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Research Update: Inhomogeneous aluminium dopant distribution in magnetron sputtered ZnO:AI thin films and its influence on their electrical properties

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The spatial distribution of Al in magnetron sputtered ZnO:Al films has been investigated in depth. Two different kinds of inhomogeneities were observed: an enrichment in the bulk of the film and an enrichment at the interface to the substrate. This has been correlated to the electrical properties of the films: the former inhomogeneities can lead to trap states at the grain boundaries limiting the free carrier mobility. The latter can promote the formation of secondary phases, which leads to an electrical inactivation of the dopant. Furthermore, this effect can contribute to the thickness dependence of the electrical properties of ZnO:Al films. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4922152]

Doped zinc oxide (ZnO:X) belongs to the class of transparent conductive oxides. These materials combine a high optical transmittance above 80% in the visible spectrum with a resistivity below $10^{-3} \Omega \text{cm.}^1$ Nowadays, these materials are used on an industrial scale in flat panel displays, for architectural glass coatings, in photovoltaic cells, etc.² Only if the free carrier concentration in these materials is very high and the mobility of the charge carriers is as high as possible, these properties can be achieved. To this purpose, the ZnO films have to be highly doped using dopant elements with concentrations up to approximately 2 at. %, i.e., one can speak of alloying the ZnO. However, the concentration of the free carriers and their mobility strongly depend on structural properties of the material such as defects, the density of the dopants, and the presence of secondary phases. In general, only a part of the dopant atoms in magnetron sputtered films creates free electrons in the conduction band and thus contributes to the doping effect. The remaining part is electrically inactive, which means that it is either not incorporated on a Zn lattice site, which is the doping mechanism for group III elements,^{3,4} compensated by acceptor-like defects, or inactivated in insulating secondary phases.

The solubility limit of Al in ZnO under thermodynamic equilibrium conditions is below 0.5 at. %.⁵ Under non-equilibrium conditions, which prevail during the magnetron sputtering deposition, the solubility is significantly higher, in the range of 2–3 at. %.^{6,7} This behaviour is also observed for silicon and for SiGe alloys. For SiGe, it was shown that the strain in the heteroepitaxial films increases the solubility significantly.⁸ Still, the formation of secondary phases has to be expected for Al concentrations which are typically present in ZnO:Al (1–3 at. %).



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The spatial distribution of the dopant element in ZnO and the segregation of secondary (oxidic) phases containing the dopant material have only been studied sporadically for ZnO in general, and especially, for films prepared by magnetron sputtering. Sieber et al.⁷ performed a study of the microstructural properties of Al-doped ZnO and showed that the Al is present in the form of Zn-Al-O phases at the grain boundaries and in a 10–20 nm thick region at the interface to the Si substrate. They prepared ZnO:Al films on Si substrates by magnetron sputtering from pure metal targets under controlled oxygen flow and used high-resolution transmission electron microscopy (HRTEM). The samples have been prepared in cross section for investigation of the microstructure. Unfortunately, they did not correlate their results to the electrical properties of the films. It seems, no other group actually proved the existence of such phases in films sputtered at moderate temperatures yet. Vasile et al.⁹ studied the distribution of the dopant in ZnO:Al active channel layers deposited by the sol-gel method and had indications of an enrichment of the Al at the grain boundaries and at the interface to the SiO2 substrate. Kinemuchi and co-workers¹⁰ found an Al enrichment at the grain boundaries of their c-axis textured ZnO:Al ceramics as well. However, their films were sintered at 1400 °C for 10 h, i.e., under thermodynamic equilibrium conditions. For large-grained, polycrystalline ZnO used, for example, in varistors, doped with elements other than Al, more data are available: Sato et al.,¹¹ for instance, performed detailed experimental and theoretical studies on the segregation of different impurities (Pr and Co) at the grain boundaries.

In this paper, we discuss the spatial distribution of the dopant Al measured by atom probe tomography (APT), Rutherford backscattering spectrometry (RBS), and transmission electron microscopy (TEM) combined with energy dispersive X-ray (EDX) spectroscopy and high angle annular dark field (HAADF) imaging on as-deposited and annealed ZnO:Al films. The microscopic results are then discussed in relation to electrical measurements on the films. The conclusions can be used to optimize the mobility of the free carriers as well as their concentration and hence the conductivity of the transparent conductive oxide films.

