Morphological TEM studies and magnetoresistance analysis of sputtered Al-substituted ZnO films: The role of oxygen

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In this article, we report on the synthesis of thin, epitaxial films of the transparent conductive oxide Al:ZnO on (0001)-oriented synthetic sapphire substrates by DC sputtering from targets with a nominal 1 at.% Al substitution. The deposition was carried out at an unusually low substrate temperature of only 250 °C in argon–oxygen mixtures as well as in pure argon. The impact of the process–gas composition on the morphology was analysed by transmission electron microscopy, revealing epitaxial growth in all the cases with a minor impact of the process parameters on the resulting grain sizes. The transport properties resistivity, Hall effect and magnetoresistance were studied in the range from 10 to 300 K in DC and pulsed magnetic fields up to 45 T. While the carrier density and mobility are widely temperature independent, we identified a low field–low temperature regime in which the magnetoresistance shows an anomalous, negative behaviour. At higher fields and temperatures, the magnetoresistance exhibits a more conventional, positive curvature with increasing field strength. As a possible explanation, we propose carrier scattering at localised magnetic trace impurities and magnetic correlations.

Cross-sectional HAADF-STEM image of an Al:ZnO film grown without oxygen in the sputtering gas. The inset is a false-colour [100] high resolution STEM image (inverted annular bright field: green, annular dark-field: red) of the ZnO crystal structure.

1 Introduction During the recent years, transparent conductive oxides have gained a considerable interest from the viewpoint of applications in optical, optoelectronic and sensing devices [1]. Indium-tin oxide (ITO) is already well established in industrial manufacturing and sets out the performance standards in terms of its low electric resistivity, high carrier mobilities and outstanding optical transparency. Transparency values of 92% for 170 nm thick films have been reported [2] together with resistivity values of typically 0.1 mΩcm and exceptionally even down to 0.072 mΩcm [3, 4].

However, the toxicity and scarceness of elemental indium, see Ref. [5], have triggered the materials research community in developing alternative TCOs based on abundantly available, non-toxic elements. Zinc oxide (ZnO), an n-type semiconductor with a wide, direct bandgap of 3.37 eV, is an especially promising candidate [6]. A standard procedure to enhance the conductivity of ZnO to
ITO-like values is the presumably substitutional incorporation of trivalent aluminium (ionic radius 67.5 pm) on the lattice sites of the divalent zinc ions (ionic radius 88 pm). Within this article, we will use the acronym ‘AZO’ for these aluminium-doped zinc oxide materials. Until date, the exact solubility limit is not precisely known, but literature data on polycrystalline AZO bulk materials point to achievable substitution ratios of 1–2 at.% of Al on the Zn sites [7, 8]. Besides the intrinsic semiconducting behaviour and n-type Al substitution, several defect types are associated with the generation of free charge carriers: Zinc interstitials are seen as shallow donors [9, 10] while oxygen vacancies and interstitial hydrogen atoms act, respectively, as deep and shallow donors [11]. As experimental evidence, we mention the metal–insulator transition achieved by the addition of hydrogen gas during the sputter deposition of nominally pure ZnO films in an oxygen atmosphere [12].

It is less evident to decide whether hydrogen, used as a deposition or annealing gas, generates hydrogen interstitials or oxygen vacancies, or both defects together. To circumvent this uncertainty, we will focus in our work on films that are not intentionally exposed to hydrogen but grown, instead, under oxygen-deficient conditions. The main percentage of the sputtering gas will be argon, meaning that, even in case of incorporation, no additional doping effects are expected. These samples will be characterised with respect to their morphology and optical transparency, followed by an in-depth study on their electronic transport properties. As a matter of fact, AZO films are known for an unexpected, weak negative magnetoresistance effect [13–15]. Pure metals, alloys and oxides with metallic-like conductance show generally a positive magnetoresistance of typically 1% resistance increase in magnetic fields in the order of 10T at temperatures below 10 K. This positive magnetoresistance, analytically described by Kohler’s rule, is indicative for the purity and crystalline quality of the material. Hereby, the resistance increase is attributed to a reduction of the carriers’ mean free path by forcing them to move on fractions of Lorentz circles. Negative magnetoresistance on the other hand is best known in the form of the giant (negative) magnetoresistance ‘GMR’ in heterostructures of magnetic metals [16] and from the colossal negative magnetoresistance ‘CMR’ in manganese perovskites [17, 18]. Negative magnetoresistance phenomena are in any case related to a magnetic ordering effect induced by an external field and, at first sight, there are no magnetic constituents present in AZO.

