

## STABILITY OF TRANSPARENT ZnO FRONT CONTACTS FOR Cu(In,Ga)Se<sub>2</sub> SUPERSTRATE SOLAR CELLS

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**ABSTRACT:** The resistivity and the thermal stability of transparent conducting ZnO:Al have been correlated with the conditions of the sputtering process. Layers deposited at low RF power density (~1.3 to 2.6 W/cm<sup>2</sup>) exhibit a low resistivity of  $9 \cdot 10^{-4} \Omega\text{cm}$ , predominantly due to a high concentration of intrinsic donor type defects. These donors are compensated during annealing at high temperature in vacuum; the resistivity increases and the conductivity of the layers are not thermally stable. Depositions at RF power densities of more than 3.2 W/cm<sup>2</sup> yield a high growth rate of 70 nm/min, and the extrinsic Aluminum dopant is incorporated on vacant cation sites. These substitutional donors are thermally stable, and the change in resistivity after annealing at 550 °C is below 20 %. The influence of Na from the glass substrates has been investigated.

Keywords: ZnO - 1: Sputtering - 2: Cu(In,Ga)Se<sub>2</sub> - 3

### 1 INTRODUCTION

Aluminum doped zinc oxide (ZnO:Al) is commonly used as transparent front contact in thin film solar cells. In combination with Cu(In,Ga)Se<sub>2</sub> (CIGS) absorber layers solar cells with efficiencies of up to 18.8 % have been obtained [1-3]. These devices are usually made in the standard substrate configuration on Mo-coated glass substrates. An alternate configuration is the superstrate solar cell where the absorber layers is deposited glass coated with the transparent front contact. This offers the technological advantage of easier and more reliable encapsulation and therefore lower costs.

However, during the CIGS deposition the transparent front contact is exposed to temperatures of about 550 °C. Under these conditions the electrical properties of the ZnO:Al layers are expected to deteriorate. Nevertheless, the sheet resistance of the front contact should be below  $10 \Omega_{\square}$  for high efficiency solar cells.

We have grown transparent conducting ZnO:Al layers under various sputtering conditions. The resistivity of these layers was investigated in the as-deposited state and after annealing in vacuum at 550 °C. This paper correlates the changes in resistivity during the annealing treatment with the deposition process.

### 2 EXPERIMENTAL DETAILS

ZnO and ZnO:Al layers have been grown on soda lime glass substrates by RF sputtering from 4”

ceramic targets of pure ZnO and ZnO mixed with 2wt% Al<sub>2</sub>O<sub>3</sub>. The sputtering system has a base pressure in the lower  $10^{-5}$  Pa range, for the depositions Ar of 99.999% purity is introduced to a pressure of 0.3 Pa. Deposition temperatures between room temperature and 400 °C have been employed, the RF power densities has been varied between 1.3 and 5.1 W/cm<sup>2</sup>.

### 3 ELECTRICAL PROPERTIES OF ZnO:Al

Figure 1 shows the dependence of the electrical properties on the RF sputtering power. For each respective temperature the resistivity shows a maximum at intermediate RF power density, whereas in the regimes of low and high power density the resistivity is lower. Especially the deposition regime at 5.1 W/cm<sup>2</sup> is technologically interesting because of the high deposition rate of 70 nm/min, compared to 10 nm/min at 1.3 W/cm<sup>2</sup>.

The behavior of the resistivity is governed by the carrier density rather than the mobility; low resistivity corresponds to high carrier density and vice versa, whereas the mobility exhibits only minor changes with varying power density. Films deposited at room temperature have mobilities in the range of 15 to 20 cm<sup>2</sup>/Vs. Layers grown at 200 °C exhibit mobilities of about 20 cm<sup>2</sup>/Vs, whereas 10 to 15 cm<sup>2</sup>/Vs are observed for layers grown at 400 °C. The mobility increases with increasing substrate temperature up to

about 200 °C because of improvements in the crystal quality. At higher temperatures a migration of the aluminum dopant towards the grain boundaries has been reported which deteriorates the crystal quality and lowers the mobility [4].

