~ 525 ^{o}C).

Keyword: aluminium-induced layer exchange; ZnO:Al coated glass; preferential (001) orientation

1. Introduction

Large-grained polycrystalline silicon (poly-Si) thin-film solar cells on foreign substrates (e.g. glass) feature the potential to combine the advantages of both crystalline silicon wafers (high material quality) and thin-film technologies (low costs). Poly-Si thin-film solar cells can be prepared by the 'seed layer approach' where in a first step a large-grained seed layer is formed on the foreign substrate and in a second step this seed layer is epitaxially thickened [1,2]. A promising way to prepare such seed layers is the aluminium-induced layer exchange (ALILE) process. The ALILE process is a special form of aluminium-induced crystallization (AIC) where a substrate/Al/a-Si stack is transformed into a substrate/poly-Si/Al(+Si islands) stack by a simple annealing step below the eutectic temperature of the Al/Si system (577°C) [3,4]. Usually the seed layers are prepared directly on nonconductive substrates like glass.

An appealing option for poly-Si thin-film solar cells would be the seed layer formation on a TCO-coated glass substrate (TCO: Transparent Conductive Oxide) because TCOs show a high transparency in the spectral region where the solar cell is operating and they provide a high electrical conductivity. TCOs are well established for thin-film solar cells based on amorphous Si (a-Si:H) or microcrystalline Si (µc-Si:H) [5-7] but are not used so far for poly-Si thin-film solar cells. The formation of poly-Si seed layers on ZnO:Al coated glass using the ALILE process has been introduced recently [8]. In this paper we report the influence of different annealing temperatures on the formation of seed layers on ZnO:Al coated glass by the ALILE process.

2. Experimental details

Glass substrates (Borofloat 33 from Schott) were cleaned with a normal glass cleaning solution (Mucasol). The ZnO:Al films were prepared on the cleaned glass substrates in an in-line system in dynamic mode using non-reactive RF-sputtering from ceramic targets. The amount of doping was determined by using a ZnO:Al_2O_3 target with 1 wt % of Al_2O_3. The

ZnO:Al films were deposited at a constant deposition pressure of 0.1 Pa and at a substrate temperature of 300 °C. The initial layer stacks for the ALILE process (Al and a-Si) were deposited onto the ZnO:Al coated glass by DC magnetron sputtering. The initial layer stacks were deposited at room temperature and with an Ar pressure of 6.5×10^{-3} mbar. The thickness of the Al layer and the a-Si layer is 300 nm and 375 nm, respectively. The ALILE process requires a thin permeable membrane between the Al and the a-Si layer which controls the diffusion of Al and Si [9]. In our case, the membrane consists of an Al oxide layer formed by exposure to air of the Al-coated substrate prior to the a-Si deposition. Our standard oxidation time is 2 h.

Subsequently the samples were annealed in a tube furnace at an annealing temperature T_A between 425 °C and 525 ^{o}C in N_2 ambient. The samples annealed at 425 °C and 450 ^{o}C were annealed for 16 hours and the samples annealed between 475 °C and 525 ^{o}C were annealed for 4 hours. In addition to the annealing experiments in the tube furnace, we carried out annealing experiments in a heating stage of an optical microscope. These experiments enable the investigation of the crystallization (nucleation and subsequent growth) during the ALILE process. The ALILE process on ZnO:Al coated glass is shown schematically in Fig. 1. Finally the resulting top-layer (Al and Si islands) was removed by chemical mechanical polishing (CMP). For CMP Syton® HT-50 colloidal silica slurry (from DuPont Air Product NanoMaterials L.L.C) was used. Samples were cleaned using hot water in an ultrasonic bath after CMP process.

Raman spectroscopy was performed to characterize the structural quality of the resulting poly-Si films. The crystallographic surface orientation and the grain size of the poly-Si films were investigated using electron backscatter diffraction (EBSD). In addition to the seed layer experiments mentioned above we examined also the influence of the annealing temperature on the properties of the ZnO:Al film (without the seed layer on top). Transmittance measurements (λ: 320 ~ 2000 nm) and 4-point probe measurements were used to characterize the optical and electrical properties of the ZnO:Al films on glass.