For sputtered films prepared from ZnO targets containing 5 wt.% Al2O3, Li et al. [13] found a normalised resistance drop $\Delta \rho / \rho (B = 0)$ of $-0.32\%$ at 5 K in a field of 2T. This agrees well with the data by Liu and Jiang [14] (also sputtering, same doping concentration) who report a drop of the normalised resistance by $-0.19\%$ at 2.5 K in a 2T field. The highest drop until now of $\Delta \rho / \rho (B = 0)$ = $-6.9\%$ at 5 K in a field of 6 T was reported by Gacic et al. [15] for pure ZnO films, prepared by laser ablation. A possible reason for this unexpected magnetoresistance behaviour could be the presence of a vanishingly small concentration of magnetic impurities such as iron or nickel incorporated into the films. Such impurities can stem from the sputtering- or laser-ablation target or from the walls of the plasma-deposition chambers. However, an intentional doping of ZnO films with 5 at.% of cobalt did not enhance the magnitude of the magnetoresistance response [15]. Nevertheless, all these prior data could be successfully brought into agreement with a model proposed by Khoshla and Fisher [19] already in 1970. This model, developed for the degenerate semiconductor CdS, treats two magnetoresistance contributions: A negative contribution, prevailing at low temperatures and low fields, results from the field-induced reduction of carrier-spin scattering at localised magnetic moments. The positive contribution, noticeable at higher fields, is a band structure effect attributed to a field-induced redistribution of carriers over different conduction bands with different relaxation times.

### 2 Experimental

#### 2.1 Thin-film preparation

The thin films were prepared by DC sputtering without magnetron assistance in a home-made sputtering system described in earlier publications by the authors [20, 21]. The sputtering target with 1.0 at.% Al content was prepared by thoroughly mixing appropriate amounts of Al2O3–ZnO powder (Zano–Al with 2.4 at.% Al, Umicore, Belgium) and ZnO powder (purity 99.99% on trace metals basis, Sigma–Aldrich, USA). This mixture was pressed into discs with 1.5 inch diameter and a thickness of 2 mm using uniaxial pressure of 8.6 GPa. Sintering was performed during 60 min at 900 °C in a vacuum oven, followed by cooling down to room temperature over 8.75 h. According to the literature [7, 8], a substitution ratio of 1 at.% Al is still below the solution limit determined for AZO powders. Moreover, thin films with this Al percentage show high electrical conductivities in combination with low optical absorption [22]. Concentrations exceeding the 1 at.% level are supposed to result in phase separation with occurrence of the insulating ZnAl2O4 spinel phase and smaller grain sizes [21]. On the opposite, a substitution below the 1 at.% ratio reduces the density of free charge carriers while the carrier mobility should in principle come close to the value of 200 cm²/Vs as reported for pure, non-substituted ZnO [1]. Furthermore, all samples were deposited at a substrate temperature of only 250 °C; this is based on the idea that transparent conducting oxides should ideally be deposited at low temperatures in order to make film growth compatible with microelectronic, polymeric and photovoltaic materials [23]. All samples were grown on (0001)-oriented synthetic sapphire (1 cm², 1.0 mm thick) with a typical root-mean squared (rms) roughness of 3 nm over an area of 900 μm² on the top side (CrysTec GmbH, Germany). The backside of the substrates was unpolished to ensure a good adhesion to the substrate heater mediated by pyrolised silver paint. For comparative optical transparency studies, substrates of double-side polished borosilicate glass were used with the same dimensions.
as the sapphire substrates. All other settings for sputtering deposition are documented in Ref. [21].

