ABSTRACT: Aluminum-doped zinc oxide are a representative for a transparent and conducting oxide thin film (TCO) and is commonly used as front contact in chalcopyrite and amorphous/microcrystalline silicon solar cells. Optimum optical and electrical properties for this application are obtained for moderate doping levels and high mobilities. State-of-the-art films, preferably deposited by magnetron sputtering or low pressure chemical vapor deposition, exhibit mobilities around 40 cm²/Vs. Post-deposition thermal treatment will usually lead to a strong increase of resistivity. If the films are capped by thin silicon layers, however, the degradation of electrical properties can be prevented and a significant increase in mobility can be obtained. The highest mobility reached in this study is 67 cm²/Vs.

Keywords: TCO, ZnO, Annealing, Electrical Properties.

1 INTRODUCTION

Material research in transparent conducting oxides has focussed on minimization of resistivity for a long time in the past. With the increasing importance of thin film solar cell technology, more attention is being laid on minimization of optical losses, especially by an extension of the window of high optical transmission into the near-infrared part of the solar spectrum. In order to fulfill the requirements for modern thin film devices this means that the carrier concentration should be kept at moderate levels in the low 10^{20} cm^{-3} range and an optimization of carrier mobility in order to achieve low resistivities is preferred over extensive doping.

For solar cells based on amorphous and microcrystalline silicon magnetron sputtering of Al-doped ZnO layers has shown to lead to films exhibiting mobilities well above 40 cm²/Vs [1]. These films can be roughened by wet chemical etching for light trapping purposes [2]. For these films the carrier concentrations were adapted by variation of target doping and best mobilities have been achieved at high substrate temperatures. Unfortunately mobilities above 50 cm²/Vs could not be produced.

In order to further increase mobility post deposition thermal treatments have been examined. Unfortunately these attempts were of only limited success and the realization of very high mobilities has not been achieved as high temperature treatments usually result in degradation of electrical properties [3].

Recently it was shown, that the thermal stability of sputtered ZnO:Al films can be strongly enhanced by capping the layers with a thin silicon cap [4]. This finding has also stimulated research in integration of ZnO:Al layers in poly-Si solar cells [5].

In this paper it is shown that, post deposition thermal treatments of capped ZnO:Al layers can strongly enhance electrical conductivity. The influence of annealing temperature and cap thickness has been investigated. Mobilities up to 67 cm²/Vs have been achieved, leading to resistivities below 140 μΩcm. In order to rule out an influence of the capping layer on electrical transport measurements have also been carried out after removal of the capping layer by plasma etching.

2 EXPERIMENTAL DETAILS

The aluminum doped zinc oxide (ZnO:Al) layers used for this investigation were all prepared by non-reactive radio frequency (RF) magnetron sputtering using a ceramic target with an Al₂O₃-concentration of 1 wt. % [6]. A substrate temperature around 300 °C was used in all cases.

Two different glass substrate were used: for the annealing studies on uncapped ZnO:Al layers, films deposited onto Corning 1737 glass were used. In the experiments on capped ZnO:Al films Schott Borofloat 33 glass with an 80 nm thick SiN diffusion barrier supplied by CSG Solar were used. This type of substrate exhibits a coefficient of thermal expansion similar to the one of silicon and is thus suitable as substrate in the production of polycrystalline Si solar cells by a solid phase crystallization process at 600 °C.

The ZnO:Al samples on the CSG substrate were thoroughly cleaned and then coated with 50 nm thick n-type amorphous silicon films by plasma-enhanced chemical vapor deposition (PECVD). It should be noted that doping of the capping layer does not influence the results as was shown for undoped layers. Here doped layers were used because this corresponds to the polycrystalline silicon thin film solar cell structure currently under development at HZB.

Annealing was carried out in a quartz tube furnace under nitrogen atmosphere in all cases. Uncapped films were directly placed into the tubes at the indicated annealing temperatures, while films with capping layers were placed into the tubes at low temperatures and ramped up to the annealing temperature at a rate of 1.6 K/min in order to prevent cracking.

Additionally some films were treated in a rapid thermal processing (RTP) system under tungsten-halogen lamps [7]. A maximum temperature of 860 °C was applied for 60 s. The electrical performance was examined by Hall measurements in standard van-der-Pauw geometry at room temperature. Optical measurements were carried out using a Perkin Elmer Lambda 19 spectrophotometer equipped with an integrating sphere in the spectral range from 250 to 2500 nm.
According to the current understanding of TCO films, the mobility of state-of-the-art films is limited by two scattering mechanisms apart from lattice scattering. First, doping of the material leads to ionized scattering centers in the form of the ionized donor atoms. There is still a debate about the right theoretical description of ionized impurity scattering [8]. Recently, Ellmer et al. proposed an expression for the contribution of ionized impurity scattering and lattice scattering based on an expression originally derived for doped single-crystalline silicon [9].

The main effect of ionized impurity scattering is a decreasing mobility with increasing doping, meaning that for low doping levels higher mobilities can be obtained in principle. Unfortunately, the zinc oxide films used as TCO material are polycrystalline, meaning that also grain boundary scattering will play a prominent role. Using the Seto model for calculation of its contribution will play a prominent role. Using the Seto model for calculation of its contribution one can see that the defect density at grain boundaries, and to a lesser extent the grain size, strongly influences the mobility. Generally, the grain boundaries lead to very low mobilities for low doping levels and an optimum doping range is obtained, in which highest mobilities can be obtained. For post-deposition thermal treatments it is thus crucial, that the carrier concentration is kept in this optimum range.