3. Results and discussion

3.1. Properties of the ZnO:Al films

In order to study the influence of the annealing temperature (425 ~ 525 ^{o}C) on the properties of the ZnO:Al we measured the electrical and optical properties of bare ZnO:Al films on glass before and after annealing. Two annealing times (4 and 16 hours) were used to determine the time dependence. The sheet resistances (R_s) of ZnO:Al films on glass as a function of the annealing temperature are shown in Fig. 2 (a). Solid squares and open circles indicate the sheet resistance of ZnO:Al films after 4 and 16 hours annealing in N_2 ambient, respectively. For comparison, the sheet resistance of as-deposited ZnO:Al films of 6.3 Ohm/square is indicated with a dashed line. The sheet resistances of the samples annealed at 425 ^{o}C for 4 hours and 16 hours are 48.5 and 91.2 Ohm/square, respectively. The sheet resistances of the samples annealed at 450 ^{o}C have similar values as the samples annealed at 425 ^{o}C. But if the annealing temperature is higher than 450 ^{o}C, the sheet resistances of the annealed ZnO:Al films are significantly increased with increasing annealing temperature. Compared to results obtained for annealing in vacuum [10] the annealing in N_2 ambient leads to higher R_s. The reason for the changes of the electrical properties upon annealing in N_2 ambient is the reduction of the free carrier density and the decreased carrier mobility [11].

Fig. 2 (b) shows the optical transmittance of the as-grown sample, the sample annealed at 425 ^{o}C for 4 hours, and the sample annealed at 425 ^{o}C for 16 hours. The transmittance of the ZnO:Al films in the UV (ultraviolet) and the VIS (visible) region shows no change upon annealing. But in the NIR (near infrared) region the transmittance is increased strongly after annealing. The transmittance of the samples annealed in N_2 ambient shows a similar behaviour compared to samples annealed in vacuum [10].

3.2. Properties of the poly-Si films

The ALILE process is based on the following steps: (1) Upon heating silicon diffuses from the a-Si into the Al layer across the Al oxide interface. (2) Silicon nuclei are formed locally within the Al layer. (3) The silicon nuclei (grains) grow laterally until neighbouring grains coalesce and finally form a continuous poly-Si film on the substrate. (4) Al is displaced and diffuses across the Al oxide interface into the initial a-Si layer.

The crystallization (nucleation and subsequent growth) was observed in a heating stage of an optical microscope [4]. Therefore the samples were placed upside down on the heating stage such that the initial ZnO:Al/Al interface could be observed through the glass/ZnO:Al during annealing. The formation of poly-Si grains at the initial ZnO:Al/Al interface leads to a local change of the reflectivity as Si reflects less light than Al. The corresponding optical micrographs were analyzed to determine the crystallized fraction. The crystallized fraction as a function of the annealing time for different annealing temperatures (T_A) is shown in Fig. 3. The annealing temperature was varied from 425 to 525 ^oC with an increment of 25 ^oC. Higher annealing temperatures led to faster crystallization. The crystallized fraction reached nearly 100 % at all annealing temperatures, which means that at all annealing temperatures continuous poly-Si film were formed on top of the ZnO:Al coated glass. The crystallization process at 425 ^oC takes less than 4 hours. The crystallization process at annealing temperatures above 500 ^oC is very fast (below 10 min).

Fig. 4 shows the normalized Raman spectrum of the poly-Si film formed on a ZnO:Al coated glass substrate at 425 ^oC (dashed line). For comparison, the result obtained on a FZ silicon wafer is also shown (solid line). As can be seen from Fig. 4, the Raman spectrum measured on the poly-Si film is almost the same as that obtained on the FZ Si wafer. The value of the FWHM (Full-Width at Half-Maximum) of the poly-Si film annealed at 425 ^{o}C is 3.8 cm^{-1} (the FWHM of the FZ Si wafer is 3.6 cm^{-1}). Hence, the poly-Si film crystallized on ZnO:Al coated glass at 425 ^{o}C has a high-quality crystalline structure.