Three types of samples were prepared, differing in deposition parameters only in the presence or absence of oxygen in the argon process gas with a standard pressure of 2.00 hPa, see Table 1. Type I films were deposited during 120 min with a partial oxygen pressure between 1 and $5 \times 10^{-3}$ hPa, being close to the detection limit of the pressure gauge. As discussed in more detail in Section 3, these samples show relatively large crystalline grains in scanning electron microscopy (SEM) analysis, an excellent optical transparency, but rather poor resistivity and mobility values as compared to the state-of-the-art for DC–magnetron sputtered films [24, 25]. Type II samples were grown during 60 min without intentional oxygen addition to the sputter gas. Small grain sizes and low transparency values are obtained in these samples, although they exhibit extraordinarily low resistivity and especially high mobility values. Oxygen built into the crystal lattice must stem directly from the sputtering target and oxygen residues in the process gas. Growth under these oxygen-deficient conditions was inspired by earlier observations stating that thermal annealing of AZO films in hydrogen gas creates oxygen vacancies and enhances the carrier concentration and mobility [26]. Type III samples, also denoted as ‘layered samples’, were deposited in the presence of oxygen during the first 30 min of deposition time and without oxygen addition during the subsequent 60 min. As can be seen from Table 1, these samples combine high optical transmission (comparable to type I sample) with the beneficial mobility and resistivity values of the type II films.

### 2.2 Optical and imaging techniques

The SEM micrographs were taken with a FEI Quanta 200 FEG-SEM at an acceleration voltage of 15 kV. UV–Vis transparency measurements were performed using a CARY 500 spectrophotometer (Agilent, USA). The transmission spectra were averaged over the wavelengths regime between 390 and 700 nm. Cross-sectional transmission electron microscopy (TEM) samples were prepared by a focused ion beam (FIB) lift-out procedure in a FEI Helios FIB system. Scanning TEM was performed on a Titan ‘cubed’ microscope, equipped with a four-quadrant high solid angle EDX detection system (energy-dispersive X-ray mapping, Bruker) as well as a probe-corrector for improved image resolution, operated at 200 kV acceleration voltage. The convergence semi-angle $\alpha$ used was 22 mrad, the acceptance inner semi-angle $\beta$ was 65 mrad for HAADF-STEM imaging (high-angle annular dark field scanning TEM and 22 mrad for ADF-STEM imaging (annular dark field - STEM). For similar TEM studies on ZnO powders prepared by spray pyrolysis, we refer to Ref. [27].

#### 2.3 Magneto-transport studies

Magneto-transport measurements were carried out after lateral thin-film patterning by UV lithography and wet-chemical etching in a 1:1000 HNO$_3$:H$_2$O solution into 6-terminal Hall bar structures. The layer thickness of these patterned films was determined by atomic force microscopy (AFM) and the values are included in Table 1. Contacting was done by wire bonding with silicon-doped Al wires and conductive silver paint. Resistivity and Hall measurements in the temperature regime between 70 and 300 K in magnetic DC fields up to 2.0 T were carried out on samples with a $87 \mu$m long and $48 \mu$m wide current path, measured between the transverse and longitudinal voltage leads. For resistivity measurements, the current was 1 mA and the current direction was reversed in order to correct for thermal voltages. Hall data were determined by inverting the current direction (current amplitude 1 mA) to compensate for misalignments of the Hall leads and under inversion of the field direction to correct for remnant magnetisations of the electromagnet.