The ZnO:Al films were deposited by 13.56 MHz radio frequency (RF) magnetron sputtering from a 3 in. diameter ceramic target containing 2 wt. % Al₂O₃ with a sputtering power of 50 W. The target-to-substrate distance was 61 mm and the process pressure was kept constant at 0.3 Pa using pure Ar as sputtering gas. The films were prepared on different types of substrates: borosilicate glass (Borofloat glass 33, Schott AG) with a size of $10 \times 10 \times 1$ mm³ for the electrical measurements, glassy carbon (Sigradur) with a size of $5 \times 10 \times 1$ mm³ for the RBS measurements, a Mo tip with a radius in the range of about 50 nm for the APT analysis, and oxidised single crystalline silicon as well as single crystalline silicon with only the native oxide layer on top with a size of $10 \times 10 \times 0.3$ mm³ for the TEM analysis. During deposition, the substrates were kept at floating potential. Additionally, the film on the silicon substrate was annealed at 600 °C for about 18 h in vacuum. The glass substrates were cleaned for 5 min in an ultrasonic bath of isopropanol at room temperature, while the glassy carbon substrates were first wiped with a wet tissue before they were ultrasonically treated for 15 min at 80 °C in isopropanol. The silicon substrates were also wiped with a wet tissue and afterwards put in the ultrasonic bath for 40 min at 80 °C. After the ultrasonic bath, all substrates were rinsed with deionized water and blown dry with pure N_2 . The silicon substrates were additionally baked out at 200 °C for 1.5 h in air.

For the depositions at elevated temperatures, the substrates were heated radiatively up to 500 $^{\circ}$ C with a boron nitride encapsulated graphite meander heater (Boralectric). The resulting film thicknesses were measured with a surface profilometer (Veeco, Dektak 8). The electrical characterization was done by Hall and conductivity measurements in the van der Pauw geometry. The contact triangles made of Ni and Au (10/150 nm) were deposited in the corners of the samples. The Hall measurements were performed at a magnetic flux of 0.86 T.

The composition of the samples was determined by RBS with 1.7 MeV ⁴He ions at normal incidence performed at the Helmholtz-Zentrum Dresden-Rossendorf. The scattering angle was 170° and the backscattered ions were detected with a surface barrier silicon diode detector with an acceptance angle of 3.36 msr, an energetic resolution of 18 keV, and a charge per sample of 100 μ C. Such an unusual high He⁺ charge was used in order to improve the measurement accuracy for the light elements O and Al by a factor of about 3 in comparison to measurements with 10 μ C.

The microstructural analysis of the samples was carried out using a Carl Zeiss LIBRA 200FE transmission electron microscope equipped with an EDX spectrometer by Thermo Fischer Scientific company. The TEM was operated at an acceleration voltage of 200 keV and the electrons were zero-loss filtered. The EDX maps were recorded with a spot size of the beam below 10 nm. Al-rich segregated particles within the film formed after thermal treatment were detected by high resolution TEM, bright-field scanning transmission electron microscopy (STEM), and high angle annular dark field imaging. To analyse the EDX spectra, the software NSS 2.2 provided by Thermo Fischer Scientific was used.

The atom probe tomography requires needle-shaped samples with a radius <50 nm. To this purpose, thin films were deposited directly on the Mo tips which were previously prepared by electropolishing at room temperature at a voltage of about 5.5 V in a solution of 4 N NaOH in water. The ZnO:Al film has been prepared without intentional heating of the Mo tip. To analyze the spatial distribution of the elements in the films, 3D laser assisted wide angle APT has been used. The APT with a local electrode was built at the University of Münster (and is now installed at the University of Stuttgart). Details of the setup can be found in Ref. 12. The field evaporation was realized with fs-pulses of a UV laser ($\lambda = 343$ nm, 200 kHz, 60 nJ/pulse) and the experimental parameters were set to maintain a detection rate of 0.02–0.04 ions per pulse. The measurements were performed in vacuum at a pressure below $p = 10^{-8}$ mbar, and the temperature of the tip was kept below 50 K. The raw data were analyzed using the 3D data software developed by the Material Physics group at the University of Rouen.

Experimental evidence for a spatially inhomogeneous distribution of the dopant material in the films has been found and two different kinds of inhomogeneities were observed: (i) an enrichment of the dopant Al in confined areas in the bulk of the film and (ii) an enrichment at the interface to the substrate.