The EBSD crystal orientation maps of poly-Si films on both ZnO:Al coated glass and bare glass are shown in Fig. 5. Fig. 5 (a) shows the surface of the poly-Si film formed on ZnO:Al coated glass at 425 ^{o}C. The surface of the poly-Si film formed at 425 ^{o}C on bare glass is shown in Fig. 5 (b). Both samples were annealed for 16 hours.

Fig. 6 shows the grain size of the poly-Si film on ZnO:Al coated glass as a function of the annealing temperature. The samples at 425 and 450 ^{o}C were annealed for 16 hours and the samples at 475…525 ^{o}C were annealed for 4 hours. The maximum grain size (open circles) and the average grain size (solid squares) of poly-Si films on ZnO:Al coated glass are about 16 µm and 5 µm at 425 ^{o}C, respectively. The maximum grain size and the average grain size of the poly-Si films on bare glass are 18 µm and 7 µm at the same annealing temperature, respectively. The grain size decreases with increasing annealing temperature on ZnO:Al coated glass as well as on bare glass. For all temperatures, the grain size of the poly-Si films on ZnO:Al coated glass is slightly smaller than that of the poly-Si films on bare glass. The process time for the ALILE process on ZnO:Al coated glass is shorter compared to the process time of the ALILE process on bare glass. Generally, the faster crystallization process leads to more nucleation sites of silicon and hence to smaller grains.

In Fig. 5 (c), the color scale for the orientation maps is shown (online color). Both poly-Si films on ZnO:Al coated glass as well as on bare glass show a strong preferential (001) orientation, as can be seen Fig. 5 (a) and (b). The fraction of the poly-Si surface showing an orientation within 20^{o} of the perfect (001) direction is defined as the preferential (001) orientation ($R_{(001)}$).

Fig. 7 shows $R_{(001)}$ of poly-Si films on ZnO:Al coated glass (solid squares) and on bare glass (open circles). For poly-Si films both on ZnO:Al coated glass and on bare glass, no significant change of $R_{(001)}$ with increasing annealing temperature was observed. In previous publication [12, 13] it was shown that the preferential (001) orientation decreases with increasing annealing temperature. The reason could be the effect of the different thermal expansion coefficients of the used glass substrates. In this study Borofloat 33 glass was used instead of Corning 1737 glass that was used in other studies. The thermal expansion coefficient of Borofloat 33 glass, crystalline silicon, and Corning 1737 glass is about 3.25×10^{-6}/K, 3.00×10^{-6}/K, and 3.76×10^{-6} /K, respectively.

A preferential (001) orientation of the poly-Si films on ZnO:Al coated glass can make these layers act as favourable seed layers for epitaxial growth of silicon absorber layers.

4. Conclusions

We investigated the structural properties of poly-Si films formed on ZnO:Al coated glass at annealing temperatures of 425 ^{o}C to 525 ^{o}C. Continuous poly-Si films are formed on ZnO:Al coated glass as well as on bare glass for all annealing temperatures (425 ^{o}C ~ 525 ^{o}C). The annealing temperature for the ALILE process on ZnO:Al coated glass should however be kept below 450 ^{o}C due to the high sheet resistance of the ZnO:Al films on bare glass after annealing at temperatures above 450 ^{o}C and due to the grain size of the poly-Si films which decreases at higher temperatures. 100 % crystallization is achieved in less than 1 hour even at 450 ^{o}C. The quality of the crystallized poly-Si film is very good as can be seen from Raman measurements. From EBSD results we learn that a preferential (001) orientation is achieved like on bare glass with $R_{(001)}$ (~ 60 %) and that grains are slightly smaller on ZnO:Al coated glass but still quite large.

All these points are very good from the point of view of solar cell production using epitaxial thickening of these seed layers on the condition that you can do the epitaxy at low enough temperature (T < 450 ^{o}C).

