Temperature stability of ZnO:Al film properties for poly-Si thin-film devices

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Abstract

The crystallization of thin silicon films at temperatures between 425 and 600 °C was investigated on glass substrates coated with Al-doped zinc oxide (ZnO:Al). Bare ZnO:Al layers degrade at the crystallization temperatures used. A silicon layer on top, however, efficiently prevents deterioration. The resistivity was even found to drop from $4.3 \cdot 10^{-4}\,\Omega$cm for the as deposited ZnO:Al to $2.2 \cdot 10^{-4}\,\Omega$cm in the case of aluminum induced crystallization and to $3.4 \cdot 10^{-4}\,\Omega$cm for solid phase crystallization. The temperature-stable conductivity of ZnO:Al films coated with Si opens up appealing options for the production of poly-Si thin-film solar cells with TCO front contacts.

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Thin polycrystalline silicon (poly-Si) films 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). This is especially interesting for the preparation of low-cost, high efficiency thin-film solar cells. Thin poly-Si films on glass for solar cells can be prepared for example by (i) solid phase crystallization (SPC) [1, 2], where amorphous Si (a-Si) is transformed to poly-Si by annealing at about 600 °C, or (ii) the 'seed layer approach' [3], where in a first step a very thin large-grained poly-Si film (seed layer) is formed and in a second step this seed layer is thickened homo-epitaxially at about 600 °C. An attractive method to prepare such large-grained seed layers is the aluminum-induced layer exchange (ALILE) [4, 5, 6, 7]. The ALILE process is a special form of aluminum-induced crystallization (AIC): A substrate/Al/a-Si stack is transformed into a substrate/poly-Si/Al(+Si) stack by a simple annealing step below the eutectic temperature of the Al/Si system (577 °C).

In both cases – SPC and ALILE - an annealing step is necessary so that only temperature-stable substrates can be used. The formation of poly-Si films on transparent conductive oxides (TCOs), however, would be an appealing option, especially for the preparation of thin-film solar cells in superstrate configuration because they allow for a simple contacting scheme and light trapping [8, 9]. In the case of cells based on a-Si:H or µc-Si:H ZnO:Al is a promising TCO material due to its high stability in hydrogen-rich plasmas [10].

Studies on the stability of ZnO:Al upon treatment at higher temperatures, as used for the crystallization of Si, have so far concentrated on annealing of thin films on glass under various conditions. Usually a strong decrease of electrical conductivity is observed during annealing in air at temperatures above 300 to 400 °C [11, 12], while much higher temperatures can be applied in vacuum [13] or, in the case of rapid thermal annealing, nitrogen [14]. As the films do not show structural degradation but rather an improved crystallinity, Minami et al. suggested oxygen to be responsible for both the decreased carrier density and mobility upon annealing in air [15]. Only recently the formation of poly-Si layers on ZnO:Al coated glass using the ALILE process has been introduced [16, 17], but no comments on the evolution of ZnO properties were given.

In this paper we show, that ZnO:Al is temperature-stable when capped with Si and thus suitable for the preparation of poly-Si thin-film solar cells. For this, we investigated two types of glass/ZnO:Al/poly-Si samples: The poly-Si was formed by either (i) the ALILE process or (ii) the SPC process.

The ZnO:Al films were deposited on the cleaned glass substrates in an in-line system in dynamic mode using non-reactive RF-sputtering from ceramic targets containing 1 wt.% Al_2O_3 at a substrate temperature of 300 °C [18]. The thickness of the ZnO:Al films, determined by fitting optical transmission and reflection spectra, was between 690 and 770 nm. These kinds of films are usually applied for the development of state-of-the-art amorphous and microcrystalline Si based single and multijunction solar cells [9].

The layers for the ALILE process (Al and a-Si) were deposited onto the ZnO:Al coated glass by DC magnetron sputtering at room temperature. The thickness of the Al layer and the a-Si layer was 300 nm and 375 nm, respectively. The initial glass/ZnO:Al/Al/a-Si stacks were annealed in a tube furnace at an annealing temperature T_A between 425 °C and 525 °C in N_2 ambient. The samples annealed at 425 °C and 450 °C were annealed for 16 hours and the samples annealed between 475 °C and 525 °C were annealed for 4 hours. Finally the resulting top layer (Al and Si islands) was removed by chemical mechanical polishing (CMP). Therefore the resulting structure is glass/ZnO:Al/poly-Si with an average silicon grain size of 5μm [17].