Furthermore, we confirmed that the measured Hall voltage was directly proportional to the strength of the magnetic field. Magnetoresistance measurements were carried out between 10 and 250 K at the KU Leuven pulsed-magnetic field facilities [28]. Here, the current paths had the same dimensions as before and the current

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**Table 1** Overview of the sputter-deposition parameters and average grain sizes of the three different types of AZO thin films, together with representative values of the room temperature resistivity $\rho$, the carrier concentration $n$, the carrier mobility $\mu$ and the average optical transparency.

<table>
<thead>
<tr>
<th>sample type</th>
<th>type I: oxygen-assisted deposition</th>
<th>type II: oxygen-free deposition</th>
<th>type III: layered growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$(O$_2$)</td>
<td>$1-5 \times 10^{-3}$ hPa</td>
<td>–</td>
<td>$1-5 \times 10^{-3}$ hPa for first 30 min</td>
</tr>
<tr>
<td>$p$(Ar)</td>
<td>2.00 hPa</td>
<td>2.00 hPa</td>
<td>2.00 hPa</td>
</tr>
<tr>
<td>discharge voltage</td>
<td>440 V for 120 min</td>
<td>380 V for 60 min</td>
<td>420 V for first 30 min, then 380 V for 60 min</td>
</tr>
<tr>
<td>discharge current</td>
<td>80 mA for 120 min</td>
<td>80 mA for 60 min</td>
<td>60 mA for first 30 min, then 80 mA for 60 min</td>
</tr>
<tr>
<td>thickness</td>
<td>110 \pm 15 nm</td>
<td>110 \pm 15 nm</td>
<td>140 \pm 25 nm</td>
</tr>
<tr>
<td>grain size</td>
<td>400 nm</td>
<td>100 nm</td>
<td>400 nm</td>
</tr>
<tr>
<td>resistivity $\rho$</td>
<td>6.55 m$\Omega$cm</td>
<td>0.094 m$\Omega$cm</td>
<td>0.69 m$\Omega$cm</td>
</tr>
<tr>
<td>carrier mobility $\mu$</td>
<td>1.82 cm$^2$/Vs</td>
<td>39.5 cm$^2$/Vs</td>
<td>27.4 cm$^2$/Vs</td>
</tr>
<tr>
<td>carrier concentration $n$</td>
<td>$5.23 \times 10^{20}$ cm$^{-3}$</td>
<td>$1.68 \times 10^{21}$ cm$^{-3}$</td>
<td>$4.82 \times 10^{20}$ cm$^{-3}$</td>
</tr>
<tr>
<td>transparency</td>
<td>90.8%</td>
<td>64.7%</td>
<td>86.0%</td>
</tr>
</tbody>
</table>
amplitude was set to 100 µA. Magnetic field exposures were done with field amplitudes up to 10 and 45 T, respectively. Both branches with increasing and decreasing strength of the magnetic field were recorded. The typical pulse duration was 30 ms for the increasing branch and 52 ms for decreasing the field back to 0. These durations hold for both exposures to 10 and 45 T maximum fields.

3 Results and discussion
3.1 Morphological characterisation Representative scanning electron micrographs of the three types of films are shown in Fig. 1. All images display a region of 2.6 x 2.6 µm². The type I sample in Fig. 1A clearly shows the hexagonal structure of ZnO with crystallites of typically 400–500 nm. In between these large crystallites, there is a manifold of small crystallites (typical diameter below 100 nm) in the initial phase of growth, without a clear or uniform crystallographic direction. Interestingly, there are crystalline seeds located precisely in the centre of the larger hexagonal structures. The type II films show overall, at lateral scales of 20 µm and more, a disordered, corrugated structure with a severely enhanced roughness, resembling almost an amorphous film growth. Within selected regions, such as shown in Fig. 1B, hexagonal ordering can be identified with less pronounced, rounded edges of the crystallites. Figure 1B also shows the regions that are not perfectly in the focus due to the global roughness. The type III samples are equally smooth as in case of type I and the hexagonal structure can still be identified although the boundaries of the crystallites show irregularities similar to the films grown in the absence of oxygen in the sputtering gas. When looking at the optical transparency data in Table 1, the type III films perform almost equally well as the type I samples and significantly better than type II materials where the corrugated morphology goes along with enhanced light scattering.