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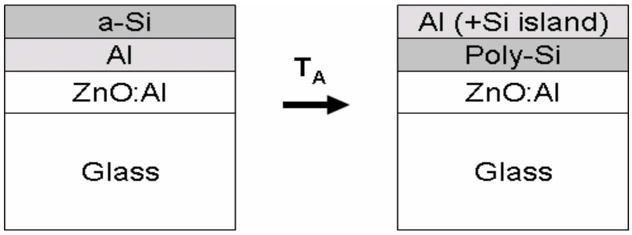
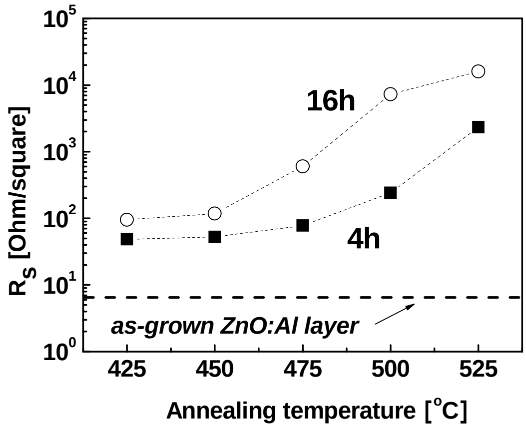
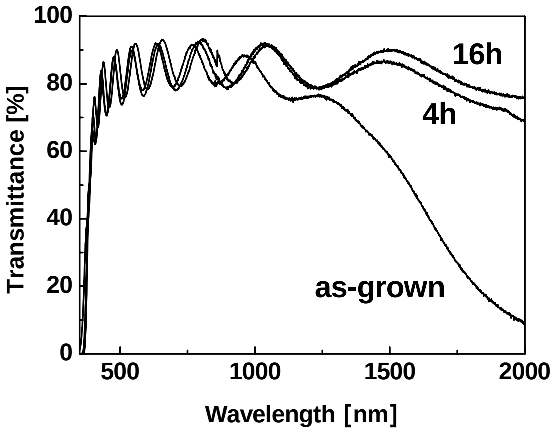


Fig. 1. ALILE process on ZnO:Al coated glass.



(a)



(b)

Fig. 2. The properties of ZnO:Al films on glass; (a) Sheet resistance (R_s) of ZnO:Al coated glass as a function of the annealing temperature after 4 hours (solid square) and 16 hours (open circle) annealing in N_2 ambient, the sheet resistance before annealing is indicated by a dashed line. (b) The optical transmittances of the as-grown sample, the sample annealed at 425 ^{o}C for 4 hours, and the sample annealed at 425 ^{o}C for 16 hours

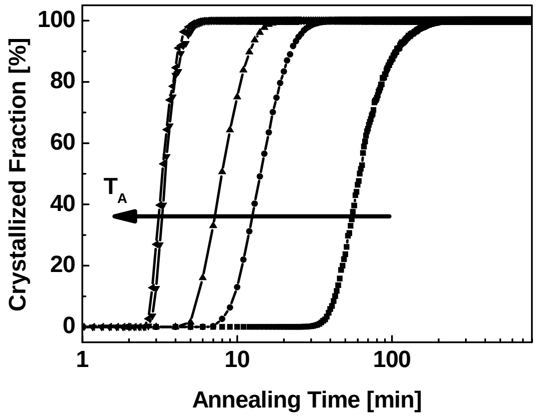


Fig. 3. Crystallized fraction versus annealing time for poly-Si films formed on ZnO:Al coated glass at five different annealing temperature, T_A (425, 450, 475, 500, and 525 ^oC). The arrow indicates increasing annealing temperature.