For the SPC-based experiments intrinsic a-Si layers were deposited on ZnO:Al coated glass by e-beam evaporation at room temperature. The thickness of the a-Si layer was about 290 nm. The initial glass/ZnO:Al/a-Si stacks were annealed in a tube furnace at 600 °C for 24 hours in N_2 atmosphere. During annealing the initially amorphous silicon was crystallized and glass/ZnO:Al/poly-Si stacks were formed.

For comparison all the different annealing steps were also applied to (i) glass/ZnO:Al samples, (ii) glass/Al/a-Si samples (ALILE process without ZnO:Al), and (iii) glass/a-Si samples (SPC process without ZnO:Al). The electrical properties were studied by 4-point probe and Hall measurements in van der Pauw geometry. The optical properties were investigated by measuring transmission and reflection spectra. In order to study the influence of the annealing temperature the electrical and optical properties were measured before and after annealing.

FIG. 1 shows the sheet resistance (R_{sh}) of the different samples as a function of the annealing temperature: glass/ZnO:Al (open circles), glass/poly-Si (open triangles), and glass/ZnO:Al/poly-Si (solid circles). For comparison the sheet resistance of as deposited ZnO:Al layers (6.3 Ω/sq) is indicated with a dashed line.

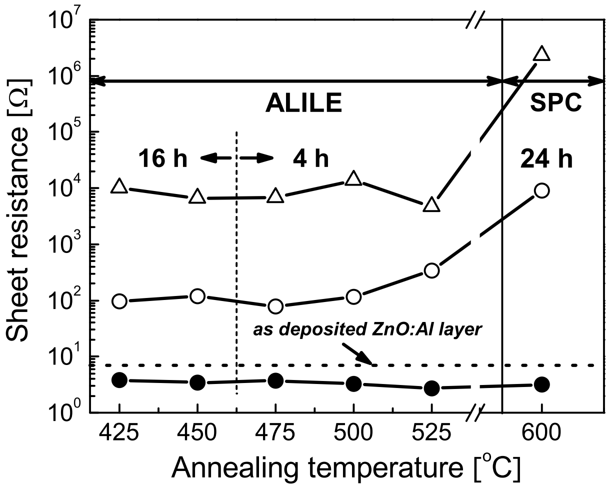

Figure 1: The sheet resistance (R_{sh}) of glass/ZnO:Al/poly-Si (•), glass/ZnO:Al (○) and glass/poly-Si (△) stacks as a function of the annealing temperature. For reference, R_{sh} of the glass/ZnO:Al layers before annealing is indicated with a dashed line. The poly-Si films were formed by either ALILE or SPC.

The sheet resistance of the annealed glass/ZnO:Al samples (open circles) is significantly increased compared to the as deposited value despite the nitrogen ambient. In contrast, the sheet resistances of the glass/ZnO:Al/poly-Si samples (solid circles) are even lower than the sheet resistance of as deposited ZnO:Al layer. This is an effect of improved ZnO:Al quality as the silicon does not contribute to the total resistance of the stack considerably. The resulting sheet resistance of the glass/ZnO:Al/poly-Si samples is almost independent of the annealing temperature (around $3\,\Omega$/sq). Hence, the Si layer on top of the ZnO:Al effectively prevents the degradation by oxygen or nitrogen. In contrast, the heat treatment even improves the zinc oxide properties and the resistivity for the sample annealed at 425 °C drops from approx. $(4.3 \pm 0.1) \cdot 10^{-4}\,\Omega$cm to only $(2.2 \pm 0.1) \cdot 10^{-4}\,\Omega$cm.

For the SPC at 600 °C for 24 hours the difference between the sheet resistance of the glass/ZnO:Al sample (open circle) and the glass/ZnO:Al/poly-Si sample (solid circle) is more than three orders of magnitude. Again the resistivity of the ZnO:Al films was improved, in this case to a value of $(3.4 \pm 0.1) \cdot 10^{-4}\,\Omega$cm. This is a very promising result regarding the application of sputtered ZnO:Al layers in poly-Si thin-film solar cells.