In order to study the microstructure of the films in more detail, we used scanning TEM on cross-sectional samples prepared by a focused ions beam lift-out procedure. Due to the layered growth, type III samples represent the morphology of both other film types together. Figure 2A is an overview high-angle annular dark field STEM (HAADF-STEM/Z-contrast) image of the sample grown without oxygen addition on a sapphire substrate (type II). The sample consists of intergrown grains with diameters between 50 and 150 nm.

The energy dispersive X-ray (EDX) spectrum in Fig. 2B taken from the same AZO layer evidences the presence of Al in the deposited layer. EDX analysis of four different regions of the AZO layer proves the Al content in the film to be 1.2 ± 0.2 at.%. This is close to the substitution ratio expected from the composition of the sputtering target. The slight excess can possibly be attributed to preferential sputtering and is not an artefact from the underlying substrate. The inset image is an EDX colour map showing Al in red and Zn in green. The Al signal is uniformly spread throughout the AZO layer, no enrichment at, for example,
grain boundaries was found. Several EDX maps of the same sample were acquired and none of them showed preferential enrichment of Al. A high-resolution HAADF-STEM image of the sapphire/AZO interface is displayed in Fig. 2C. Most of the ZnO grains are c-oriented, as indicated also by previous X-ray diffraction studies [21]. It is important to point out that no amorphous interlayer is present between the AZO film and the substrate, indicating the efficacy of the growth methodology.

Finally, a cross-sectional annular dark field (ADF)-STEM image of the layered film sample (type III) is presented in Fig. 2D. ADF conditions were chosen to easily visualise the grains within the film through a higher contribution of diffraction contrast to the image formation process. In this way, it can be seen that the ZnO grain sizes in the first deposition phase, in the presence of oxygen, are significantly smaller than those in the second deposition (vertical white arrows). Overall, the layer thicknesses seen in Fig. 2 slightly exceed the thicknesses given in Table 1 as determined by AFM imaging. The reason hereof is the wet-chemical etching of the samples used in magneto-transport studies, resulting in a partial removal of the material.

3.2 Resistivity and Hall studies

Within this paragraph, we will analyse the temperature dependence of the resistivity $\rho$, the charge-carrier density $n$ and the carrier mobility $\mu$ for selected samples of the three different film types. Of each film type, at least three different samples were prepared and the samples chosen for magneto-transport measurements were selected on basis of a low sheet resistance in combination with a homogeneous and shiny appearance. There was only a limited scattering of properties between samples belonging to a given type, meaning that the data presented below have a representative character. Starting with type I samples, see Fig. 3, we note that the resistivity follows a linear temperature dependence according to Eq. (1). This can be seen as an approximation of an exponential function governed by the band-gap behaviour:

$$\rho(T) = \rho_0 - \alpha \cdot T.$$  

The parameters are $\rho_0 = 8.25 \, \text{m}\Omega\text{cm}$ and $\alpha = 5.48 \times 10^{-2} \, \text{m}\Omega\text{cm/K}$ with an $R^2$ value of 0.99. The absolute value of the room temperature resistivity is rather high as compared to the state of the art where $\rho(300 \, \text{K}) = 0.14 \, \text{m}\Omega\text{cm}$ for polycrystalline films has been reported [24, 25].

