Abstract

The damp heat stability and subsequent vacuum annealing behavior of aluminum doped zinc oxide (AZO) films was investigated using Hall effect measurements, x-ray diffraction (XRD) and optical spectrometry techniques. The AZO films were deposited on glass or silicon wafers using reactive and non-reactive magnetron sputtering from metallic and ceramic targets, respectively. Additionally, we characterized surface textured AZO films, which are used as light scattering transparent conductive oxide (TCO) in silicon thin film solar cells. For all films a degradation of the electrical film properties was found after the damp heat treatment. For thick compact films, with large grain size, only a small increase in the electrical resistivity was observed, whereas less compact films prepared at high deposition pressures or very thin films (< 300 nm) showed an increase in resistivity by up to a factor of three already after 300 hours. The conductivity degradation during damp heat treatment could be largely reversed by annealing in vacuum. However, annealing temperatures of at least 150 °C were required. Possible mechanisms explaining the experimental results are discussed.

Keywords: sputtering, aluminum doped zinc oxide (AZO), damp heat, annealing
1. Introduction

Aluminum doped zinc oxide films (AZO) are used as transparent electrodes, and particularly as front contacts for solar cells based on thin film silicon [1] and Cu(In,Ga)(S,Se)$_2$ (CIGS) [2]. Good long-term stability of solar cells under typical environmental conditions is very important in achieving long module lifetime, which has led to recent widespread interest in damp heat treatments [3-9]. In general, it is found that cells suffer from a degradation of the electrical properties of the ZnO contacts. Hence it follows that specially designed encapsulation is required to protect the ZnO films in solar modules. In this work, the damp heat stability and the subsequent vacuum annealing behavior of AZO films prepared by reactive and non-reactive in-line magnetron sputtering were investigated. The films were found to be highly conductive with good transparency in both visible and near infrared regions. The mechanism of film degradation during the damp heat test was investigated by studying the dependence of degradation on the initial film properties and the annealing behavior in vacuum following damp heat treatment.
2. Experimental

AZO films were prepared using an in-line magnetron sputtering system on Corning (1737) glass or crystalline silicon substrates. The sputtering system was operated in mid frequency (mf) and radio frequency (rf) mode using metallic and ceramic targets, respectively. The oxygen flow during reactive sputtering was controlled by plasma emission monitoring (PEM). The intensity of the 307 nm Zn emission line was used to characterize the process. High PEM-intensities correspond to a more metallic sputtering mode. More details of the sputtering system and the process stabilization are described elsewhere [10-12]. Three groups of AZO films were prepared under various deposition conditions by reactive mf sputtering. Additionally, one group of a non-reactive rf-sputtered film, which is commonly used as front contact for silicon thin film solar cells at IPV (for more details see [12,13]), was prepared and etched in diluted hydrochloric acid (0.5 % HCl) for 40 s. The sputtering conditions of each group are shown in table 1. After deposition, all films were damp heat treated with 85% relative humidity at a temperature of 85 °C for up to 1000 h in a climatic chamber (NEMA, NCC 4020). After 300 h damp heat treatment, one set of films was annealed in vacuum at a pressure of 10⁻⁵ Pa with subsequent temperatures of 25 °C, 85 °C, 155 °C, 225 °C and 250 °C. Each annealing step was performed for one hour. The electrical properties of the films were studied by Hall effect measurements. Optical properties were obtained using a dual beam spectrometer (Perkin Elmer, Lambda 19). The crystal structure and grain size were analyzed by X-ray diffraction (XRD). Additionally, the grain size was calculated by the Scherrer formula from the XRD (002) peak. Gas effusion measurements with heating rate of 20 °C/min were performed as described elsewhere [14].
3. Results and Discussion

3.1 Damp heat results

Fig. 1 shows the electrical properties of the etched and as-deposited rf-sputtered films (group a), after damp heat treatment and subsequent annealing in vacuum. The resistivity of the films increases due to the decrease of both carrier concentration and mobility with increasing damp heat time. Neglecting the difference between the etched and as-deposited sample, the film degradation is similar in both cases. The annealing behavior is discussed in the next section. Similar profiles were found for the thickness series (group d) of reactively sputtered films as shown in Fig. 2. The films become more stable with increasing thickness. Those degradation profiles are typical for AZO and have also been observed for group b and c, which were deposited by reactive sputtering under different deposition pressures and working points, respectively.