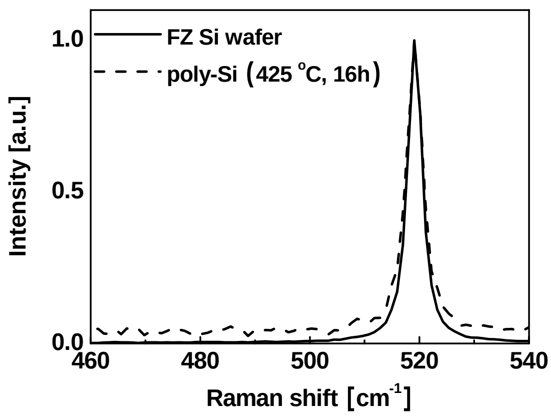
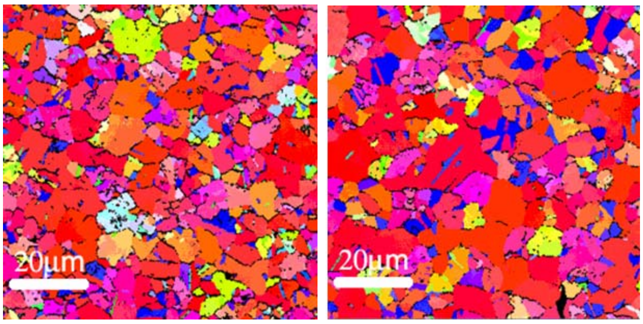
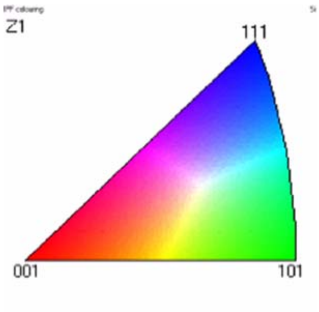


Fig. 4. Normalized Raman spectrum of a poly-Si film formed on ZnO:Al coated glass annealed at 425 ^{o}C for 16 hours (dashed line). The Normalized Raman spectrum of a FZ silicon wafer (solid line) is shown as a reference.



(a) (b)



(c)

Fig. 5. (Online color) Orientation maps of the poly-Si surface measured by EBSD. The samples were annealed at 425 ^{o}C for 16 hours: (a) poly-Si on ZnO:Al coated glass, (b) poly-Si on bare glass, (c) the color scale for the orientation maps: Red color is (001) orientation, blue color is (111) orientation, and green color is (101) orientation.

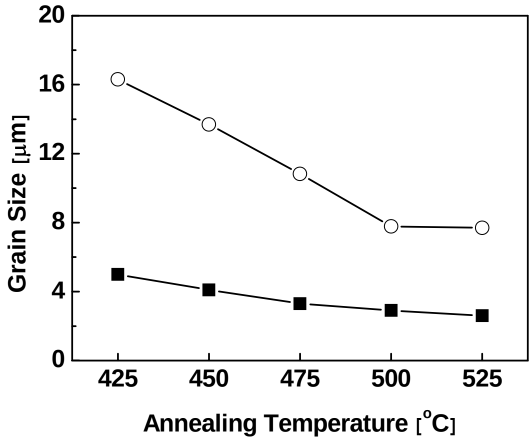


Fig. 6. Grain size of poly-Si films on ZnO:Al coated glass as a function of the annealing temperature: Maximum grain size (open circles), average grain size (solid squares)

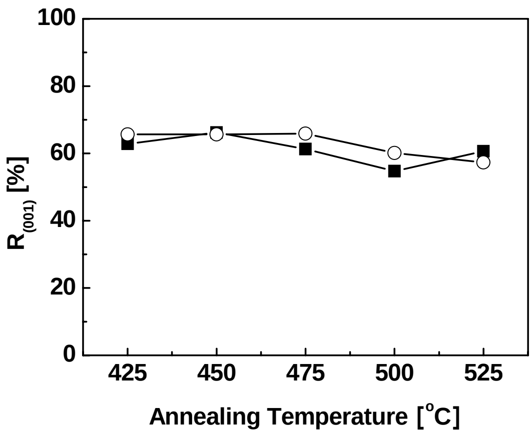


Fig. 7. Preferential (001) orientation $R_{(001)}$ of poly-Si films prepared on both ZnO:Al coated glass (solid squares) and on bare glass (open circles).