Figure 1(a) shows the results of the APT measurement, i.e., a three-dimensional reconstruction of Zn, O, and Al atom positions within an investigated volume of about $30 \times 30 \times 108$ nm³. Al-rich clusters are visualized using a threshold of >1.8 at. % Al in Figure 1(b).

Whereas small Al-rich particles of spherical morphology are visible in the upper part of the investigated volume in Figure 1(b), a continuous surface on the bottom (at the interface to the Mo tip) can be seen. The chemical composition of the small particles and of the thick layer at the Mo interface is obtained by means of the cluster search module (threshold for Al >1.8 at. %). The concentration of Al in the small clusters corresponds to 4.8 ± 1.4 at. % and of the thick layer up to about 34 ± 3 at. %.

The enrichment of the Al at the interface to the substrate becomes obvious also from the results of the Rutherford backscattering experiments for ZnO:Al films deposited at different temperatures



FIG. 1. (a) 3D reconstruction of Zn, O, and Al atom positions in an investigated volume of $30 \times 30 \times 108$ nm³ of a ZnO:Al film deposited on a Mo tip without intentional heating. (b) Al-rich clusters (aubergine color), obtained using a cluster search module with a threshold for Al-rich clusters of >1.8 at. %. (c) Concentration depth profiles for Al, O, and Mo taken along a cylinder of 1 nm radius located in the middle axis of the investigated volume in (b).



FIG. 2. RBS raw data for a ZnO:Al thin film prepared at 500 °C on glassy carbon. A background subtraction has been performed. The marked peak (*) stems from carbon on the surface of the film, formed during the long irradiation time by He ions, leading to a decomposition of hydrocarbons from the restgas on the sample surface.

on glassy carbon (Sigradur) substrates. Figure 2 shows the RBS spectrum of the sample prepared at room temperature. We also see a weak signal from the process gas ($c_{Ar} < 0.5$ at. %) built into the films during the deposition.

Figure 3 shows the details of the different element peaks (solid lines) and simulated spectra (dotted lines) for the samples prepared at different deposition temperatures. Obviously, the Al segregation is much stronger for higher deposition temperatures.

Especially for the film deposited at 500 °C, a strong enrichment of Al at the interface between the film and the substrate is visible. Using a two layer model for the film in SIMNRA¹³ to fit the



FIG. 3. RBS raw data (solid black lines) and simulated spectra (dotted red lines). A background subtraction was performed prior to data analysis, which was done with SIMNRA.¹³ (Top and center) Simulation using a 2 layer model for the film, (bottom) simulation using a 1 layer model.

to the substrate interface of the film.							
T _{dep} (°C)	Al conte						
	Interface	Surface	Film thickness (nm)				
500	6.2 ± 0.2	3.0 ± 0.2	165				
300	2.2 ± 0.2	2.0 ± 0.2	140				
30	1.9 ± 0.2	1.7 ± 0.2	120				

TABLE I. Al concentration determined by a simulation with SIMNRA¹³ using a two layer model to describe the depth dependence from the surface to the substrate interface of the film.

Al content in the main part of the film and the interface region, an Al content of (6.2 ± 0.2) at. % is determined for the interface region, while the Al content in the main part of this film is only about (3.0 ± 0.2) at. %. The marked interface region has a thickness of approximately 35 nm. For the films deposited at lower temperatures, there is only a slight increase of the Al content from the film surface to the interface to the substrate. At first glance, this is in contrast to the results of the atom probe tomography measurement for the film prepared at room temperature, where an enrichment of the Al at the interface can be detected as well (see Figure 1). A plausible explanation is the temperature increase of the Mo tip by the energetic bombardment and by the condensation of the film forming atoms during the deposition of the ZnO:Al film. Due to the small heat capacity of the Mo tip and the quite weak thermal conduction to the support, the temperature can increase significantly. With the two layer model, the following compositional changes were determined (see Table I).

We validated our results by a third measurement technique—energy dispersive X-ray spectroscopy on samples in cross section of ZnO:Al films prepared on different substrates. Figure 4 shows the results of a film prepared on Si at a substrate temperature $T_{sub} = 300$ °C.