Fig. 3 shows the optical transmittance spectra in the wavelength range 300-1300 nm of an AZO film (group a, as-deposited) measured before and after 300 h damp heat treatment. The optical transmittance is above 80% in the visible range. In the near infrared range, the transmission is slightly reduced by free carrier absorption. The spectral transmittance did not change upon damp heat treatment in the wavelength range investigated. Similar observations were found for almost all films, although changes in the electrical properties were observed.

3.2 Vacuum annealing

As shown in Fig. 1a, the resistivity increased by up to a factor of three after 300 h damp heat treatment. Afterwards, these films were annealed in vacuum with stepwise increased temperatures. The film resistivity is nearly constant at low temperatures and starts to decrease at temperatures more than 150 °C. Higher conductivity is a consequence of an increase of both carrier concentration and mobility. Fig. 2 shows the annealing behavior of the thickness series (group d). Also in this case, the electrical conductivity begins to improve after the annealing
temperature exceeds 150 °C. Annealing behavior is summarized in Fig. 4, which shows the relative decrease in resistivity for all films (see Tab. 1) as a function of stepwise applied annealing temperature. Annealing temperatures of at least 150 °C are necessary for all films to partially recover the electrical conductivity after the damp heat treatment. This specific minimum annealing temperature indicates that the damp heat treatment chemically modifies the ZnO film structure. These changes can be partially reversed by thermal annealing.

We now consider the damp heat stability and annealing behavior for the different samples described in Tab. 1, concentrating on the properties in the initial state, after 300 h damp heat treatment and after 300 h damp heat treatment with subsequent vacuum annealing at 250 °C. In addition, as-deposited films were annealed at 250 °C for 1 h in vacuum. Fig. 5 shows the grain size determined by XRD and the resistivity after different treatments of the films prepared by reactive sputtering at various deposition pressures (group b, fig. 5a), working points (group c, fig. 5b) and with different thickness (group d, fig. 5c), respectively. The graphs show the resistivity as a function of the corresponding deposition parameter for the four different treatment states. From the XRD measurement, we found that all films are highly textured with the (001) direction perpendicular to the substrate. The grain size was evaluated from the full width at half maximum (FWHM) of the (002) peak, neglecting the influence of micro stress. The resistivity of some as-deposited films improved by annealing at 250 °C. These films initially showed rather poor electrical properties, while thick films prepared at low pressure and at high PEM-intensities are at best only slightly improved by heat treatment in vacuum. Fig. 5a summarizes the results of the pressure series. Films prepared at high deposition pressure have a rather small grain size. A large increase in resistivity of these films after damp heat treatment can be observed, and significant recovery following annealing at 250 °C in vacuum is obtained. On the other hand, films prepared at low pressure are dense and have a relatively large grain size, which indicates compact film structure. For these films, only small or moderate changes of resistivity both after damp heat or thermal vacuum treatments were observed. A similarly large increase in the
resistivity after 300 h damp heat was found for films prepared close to the oxide mode and for very thin films (< 300 nm) as shown in Figs. 5b and 5c, respectively. In both these cases a significant recovery of the resistivity was observed after annealing in vacuum at 250 °C.

To summarize: compact films with large grain sizes and high thickness (> 700 nm) show quite stable electrical properties while less compact and very thin films show a much more severe degradation of the electrical properties upon damp heat treatments. However, these films also show distinct recovery of the electrical film properties after annealing in vacuum at temperatures exceeding 150 °C. For an explanation of the observed effects, we speculate that water vapor is adsorbed at the grain boundaries, leading to an enhanced scattering of carriers and also to trapping of free carries thus reducing carrier concentration and carrier mobility. For thick and compact films, only the film surface is affected by the damp heat treatment and only a small deterioration of the film properties occurs. Consequently, for thin films or less compact films, the damp heat treatment has a more pronounced impact on the electrical properties. Moreover, the critical temperature of 150 °C indicates that the water vapor is rather strongly bound to the ZnO grains and can only be re-evaporated after the critical temperature is exceeded. Indeed, effusion measurements show some enhancement of water vapor and hydrogen effusion after damp heat treatment (see Fig. 6). However, an enhancement of CO₂ desorption is also observed (not shown).