4 RESULTS

4.1 Annealing of uncapped layers

Results on annealing studies of uncapped zinc oxide films vary strongly in literature. There is a strong dependence on the deposition method and conditions. Nevertheless, most authors who used annealing at temperatures above approx. 400 °C report an increase in resistivity. This is especially true if films are annealed in air or oxygen.

In our first experiments we used a nitrogen atmosphere as it is currently used for solid phase crystallization of amorphous silicon. A strong increase of resistivity was found and Hall measurements confirmed that both carrier concentration and mobility decrease (see Figure 2). The decrease of mobility can be understood well considering the dominant scattering mechanisms discussed in the previous section. Grain boundary scattering leads to an automatic reduction of mobility when the carrier concentration diminishes strongly, thus no structural deterioration of the films can be concluded. This is also shown in Figure 2, where we compare the data to curves calculated using the scattering theories discussed in the previous section. While the agreement between theory and experiment is not optimum, the general trend is nicely described.

![Figure 1: Theoretical limits of electron mobility in zinc oxide. The blue curve shows the limit proposed by Ellmer et al. for the combined contribution of ionized impurity scattering (IIS) and lattice scattering. The green curves additionally considered the contribution of grain boundary scattering as calculated from Seto's model for various defect densities $Q'$ at the grain boundaries.](image)

![Figure 2: Mobility as a function of carrier concentration for uncapped Al-doped zinc oxide films annealed in nitrogen. Increasing annealing time leads to lower carrier concentration. The mobility decrease found along the decrease in carrier concentration agrees with grain boundary scattering, which plays an increasing role for decreasing carrier concentrations.](image)

4.2 Annealing of capped layers

In order to prevent the degradation of the electrical conductivity of the ZnO:Al layers, we introduced a capping layer of amorphous silicon deposited by PECVD on top. In order to prevent cracking the samples were placed into the tube furnace at 200 °C and the temperature was raised subsequently to the final annealing temperature at a rate of 1.6 K/min. After maintaining the annealing temperature for different times the samples were cooled down again to 200 °C at the same rate and retrieved from the furnace.

The impact of the annealing procedure on resistivity of the films can be seen in Figure 3. In comparison to the as-deposited state ($\rho \sim 270 \mu\Omega\text{cm}$) the resistivity could be reduced to below 140 $\mu\Omega\text{cm}$. Resistivities in this range are so far only reported for pulsed laser (PLD) deposited films with significantly higher carrier concentrations [10].

Hall measurements on these films showed a slight increase in carrier concentration and, most remarkably, a strong increase in mobility. The mobility values are also shown in Figure 4. While as deposited films had mobilities around 42 cm$^2$/Vs, annealed films showed mobilities up to 67 cm$^2$/Vs. As for the resistivity higher annealing temperatures led to better electrical performance.

The mobility values measured in this study are well above values reported for as-deposited films and similar mobilities were only shown for epitaxial films on
sapphire substrates [11, 12].

**Figure 3:** Resistivity of capped ZnO:Al after thermal annealing at different annealing temperatures as a function of plateau time. As-deposited films showed a resistivity around 270 μΩ·cm.

**Figure 4:** Mobility of capped ZnO:Al after thermal annealing at different annealing temperatures as a function of plateau time. As-deposited films showed mobilities around 42 cm²/V·s. After annealing a maximum mobility of 67 cm²/V·s was measured.

In order to exclude an influence of the capping layer the silicon cap was also removed after the annealing procedure by a plasma etching using an NF₃ plasma. Hall measurements on these samples showed a wider scattering of measured mobility values, but deviation from the values measured on the capped films was in all cases less than 10%. Mobilities measured on the decapped samples could be slightly higher or lower than in the capped state. A possible reason could be the influence of the plasma treatment on the conductivity of the surface of the ZnO:Al layer.

4.3 RTP processing

Some of the films already annealed at 500 °C were further treated by a rapid thermal annealing process which was developed for post-deposition treatment of thin film poly-Si films [7]. A maximum temperature of 860 °C was applied for 60 s.

It could be shown, that the capped films also withstand this high temperature treatment for short times, thus the stack can be readily used as a substrate for poly-Si device preparation. Moreover again a positive effect on resistivity and mobility could be proven (see Figure 5).

**Figure 5:** Change of resistivity and mobility of capped ZnO:Al films annealed at 500 °C for different times upon rapid thermal annealing in nitrogen with a maximum temperature of 860 °C.

3 SUMMARY

In summary it could be shown, that annealing of capped ZnO:Al layers can lead to a considerable improvement of mobility well above as-deposited values reported for deposition onto glass substrates. The maximum mobility was reached for annealing at 650 °C with 67 cm²/V·s.

The capping layer successfully prevents degradation of carrier concentrations during high temperature treatments, including RTP processing at temperatures up to at least 860 °C. Thus the substrates used in this study form suitable substrates for the development of poly-Si devices formed by solid phase crystallization of amorphous silicon. This enables the development of superstrate cells using the same light-trapping schemes that have already been developed for microcrystalline silicon (μc-Si:H) solar cells.

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5 REFERENCES