Again, an increase of the Al concentration in a region close to the substrate can be observed. Assuming that the increase of the counts at the interface to the substrate is proportional to the increase of the Al concentration, neglecting fluorescence and absorption effects, the Al concentration at the interface must be in the range of 3.4 at. % when it was approximately 2.1 at. % in the bulk (as determined from the RBS measurements). The width of this region is approximately (40 ± 10) nm (see markers in Figure 4). This width is in quantitative agreement with the results from the RBS measurements on the sample grown at 500 °C.

The TEM image in Figure 5(a), taken close to the region where the EDX measurement was performed (Figure 4), shows a lower crystallographic quality in the first 30–50 nm. Fine crystallites of ZnO (<5 nm) at the interface between the film and the substrate are clearly observed in Figure 5(b), which shows the bright field micrograph of the ZnO:Al film deposited on glass. Similar observations have been made by Sieber *et al.*⁷ who found an interface layer with a thickness of 10–20 nm



FIG. 4. (a) Depth profiles of the elements determined from EDX maps of a cross section of a ZnO:Al film deposited at 300 °C on a Si substrate. The uncertainty of the data is indicated for selected data points. The errors were determined from the variation of the signal in lateral film direction for the area measured. (b) Zoom display of the data. The general increase of the element signal with increasing depth is due to the wedge-like shape of the cross-sectional sample.



FIG. 5. (a) TEM image of a ZnO:Al film deposited at $300 \,^{\circ}$ C on Si. The image was taken in a region close to the area, where the EDX measurement was performed. (b) TEM micrograph of the ZnO:Al film deposited at room temperature on glass showing fine crystallites at the interface.

which exhibited small crystallite sizes in the range of 4–7 nm depending on the oxygen flow rate during their sputtering process, and Vogel-Schäuble *et al.*¹⁴ who found a defective nucleation zone at the interface to the substrate with a thickness of roughly 50 nm in their RF magnetron sputtered ZnO:Al films on glass by TEM investigations.

The Al enrichment at the interface has also been observed by EDX for films prepared on glass substrates (not shown here). Since the RBS samples were prepared on glassy carbon (Sigradur) and the APT samples were prepared on Mo, the Al enrichment at the interface occurs on different substrate types. However, measurements on films grown on single crystalline ZnO or Al₂O₃ substrates did not show an enrichment of Al at the interface to the substrate in EDX measurements.

The observation of the fine crystallites and the increased defect density suggests a possible correlation between this defect rich interface region and the enhanced Al concentration. This is not surprising, because the concentration of Al can exceed the solubility limit in the interface layer of the magnetron sputtered ZnO:Al films leading to the precipitation of secondary phases and a degradation of the crystalline quality. However, in contrast to Sieber *et al.*,⁷ we were not able to detect secondary phases at the grain boundaries or at the interface in the as-deposited film on Si.

In order to study the effect of high temperature treatments on secondary phase segregation, a TEM analysis was carried out on a ZnO:Al film on oxidised Si after annealing at 600 °C in vacuum. The bright field image in Figure 6(a) shows the presence of a region of fine precipitates at the film-substrate interface as well as within the film at the boundary of columnar grains of ZnO (marked by arrows).

The STEM HAADF image in Figure 6(b) clearly shows these precipitates. The size of these precipitates was between 10 and 25 nm. The contrast difference between the matrix of ZnO and these precipitates originates from the difference in their atomic numbers and hence indicates that these precipitates are enriched in Al. The EDX analysis shown in Figure 6(c) confirms the enrichment of Al in these precipitates. Locally resolved EDX measurements revealed an inhomogeneous distribution of Al within the film as well. High-resolution image analysis of the region marked in Figure 6(d) points to a cubic structure of these precipitates—either $ZnAl_2O_4$ or γ -Al_2O₃ (see fast Fourier transform (FFT) in the inset). However, a clear distinction between $ZnAl_2O_4$ and γ -Al_2O_3 was not possible with this technique since the space group of both phases are identical ($Fd\bar{3}m$) and the lattice parameters are nearly the same $(a_{ZnAl2O4} = 8.0848 \text{ Å and } a_{\gamma-Al2O3} = 7.914 \text{ Å})$ [JCPDS 05-0669 and 79-1557, respectively]. For analysis by XRD, on the other hand, the relative amount of those precipitates is too small. The observation in the present study suggests that during the annealing step, the super-saturation of Al in ZnO is partially relieved by the precipitation of ZnAl₂O₄ or Al_2O_3 at grain boundaries and at the interface. The relaxation of the ZnO lattice due to the annealing treatment was also indicated by the observation of stacking faults in the film. From the FFT analysis, the following epitaxial relationship between the ZnO and the new cubic structure can