From the substitution ratio of 1 at. % Al, and assuming that each aluminium atom provides one free charge carrier, the estimated carrier density is $n^* = 4.1 \times 10^{20} \, \text{cm}^{-3}$. Therefore, the sample is expected to be on the metallic side of Mott’s metal–insulator transition for this specific compound, being in the order of $5 \times 10^{18} \, \text{carriers/cm}^2$ [29]. According to the Hall data in Fig. 3B, the carrier density is practically temperature independent with $n \approx 5.2 \times 10^{20} \, \text{cm}^{-3}$ and this temperature independence can be seen as an indication for metallic-like
conduction such as in degenerate semiconductors. Furthermore, the experimentally determined carrier concentration agrees very well with the $n^*$ value expected from the substitution ratio. The mobility values were calculated from the resistivity and carrier concentration according to $\mu = (n \cdot e \cdot \rho)^{-1}$ with $e$ being the elementary charge. In analogy with the high resistivity, the room temperature value of the mobility is 20–30 times lower than record-high values in literature, where $\mu = 57 \, \text{cm}^2/\text{V}s$ has been documented [24, 25]. There is little variation in temperature and there is no obvious reason why the mobility should increase with increasing temperature. Nevertheless, this agrees with previous observations on ZnO films with 2.4 at.% Al substitution [21]. Increasing mobility values with increasing temperatures are also known from oligomer films (sexithiophene and octithiophene) and were explained by a less efficient charge-carrier trapping in grain boundaries as temperature increases [30]. The absolute change of the mobility between 75 and 300 K is, however, small and overinterpretation of the data in terms of identifying underlying mechanisms should be avoided.

Performing the same resistivity and Hall analysis on type II samples, deposited without addition of oxygen to the sputtering gas, gives surprising results, see Fig. 4. The room temperature resistivity drops by almost 2 orders of magnitude as compared to the type I samples and $\rho (300 \, \text{K}) \approx 90 \, \mu\Omega\text{cm}$ can be compared to an impure metal or metal alloy. One might infer that oxygen-deficient deposition can result in films with a content of pure, nonoxidised zinc or aluminium metal and their alloys. In turn, the low resistivity might therefore be due to percolating, metallic current paths. However, metallic phases could neither be found by X-ray diffraction nor by SEM analysis. Both methods are not sufficiently sensitive in case that potential metallic inclusions are either amorphous or occupy only a minor volume fraction. However, also the high-resolution TEM imaging discussed in Section 3.1 did not give any indication for local- or path-like deviations from the zinc-oxide phase. Therefore, we can safely conclude that metallic volume fractions, if any, are well below the detection limit of several analytical methods. The only possibility might be a certain excess of Zn atoms, located at interstitial positions, which can in principle also

Figure 3 Temperature dependence of the longitudinal resistance $\rho$ (panel A) and of the carrier concentration $n$ and mobility $\mu$ (panel B) of a type I sample, prepared by oxygen assisted deposition. The solid line through the $\rho(T)$ data is a linear fit [Eq. (1)] while the carrier concentration is temperature independent. The increase of the mobility with increasing temperature points to carrier release from grain boundaries. The dashed lines in panel B are guides to the eye.

Figure 4 Temperature dependence of the longitudinal resistance $\rho$ (panel A) and of the carrier concentration $n$ and mobility $\mu$ (panel B) of a type II sample, deposited in pure argon atmosphere without additional oxygen in the process gas. The fit curve of $\rho(T)$ is based on Eq. (4). The dashed lines in case of the carrier mobility and concentration data are guides to the eye.
act as electron donors [9, 10]. The low room temperature resistivity and high mobility values agree very well with state-of-the-art data on films subjected to post-deposition annealing in hydrogen [31].

So far, also these post-annealed samples are assumed to be phase pure and free of metallic percolation paths. As shown in Fig. 4B, the substantial resistance drop in comparison to type I samples is due to two elements: First, the charge carrier density increases by a factor of 3 to \( n \approx 1.6 \times 10^{21} \, \text{cm}^{-3} \), which is temperature independent and well above the critical concentration for Mott’s MI transition. Second, mobility increases more than 20 times at all temperatures. This is somehow counter intuitive as compared to the reduced crystallite sizes of the type II material (compare with Table 1) and will be subject to further studies. The absolute value of the carrier density is four times higher than \( n^* \) expected from substitutional doping; this indicates that films grown in the absence of oxygen must have oxygen vacancies and possibly also interstitial zinc atoms. Both defect types were indicated previously as possible electron donors [9–11].