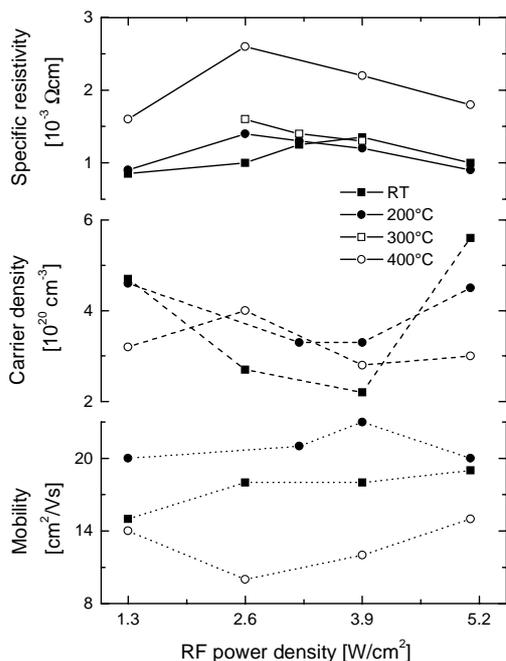


Figure 1: Dependence of the electrical properties of ZnO:Al on the RF sputtering power. The behavior of the resistivity is governed by the charge carrier density rather than the mobility.

### 3.1 Thermal stability of ZnO:Al

Figure 2 presents the relative changes of the electrical properties of the ZnO:Al layers after annealing at 550 °C. The changes in the resistivity strongly depend on the RF power density. In the low power regime the resistivity is observed to increase up to 800 %, in contrast, highly stable layers with increments of less than 20 % are observed in the intermediate range of power densities. Layers deposited in the regime of high power density show higher increments between 40 and 200 %.

The behavior of the resistivity is mostly related to the carrier density. Losses of up to 80% are observed for layers grown at low and high RF power, whereas smaller loss is observed in case of layers grown in the intermediate regime of power density.

The mobility is affected by annealing only in the case of room temperature deposited layers. At low RF power density these layers exhibit a decrease of more than 80 %, whereas the films grown at high RF power density actually show an increase in the mobility of up to 60 %. This increase compensates the effect of the charge carrier loss which leads to an moderate

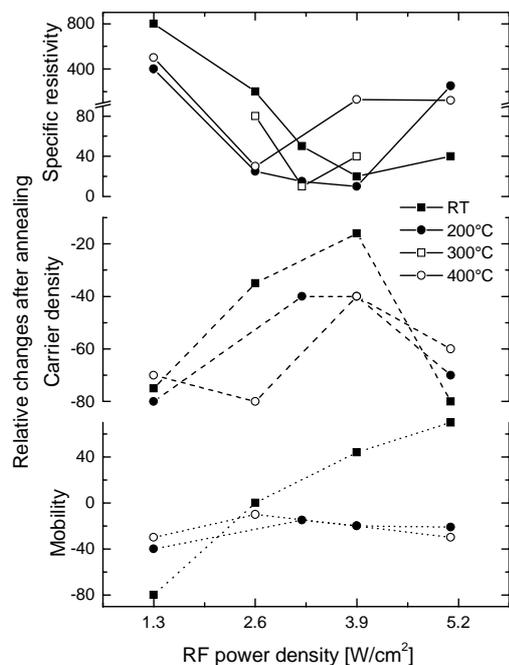


Figure 2: Relative changes of the electrical properties after annealing vacuum at 550°C. The changes in resistivity and carrier density exhibits a strong dependence on the power density.

overall increase in resistivity of 20-40 % for layers grown at room temperature and high power density. The layers deposited at elevated temperatures do not show this behavior, uniform loss of about ~30 % of the initial mobility is observed.

### 3.2 Conduction mechanism

We think that the variations in the electrical properties can be explained by an effect of ion bombardment on the formation of donor type intrinsic defects. Impinging ions from the plasma are reported either to damage the growing film [5] or to enhance the surface mobility of adatoms, thereby leading to an improved crystal quality [6-8]. This trade-off between damaging and beneficial effects of the ion bombardment is reflected in the three regimes of resistivity and carrier concentration which is visible in Figure 1.