FIG. 6. (a) Microstructure of a ZnO:Al film on oxidised Si after annealing at 600 °C showing the presence of fine precipitates at the interface and within the film at the columnar grain boundaries (marked by arrows). (b) STEM HAADF image clearly showing dark regions due to precipitates of lower mean atomic number. (c) EDX spectra from the matrix (black) and a precipitate (red) showing an enrichment of Al in the precipitate. (d) HRTEM image of the cubic spinel phase in the ZnO:Al film. The inset displays the FFT from the region circled which can be assigned to a hexagonal and a cubic fcc phase.

be inferred: $(0002)_{ZnO} \parallel (11\overline{1})_{fcc}$ and $[11\overline{2}0]_{ZnO} \parallel [011]_{fcc}$. The formation of the spinel ZnAl₂O₄ after annealing of ZnO and Al₂O₃ has been reported by many authors with different epitaxial relationships with $(0002)_{ZnO} \parallel \{111\}_{ZnA12O4}$.^{15–17} Hence, the cubic phase observed in our study could be the ZnAl₂O₄ spinel.

The Al enrichment shown by the atom probe tomography also indicates the formation of secondary phases in the region near to the substrate: While the measured Al and O contents in the bulk of the film are very low, they are higher at the interface to the substrate (see Figure 1(b)). This effect may partly be a measurement artefact, possibly caused by a preferred field-enhanced evaporation of the oxygen during the laser pulse in the course of the APT analysis of the bulk of the film. However, at the same time, the APT points to the presence of compounds with a higher dissociation energy, because at the substrate interface the evaporation takes place only at higher laser pulse energies. This could be Al_2O_3 or $ZnAl_2O_4$ which is consistent with the results from the high-resolution TEM (see Table II).

The composition of the Al-rich layer near the substrate as measured by APT is, within the error bar, closer to the composition of $ZnAl_2O_4$ than to that of Al_2O_3 .

It is likely that the enrichments of Al in the bulk of the film are correlated to the presence of grain boundaries. Such effects are known since a long time and have been investigated to understand and

Jopant elements.						
Compound	$\Delta_{f}H^{0}\left(eV\right)$	Reference				
ZnO	-3.6	18				
Al ₂ O ₃	-17.3	18				
Ga ₂ O ₃	-11.2	18				
$ZnAl_2O_4$	-21.4	19				

-15.2

19

ZnAl₂O₄

ZnGa₂O₄

TABLE II. Enthalpy of formation of ZnO and secondary phases containing

tailor the mechanical properties of materials.²⁰ The segregation of dopants at a bicrystal boundary has directly been observed for Co and Pr co-doped ZnO bicrystals by Sato *et al.*¹¹ Also, Kinemuchi *et al.*¹⁰ found an increased Al content at the grain boundaries by energy dispersive X-ray spectroscopy in their sintered ZnO:Al ceramics. The segregation of dopants to grain boundaries has also been treated by density functional theory (DFT) calculations. For instance, Körner and Elsässer calculated segregation energies of Al and Ga at grain boundaries of up to 1.5 eV.²¹ In magnetron sputtered In₂O₃:Sn films, Morikawa *et al.*²² were able to prove grain boundary segregation of Sn by means of electron energy loss spectroscopy and X-ray photoelectron spectroscopy. The segregation of Cr to the grain boundaries in electron beam evaporated In₂O₃:Cr thin films was detected by APT by Payne and Marquis.²³

The Al enrichment at the substrate-film interface could be explained by a preferential condensation of Al atoms or Al rich phases (or the preferential re-evaporation of Zn atoms) in the initial stage of the film growth. The influence of condensation and re-evaporation during a deposition has already been recognized a long time ago by Langmuir²⁴ when investigating the condensation and re-evaporation of cadmium on glass. In a first approach, one can relate the condensation and re-evaporation to the vapour pressures of the deposited species only. In our case, Zn has a much higher tendency to re-evaporate from the substrate compared to Al.²⁵ On the other hand, the tendency of metal oxides to condensate on the substrate is significantly higher because of their much lower vapour pressure in comparison to that of the pure metals. Since the formation of Al_2O_3 or $ZnAl_2O_4$ is energetically preferred over the formation of ZnO, this means that Al rich oxygen containing phases are preferentially remaining on the substrate surface in the initial stage of the film growth at higher T_{sub} . This could explain the high Al content in the early stage of the film growth as well as the preferred formation of secondary phases in the interface layer. The dependence on the substrate temperature is then a result of the exponential temperature dependence of the vapour pressures, which leads to a much stronger re-evaporation of Zn from the substrate for higher deposition temperatures. However, the vapour pressure and the enthalpies of formation of the oxide phases alone cannot explain the depth dependence of the Al concentration, i.e., the fact that the enrichment is only limited to an interface region of approximately 30 nm-50 nm thickness.