To verify the hypothesis outlined above and to get a deeper understanding of the effects discussed in this paper, more detailed investigations of the microstructure have been started.
4. Conclusions

We investigated the damp heat stability (85% relative humidity and 85 °C up to 1000 h) and subsequent vacuum annealing behavior of aluminum doped zinc oxide (AZO) films prepared by magnetron sputtering. For all films a degradation of the carrier concentration and the mobility was found following damp heat treatment up to 1000 h. For films prepared at high deposition pressure, close to the oxide mode, or for very thin films, strong degradation occurs, whereas very compact films prepared at low pressure are quite stable. Damp heat treatment had no strong effects on the optical properties of the films although the carrier concentration changes. The deterioration of the electrical properties upon the damp heat treatment could be partially reversed by thermal annealing in vacuum, once a critical temperature of 150 °C is exceeded. Very thin films (< 300 nm) or films prepared at high pressure or close to the oxide mode conditions, e.g. at high deposition pressures or, in the case of reactive sputtering, close to the oxide mode, are strongly affected by the damp heat treatment and also show a more pronounced recovery of electrical properties on thermal annealing. These films have a relatively small grain size and a less compact film structure than films prepared under optimized conditions. These results suggest that adsorption of water vapor at the grain boundaries occurs during the damp heat treatment, and evaporation of the water takes place during vacuum annealing. Adsorbed water could lead to a capture of free electrons and strengthen the contribution of the grain boundary scattering to the carrier transport.

Acknowledgements

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References


Figure captions

Fig. 1 Electrical properties of as-deposited (unetched) and 40 s etched films (group a) as function of damp heat treatment time (DH time) and subsequent vacuum annealing temperature ($T_{\text{Annealing}}$): (a) resistivity, full symbols correspond to annealing at 250 °C of as-deposited films without damp heat treatment, (b) carrier concentration (open symbols) and electron mobility (full symbols). Details of the deposition conditions can be found in Tab. 1.

Fig. 2 Electrical properties of thickness series (group d) as function of damp heat treatment time (DH time) and subsequent vacuum annealing temperature ($T_{\text{Annealing}}$): (a) resistivity, full symbols correspond to annealing at 250 °C of as-deposited films without damp heat treatment, (b) carrier concentration (open symbols) and electron mobility (full symbols). Details of the deposition conditions can be found in Tab. 1.

Fig. 3 Optical transmittance spectra of as-deposited films (unetched, group a) before damp heat (black dashed line) and after 300 h damp heat treatment (grey solid line).

Fig. 4 Resistivity of various films as a function of the annealing temperature after 300 h damp heat treatment. The resistivity $\rho$ was normalized to the resistivity $\rho_{300}$, measured after 300 hours damp heat treatment before vacuum annealing.
Fig. 5 Grain size (dotted line, open symbols) and resistivity (closed symbols) after different treatment states of AZO films as a function of the corresponding deposition parameter during reactive mf sputtering: (a) pressure series (b) working point series, (c) thickness series. The resistivity values were measured in the initial state (squares, solid line), after 300 h damp heat treatment (DH, circles, dashed line) and after 250 °C vacuum annealing before (A, stars, dash-dotted line) and after damp heat treatment (DH + A, triangles, short-dashed line).

Fig. 6 Gas effusion measurements of etched rf sputtered films before and after 300 hours damp heat treatment. The graph shows the measured intensity of mass 2 (H₂) and mass 18 (H₂O) in relative units as function of the sample temperature. The heating rate was 20 °C per minute.
Table captions

Table 1. Deposition conditions for films prepared by radio frequency excitation from ceramic ZnO:Al₂O₃ targets (group a) and by mid frequency (mf) sputtering from metallic Zn:Al targets (other groups): substrate temperature Tₛ, deposition pressure pdep, PEM intensity, thickness d and etch time tetch.
Table 1

<table>
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<tr>
<th>Series</th>
<th>$T_S$ (°C)</th>
<th>$p_{dep}$ (Pa)</th>
<th>PEM (%)</th>
<th>$d$ (nm)</th>
<th>$t_{etch}$ (s)</th>
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<tr>
<td></td>
<td>A2</td>
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<td>0.1</td>
<td>-</td>
<td>750</td>
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<td>c) Working point</td>
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Fig. 1 (a)

Fig. 1 (b)
Fig. 2 (a)

Fig. 2 (b)
Fig. 3
Fig. 4
Fig. 5 (a)

Fig. 5 (b)
Fig. 5 (c)
Fig. 6