Taking the constant carrier density \( n \) as given, the temperature dependence of the resistivity (and also of the mobility) can be understood on established grounds with electron–phonon scattering. The fit curve in Fig. 4A is given by

\[
\rho(T) = \rho_0 + \beta \cdot T^2. \tag{2}
\]

Here, \( \rho_0 = 82.5 \, \mu\Omega \, \text{cm} \) stands for temperature-independent scattering processes while \( \beta = 1.34 \times 10^{-4} \, \mu\Omega \, \text{cm/K}^2 \). The coefficient of determination of the fit based on Eq. (2) is \( R^2 = 0.999 \). The second term is related to electron–phonon scattering and the proportionality to \( T^2 \) (rather than being linear in \( T \)) is given by the fact that data are measured not far below the Debye temperature of ZnO with \( \theta_D \approx 400 \, \text{K} \) [32–35]. Again, we point out that relative resistivity and mobility changes between 75 and 300 K are small as compared to the absolute room- or low-temperature temperature values, dominated by defect scattering.

When addressing the type III samples, see Fig. 5 for the experimental data, we note that the nominal carrier density \( n \approx 5 \times 10^{20} \, \text{cm}^{-3} \) is similar to the type I films prepared in the presence of oxygen in the process gas. Nevertheless, the temperature dependence of the resistivity and the mobility both resemble the behaviour of type II samples. The fit parameters for \( \rho(T) \), based on Eq. (2), are \( \rho_0 = 0.63 \, \text{m\Omega cm} \) and \( \beta = 6.93 \times 10^{-4} \, \mu\Omega \, \text{cm/K}^2 \). The similarity with type I samples is expected since we are dealing approximately with a \( d_2 = 110 \, \text{nm} \) thick capping layer of AZO deposited in pure argon on top of a 55 nm \( (d_1) \) thick base layer deposited with oxygen present. Considering the sandwich structure as two resistors in parallel, the resistivity \( \rho_{\text{dl}} \) of the layered structure should be given by Eq. (3):

\[
\frac{1}{\rho_{\text{dl}}} = \frac{1}{\rho_{\text{Type I}}} + \frac{1}{\rho_{\text{Type II}}}. \tag{3}
\]

Inserting the room temperature resistivities given in Table 1, we would expect \( \rho_{\text{dl}} \approx 0.11 \, \text{m\Omega cm} \). However, the experimental value for double-layered films is six times higher than this estimate and therefore we assume that there is a possible redistribution of oxygen atoms within this AZO stack. Further research is required for a conclusive explanation, but an imaging of the oxygen density with atomic resolution is beyond the present state-of-the-art. Nevertheless, we can state that type III samples come close the outstanding electronic features of type II samples (especially regarding the mobility) and their optical transparency resembles the remarkably high values of type I material.

### 3.3 Negative magnetoresistance effect

The first set of data in pulsed magnetic fields on type III samples was taken between 10 and 150 K in field amplitudes limited to 10 T. As shown in Fig. 6, the MR amplitude reaches maximally \(-0.8\% \) (10 K, 10 T) and, under the same field, the resistance drop is only \(-0.1\% \) at 150 K. In this field and temperature regime, there is no indication for a positive MR and the amplitudes found here are fully within the
order identified in earlier work [13–15]. The fit function, according to the model derived by Koshla and Fisher [15, 19], is given by Eq. (4):

$$\frac{\Delta \rho}{\rho(B = 0)} = -a^2 \ln(1 + b^2 B^2) + \frac{c^2 B^2}{1 + d^2 B^2}. \quad (4)$$