Condensation and re-evaporation also depend on the specific type of substrate and its crystallinity.^{26,27} Although experimental data on the energies binding the film forming species to the substrates used here have not been found, it might be hypothesized that the condensation of Zn or Zn-O phases is easier on crystalline materials. This could explain the absence of the enrichment in films grown on the single crystalline substrates (ZnO and Al₂O₃) in comparison to the amorphous substrates or substrates with an amorphous top layer (glassy carbon, Si, glass). Furthermore, it would explain the limited width of the enriched layer: the (poly-) crystalline nuclei formed in the initial stages of the film growth could facilitate the condensation of ZnO and hence, the Al concentration decreases to a lower equilibrium value. On the contrary, Lorenz et al.²⁸ observed an enrichment of the dopant scandium at the substrate-film interface in ZnO:Sc films grown on single crystalline substrates. Within our model, this could only be explained by an even higher tendency of the Sc to form precipitates and changed initial conditions due to the different deposition techniques. A difference of the binding energy of the film forming species to the substrate material itself could explain the fact that an enrichment of Al is barely detectable with the RBS measurements for the films grown on glassy carbon at $T_{sub} = 300 \,^{\circ}$ C (see Figure 3 and Table I), while the films grown on Si at this temperature clearly show an enrichment in the EDX measurements. The detection limits of the different techniques cannot cause this discrepancy, because, based on the EDX measurement, the increase is about 1 at. % Al, which would be well detectable by RBS.

As already pointed out, the inhomogeneity of the Al in the bulk of the film can be related to the segregation of Al to grain boundaries. As Sato *et al.*¹¹ discussed in their work on Pr and Co-codoped ZnO bicrystals and as it was confirmed by our investigation,²⁹ the segregation of Al is most likely responsible for the formation of electron trap states at the grain boundaries. The filling of these trap states by electrons leads to potential barriers at the grain boundaries which reduce the effective mobility of the free carriers. This assumption is supported by literature data: Figure 7 shows the transport data of ZnO:Al films, i.e., the Hall mobility μ_n of the free carriers as a function of their concentration *n* of films prepared with different Al contents.



FIG. 7. Hall mobility μ_n as a function of the free carrier concentration *n* for doped ZnO films prepared from targets with different dopant concentrations (color codes target composition according to scale on the right). The data were taken from Agashe *et al.*³⁰ (circles, ZnO:Al), Berginski *et al.*³¹ (squares, ZnO:Al), Cornelius and coworkers⁶ (triangles up, ZnO:Al), Suzuki *et al.*³² (diamonds, ZnO:Al), Terasako *et al.*³³ (triangles down, ZnO:Ga), and our own data (all open symbols, part of the data was taken from Ref. 34). The solid blue line models the transport data of the single crystalline ZnO and hence mainly the mobility limited by ionized impurity scattering. The dotted green lines are fits with a combined transport model taking into account ionized impurity scattering and grain barrier limited transport (grain size L = 50 nm).³⁵ The inset shows the trap state densities at the grain boundaries as a function of the dopant concentration in the target determined by a fit to the different datasets. The dashed line shows a fit with a function of the form $A(1 - \exp(-B \cdot c_A))$.

A fit of the data with a transport model combining ionized impurity scattering and grain barrier scattering of the charge carriers (for details on the model see Ref. 35) shows a clear trend: with increasing Al concentration in the film/target, the trap density at the grain boundaries N_t increases, which means that more Al in the films leads to a stronger grain boundary scattering (see Table III). For the modelling, the best fits were usually obtained for a grain size L = 50 nm. The effective mass m^* was adjusted to the free carrier concentration range considering the degeneracy of the electron gas, which leads to a dependence of m^* on the electron concentration (for details on the $m^*(n)$ dependence, see Ref. 35).