At low RF power only a small amount of energy is transferred to the substrate by argon ions. Also the energy in the plasma is not sufficient for a complete dissociation of  $Al_2O_3$ . Sputtered particles move to the substrate and stay at whatever place they arrive; therefore surface diffusion and reorganization is limited. Thus the layer has small grains and defects like zinc interstitials and oxygen vacancies are formed. The conduction mechanism is governed by a high concentration of donor type intrinsic defects which results in low resistivity. Upon annealing the donor type defects recombine with oxygen which is des-

orbed from the grain boundaries and that leads to a large increase in the resistivity [9].

At intermediate powers a higher flux and higher energies of argon ions provides enough energy for the dissociation of  $\text{Al}_2\text{O}_3$  and to enhanced surface diffusion of adatoms. Larger grains with less defects are formed, the conductivity is no longer governed by a high concentration of intrinsic defects but by extrinsic donors (aluminum on the zinc site), thus the resistivity is slightly increased. However, extrinsic donors on substitutional sites show a higher thermal stability than intrinsic donor type defects [10], thus the resistivity increases only marginally upon annealing.

At high powers the growth rate is high and donor type defects are produced due to impinging ionized species which lower the resistivity. XRD measurements of these layers additionally show that the growth kinetics are changed and a loss in the preferential [0002] texture is observed. Annealing of these layers removes the defect type donors which gives rise to increased resistivity.

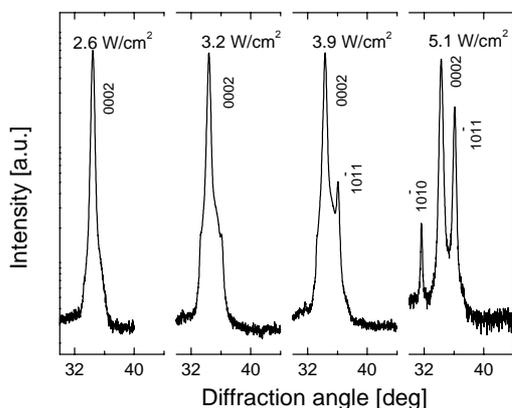


Figure 3: X-ray diffractograms of ZnO:Al layers grown at different RF power densities.

#### 4 INFLUENCE OF Na

ZnO:Al layers were deposited on Na-free glass in order to study the influence of Na diffusion from the substrate during the deposition and/or annealing at  $550^\circ\text{C}$ . In the case of room temperature depositions there is no difference in the electrical properties, neither initially nor after the annealing. However, layers deposited at  $400^\circ\text{C}$  on Na-free glass show a lower resistivity compared to those on Na-containing glass, due to higher mobility and carrier density. After annealing the relative changes in resistivity are same due to loss in the carrier density.

The measurements suggests that Sodium is incorporated into the layer only during growth at high temperatures where it forms an acceptor. The relative changes of the electrical properties due to annealing are similar for Na-containing and Na-free substrates,

which means that Na does not contribute to the loss in conductivity of ZnO:Al at high temperatures; perhaps Na which diffuses after the deposition is not electrically active.

### 5 SUPERSTRATE SOLAR CELLS

ZnO:Al covered with a 100 nm thick buffer layer of undoped ZnO was used for the fabrication of superstrate solar cells. The  $2\ \mu\text{m}$  thick  $\text{Cu}(\text{In,Ga})_x\text{Se}_y$  absorber layer was grown by vacuum evaporation of the elements. Finally, a 50 nm thick Au layer was evaporated as metallic back contact.