In addition to the electrical properties the influence of the annealing on the optical properties was also studied. FIG. 2 shows the absorption spectra of three different samples before

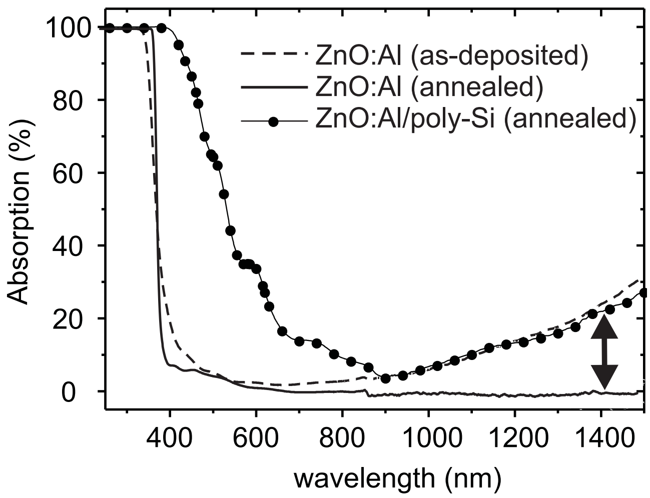

Figure 2: Absorption spectra of ZnO:Al films on glass before (dashed line) and after (solid line) annealing, as well as of a glass/ZnO:Al/poly-Si stack after annealing (solid circles). Annealing was performed at 600 °C for 24 hours in N_2 ambient (SPC experiments). The arrow indicates the remaining free carrier absorption of the glass/ZnO:Al/poly-Si stack after annealing.

Table I: Resistivity ρ, carrier concentration N_e and hall mobility μ of the as deposited ZnO:Al film and ZnO:Al films coated with poly-Si produced by the ALILE and the SPC process.

Sample	Crystallization conditions	ρ $[10^{-4}\,\Omega\mathrm{cm}]$	N_e $[10^{20}\,\mathrm{cm}^{-3}]$	μ $[\mathrm{cm}^2/\mathrm{Vs}]$
ZnO as dep.	-	4.3 ± 0.1	3.5 ± 0.1	42.0 ± 0.1
SPC	24 h @ 600 °C	3.4 ± 0.1	3.5 ± 0.1	52.6 ± 0.1
ALILE	16 h @ 425 °C	2.2 ± 0.1	6.8 ± 0.2	41.8 ± 0.2

and after annealing at 600 °C for 24 hours (SPC experiments): (i) glass/ZnO:Al before annealing (dashed line), (ii) glass/ZnO:Al after annealing (solid line), (iii) glass/ZnO:Al/poly-Si after annealing (solid circles). It can be clearly seen that the heat treatment of the glass/ZnO:Al samples leads to a disappearance of free carrier absorption in the NIR. The disappearance of free carriers can explain the strong increase of sheet resistance seen in FIG. 1. For the glass/ZnO:Al/poly-Si stack, however, the free carrier absorption in the NIR is preserved (indicated with an arrow) although the stack has been annealed for the same time. Bare poly-Si films have no absorption in this spectral region.

For a better understanding of the change of electrical properties during crystallization

Hall measurements were carried out on three samples, namely the as deposited ZnO:Al film, the glass/ZnO:Al/poly-Si stack formed by ALILE and CMP for annealing at 425 °C and the glass/ZnO:Al/poly-Si stack formed by SPC. It should be noted that in all cases the Si layer does not contribute to the electrical transport noticeably, so the measured values could be solely attributed to the ZnO:Al layer. The results are summarized in Table I.

While the improved conductivity of the ALILE sample is mostly due to higher carrier concentration N_e in the ZnO:Al film, no change in carrier concentration can be observed for the SPC. Instead the mobility μ increases strongly. The measured value of $52.6\,\mathrm{cm^2/Vs}$ is close to the theoretical limit proposed by Ellmer [19], and thus higher than the experimental limit found on the sputtering coater used in this study [18]. This indicates two different processes are responsible for the increase of conductivity. The higher mobility for the SPC sample is most likely caused by an improved crystallinity of the ZnO:Al film after the annealing. The increased electron concentration of the ALILE sample probably results from a diffusion of Al into the ZnO:Al film during the annealing and thus is a peculiarity of the ALILE process. The effect of the improved crystallinity of the ZnO:Al film expected after the annealing on mobility is probably compensated by increased ionized impurity scattering.

In conclusion it was shown that crystallization of a-Si layers can also be carried out on ZnO:Al coated glass substrates using both ALILE and SPC. While uncoated ZnO:Al films show a strong increase of resistivity upon heat treatment, Si coating of the ZnO:Al layers used in this study resulted in electrical properties that were not only stable but considerably improved. While for SPC this is a consequence of a higher mobility, a strong increase of carrier density was observed during the ALILE process. The temperature-stable conductivity of glass/ZnO:Al/Si layer stacks opens up appealing options for poly-Si thin-film devices including transparent conductive oxides (TCOs), e.g. solar cells.

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