This effect is important for practical applications of the films: since the mobility of the charge carriers should be as high as possible, a high number of trap states are undesirable. Hence, the amount of Al in the films must be reduced. This, however, would decrease the free carrier concentration, which is, according to the relation $\sigma = en\mu$, detrimental for the conductivity of the samples and also undesirable. However, the electrical activation of the dopant is usually well below 100%, which means only a part of the Al atoms donates a free electron. Therefore, the aim must be to increase the electrical activation or to find dopants with a higher activation to reduce the amount of dopant material and hence increase the mobility while maintaining a high free carrier concentration. A possible candidate is Ga. First systematic studies by Cornelius³⁶ as well as Gabas *et al.*³⁷ already indicate a higher electrical activation of Ga in comparison to Al in magnetron sputtered films. This effect can tentatively be explained by a simple interpretation. The covalent bond lengths of Ga-O (192 pm) and Al-O (192 pm) in the tetrahedral configuration are nearly the same, i.e., both Al and Ga fit well into the host lattice with a bond length of Zn-O (197 pm).^{38,39} However, Ga has a lower tendency to form secondary phases such as Ga₂O₃ or ZnGa₂O₄ in comparison to Al with Al₂O₃ or ZnAl₂O₄ (see Table II), i.e., a larger portion of the Ga should remain in an electrically active configuration.

Film	$m^*(m_{\rm e})$	c _{dopant} (at. %)	Method	$N_t (10^{13} \text{ cm}^{-2})$	Reference
ZnO:Ga	0.33	0.13	IP	2.0 ± 0.5	33
ZnO:Al	0.33	0.16	RF-MS	2.0 ± 0.5	31
ZnO:Al	0.4	0.4	RF-MS	5.0 ± 1.0	31
ZnO:Al	0.41	0.4	RF-MS	5.0 ± 1.0	30
ZnO:Al	0.46	0.59	PLD	8 ± 3	32
ZnO:Al	0.45	0.79	RF-MS	6.0 ± 1.0	31
ZnO:Al	0.47	0.79	RF-MS	8.5 ± 0.5	30
ZnO:Al	0.42	0.87	DC-RMS	7 ± 1.5	6
ZnO:Al	0.47	1.57	RF-MS	7.0 ± 1.0	31
ZnO:Al	0.55	1.57	RF-MS	11 ± 2	30
ZnO:Al	0.42	1.57	DC,RF-MS	6 ± 3	This work
ZnO:Ga	0.55	1.73	IP	11 ± 3	33
ZnO:Al	0.49	2.02	DC-RMS	9 ± 2	6
ZnO:Al	0.58	3.07	RF-MS	13 ± 3	30

TABLE III. Trap state densities at the grain boundaries N_t for doped ZnO films deposited on glass substrates. The values were determined by modelling $\mu_n(n)$ data, reported by the various groups, with a combined transport model. IP: ion plating, MS: magnetron sputtering, RMS: reactive magnetron sputtering, RF-MS: radio-frequency magnetron sputtering DC-MS: direct current magnetron sputtering, PLD: pulsed laser deposition.

The enrichment of the Al at the interface to the substrate might also play a role in the low electrical activation of the dopant in ZnO:Al films. From thermodynamic considerations, the preferred formation of secondary phases in this layer is expected. Since the dopant is electrically inactive in these phases, this reduces the overall electrical activation and might hence contribute to the low electrical activation of only 30%–50% for the films investigated here. This provides also a basis to understand the thickness dependence of the electrical properties of thin ZnO:Al films.^{30,40–44} We found that initially the resistivity strongly decreases with film thickness, while it reaches a plateau for film thicknesses above 50 nm (see Figure 8). This corresponds quite well to the thickness of the enriched layer with the small crystallites and its increased amount of Al and/or Al containing secondary phases. The thickness dependence of the resistivity can be fitted with the Fuchs-Sondheimer (F-S) theory,^{45,46}

$$\frac{\rho(d)}{\rho(\infty)} = 1 + \frac{l_e(1-p)}{8(d-d_0)},\tag{1}$$

where l_e is the electron mean free path, p is the diffuse reflection coefficient for the electrons at the surface and interface, respectively, d is the film thickness, and d_0 is an interface layer which does not