#### 5.1 Morphology of CIGS layers

The morphology of the CIGS absorber layers was investigated with a scanning electron microscope (SEM). The layer corresponding to the upper image in Figure 4 was grown at constant flux of all sources. This one stage process usually yields layers with a grain-size below  $1\ \mu\text{m}$ . The growth of the second layer was started under Cu-rich conditions and finished with low Cu-flux in order to adjust the composi-

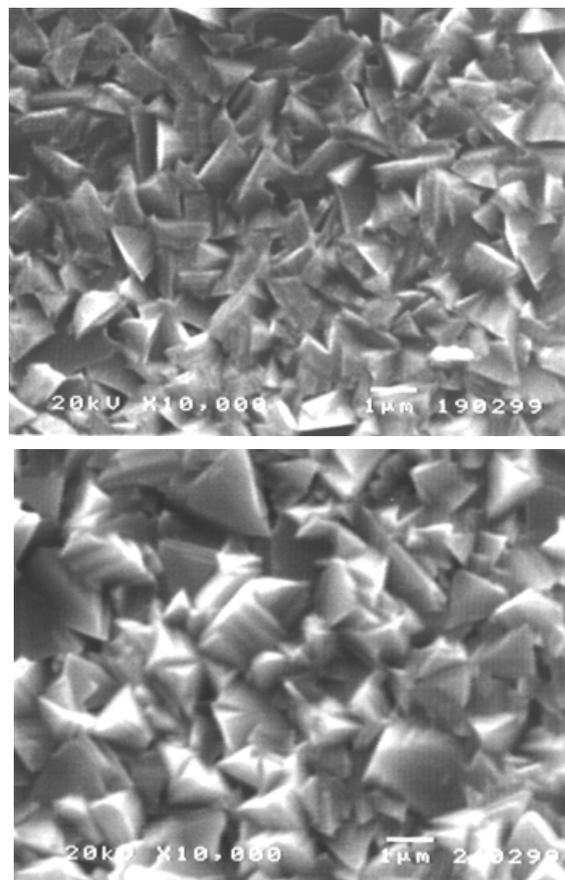


Figure 4: SEM morphology of CIGS absorber layers on ZnO/ZnO:Al coated glass. The compositions are slightly III-rich. The layer corresponding to the upper image was grown with constant source fluxes, the increases grain size of the second layer is a result of Cu-rich initial conditions (bilayer process).

tion. This two stage process results in layers with increased grain size of up to 3  $\mu\text{m}$ .

## 5.2 I-V characteristics

Figure 5 shows the I-V characteristics of a solar cell with a slightly Cu-deficient absorber. Light soaking under one sun generally improves the I-V diode characteristics which is attributed to the saturation of recombination centers near the junction and traps in the ZnO layer. The highest efficiency superstrate solar cell has  $V_{oc} = 500$  mV,  $I_{sc} = 30$  mA/cm<sup>2</sup>, FF = 57 %, and  $\eta = 8.5$  %

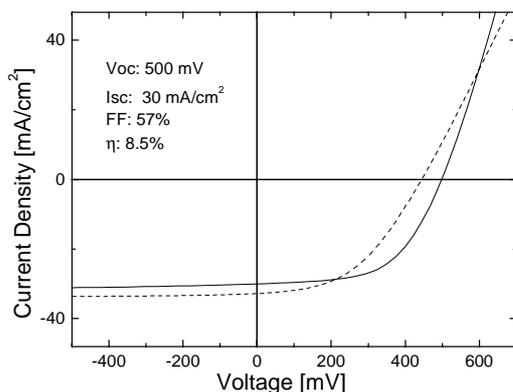


Figure 5: I-V characteristic of a CIGS/ZnO/ZnO:Al superstrate solar cell.

## 6 CONCLUSIONS

The influence of deposition parameters on the electrical properties of ZnO:Al has been investigated. For the dependence on the RF power density three regimes are identified. Low and high power density yield layers with low resistivity, however, they are not thermally stable because the conduction is dominated by donor type defects which are compensated during annealing. A regime of intermediate power density has been identified which in combination with substrate temperatures between 200 and 250°C yields layers with thermally stable conductivity because the conduction mechanism is governed by the aluminum dopant on a zinc site. The influence of sodium diffusion from the substrate has been investigated; electrically active Na is incorporated only during deposition at high temperatures.

Optimized ZnO:Al layers have successfully been used for CIGS depositions at 550 °C. Superstrate solar cells with efficiency of up to 8.5 % have been obtained.

## 7 ACKNOWLEDGEMENTS

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