FIG. 8. Resistivity of ZnO:Al films prepared with different thicknesses on borosilicate glass by RF magnetron sputtering at 300 °C. The dotted line shows a fit according to Eq. (1).

contribute to the electrical transport. From the fit, we obtain $l_e(1 - p) = 12$ nm and $d_0 = 29.5$ nm. According to Sondheimer,⁴⁶ the mean free path can also be calculated by (*h*: Planck's constant, *e*: elementary charge)

$$l_e = \left(\frac{3}{8\pi}\right)^{1/3} \frac{h}{e^2 \rho \, n^{2/3}},\tag{2}$$

which yields $l_e \approx 3$ nm. This value is smaller than $l_e(1-p)$ determined from the $\rho(d)$ fit which also indicates that the electrical transport in ZnO is influenced at the interface.

Secondary phases do not only reduce the electrically active fraction of the dopants, but they also introduce additional scattering of the charge carriers due to the inhomogeneities in the material, which reduce the free carrier mobility. This has a negative influence on the conductivity of the films as well as the near-infrared transmittance, which needs to be avoided.⁴⁷ A possible route to circumvent the enrichment of Al in the early stages of the film growth might be the use of buffer or seed layers. Experiments with buffer layers have been reported occasionally for ZnO:Al,^{42,43,48,49} but usually they are introduced to avoid the defective interface layer and improve the crystalline quality of the subsequent layer. Improved crystallinity may indeed decrease the free carrier scattering and thus contribute to a higher conductivity. However, the buffer layers might also have a positive influence on the amount of secondary phases and hence on the free carrier concentration and their mobility. According to the tentative results obtained from the different substrate types, an undoped ZnO layer with a high crystalline quality should be used as buffer.

Unfortunately, there are only very few reports on the depth dependence of the electrical film properties with or without a buffer layer in the literature. This data could be used to further investigate the possible effects of buffer layers on the phase segregation. However, the reports are ambiguous: Look *et al.*⁴² reported a homogeneous free carrier concentration throughout the whole film for their RF-magnetron sputtered ZnO:Al with or without a thin ZnON buffer layer. Itagaki and co-workers⁴³ on the other hand reported an increased average free carrier concentration when using solid-phase crystallized ZnON buffer layers for their RF-sputtered ZnO:Al films. Using RF sputtered ZnO:Al seed layers, Dewald *et al.*⁵⁰ were also able to slightly increase the average free carrier concentration of DC sputtered films. However, Sago *et al.*⁴⁴ recently measured a lower free carrier concentration close to the substrate in their magnetron sputtered ZnO:Al films, which is in agreement with our results.

Obviously, further research is necessary to clarify the effect of buffer or seed layers on the structural and especially the depth dependent electrical properties. This knowledge can then be used to examine the effect of a buffer layer on the suppression of the formation of secondary phases and hence to increase the electrical activation of the dopant, which is an additional route to improve the properties of ZnO:Al to become competitive with tin-doped indium oxide (ITO).

The spatial distribution of the dopant element Al in ZnO:Al (2 at. % Al) films, deposited by RF magnetron sputtering, has been investigated by means of atom probe tomography, Rutherford backscattering spectroscopy, and transmission electron microscopy with energy dispersive X-ray spectroscopy and high angle annular dark field imaging. Two types of inhomogeneities were found: (i) an enrichment of the dopant in a layer (40 ± 10) nm thick at the substrate-film interface and (ii) a spatially inhomogeneous distribution within the bulk of the film. The former seems to be related to a preferential condensation of Al or Al-O phases in the first stage of the growth on amorphous substrates, while the latter is most likely related to the segregation of the dopant element Al to the grain boundaries. We also derived, by combining the literature data with our own measurements, that the amount of dopant in the films determines the density of trap states N_t at the grain boundaries, which is another indication of a segregation of the dopant to the grain boundaries in the form of secondary phases like Al₂O₃ or ZnAl₂O₄. The increased density of trap states leads to a stronger grain boundary scattering which needs to be suppressed. Also, in these phases, the dopant is electrically inactive and can hence not contribute to the free carrier concentration. This is an additional source of degradation of the film quality, which might also play a role in the thickness dependence of the film properties usually reported in literature. Further research on buffer or seed 060701-12 Bikowski et al.

layers to suppress the formation of such an interface layer can provide additional routes to improve the ZnO:Al films.

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