Within the first (negative) magnetoresistance part, the parameters $a$ and $b$ depend mainly on temperature, magnetisation, strength of the localised moments, the exchange integral and the density of states at the Fermi level. This part describes the reduction of carrier scattering at localised magnetic moments. The second (positive) part originates from a field-induced rearrangement of the carrier-band occupations. The parameters $c$ and $d$ are functions of the absolute carrier concentration and conductivity. As can be seen from Fig. 6, this four-parameter fit is in excellent agreement with the experimental data. The fitting parameters $a$, $b$, $c$, $d$ and the resulting $R^2$ values are summarised in Table 2. Hereby, we note that the fitting parameters do not follow a strictly systematic trend with changing temperature. Moreover, data show little variation and also simplified parameter sets can generate fits with almost the same quality. For comparison, we assumed $c = 0$ and thus considered only the negative magnetoresistance contribution. The remaining two-parameter fits with only $a'$ and $b'$ are practically as good as the full four-parameter fits and the data sets (with $a'$, $b'$ and the resulting $R^2$) are also included in Table 2 (data in brackets). In the limit of extremely high fields, Eq. (4) can be rewritten in the form

$$\frac{\Delta \rho}{\rho(B = 0)} = \text{const.} - a^2 \ln(1 + b^2 B^2). \quad (5)$$

In other words, the magnetoresistance should remain negative and scale with the logarithm of the square of the field strength $B$. For peculiar sets of the four fit parameters in Eq. (4), one can indeed observe a crossover from negative to positive and again to negative magnetoresistance. This rather uncommon situation was observed experimentally for Co-substituted ZnO films prepared by laser ablation [15]. This gives confidence that the physical picture developed by Koshla and Fisher should at least be valid within certain experimental circumstances in the sense of temperature, field region and doping level. For an experimental verification of the high-magnetic field magnetoresistance of our AZO films, we performed resistance measurements in pulsed magnetic fields up to 45 T. In order to avoid artefacts from induction-induced data noise, we will consider here only the decreasing branch of the magnetic field from 45 to 0 T.

The data in Fig. 7 show again the weak resistance drop below 10 T, which was discussed and rendered with higher precision in Fig. 6. After a shallow minimum around 10 T, the resistance is clearly increasing with increasing field and this resembles fully the behaviour of conventional magnetoresistance. According to Kohler’s rule for non-magnetic materials, we expect a scaling according to $\Delta \rho \sim B^\alpha$, where the exponent should have the value $\alpha \approx 2$. We point out that the scaling law given in Eq. (5) cannot be brought into any agreement with the data shown in the subsequent Fig. 7.

The fit curves in Fig. 7 were therefore calculated on the basis of the following Eq. (6), which takes into account a negative magnetoresistance contribution due to scattering at

![Figure 6](image_url)
magnetic trace impurities and a positive contribution due to ordinary magnetoresistance (Table 3).

$$\frac{\Delta \rho}{\rho(B = 0)} = -a_1 \ln(1 + b_1 B^2) + c_1 B^2.$$  

(6)

All fits shown in Fig. 7 are of high quality with coefficients of determination of at least 0.99. Contrary to the expectations for a paramagnetic material, the exponent $\alpha$ deviates from 2 and varies between 0.97 (150 K) and 1.49 (70 K). In principle, such unusual low exponents have been reported before for nominally non-magnetic materials including Ag$_2$Se with a minute excess of silver and a widely linear positive magnetoresistance ($\alpha \approx 1$) up to 55 T [36]. Another example are ultrathin graphite flakes with $\alpha \approx 1.6$, where the lowered exponent was associated with either magnetic impurities or defects in the carbon lattice causing local magnetic moments [37]. We point out that $\alpha \approx 1$ should be expected in case of a ferromagnetic conductor and the assumption of local ferromagnetic correlations in AZO is not too farfetched: A recent study by Khalid and Esquinazi [38] could indeed prove the existence of ferromagnetism in ZnO single crystals upon implantation of hydrogen ions. There is also experimental and theoretical evidence that defects on zinc sites and interstitial zinc atoms cause ferromagnetic correlations irrespective of intentional substitution with transition metals [39, 40]. Defect-induced magnetic correlations are also observed in other, nominally non-magnetic materials such as graphene with vacancies in the carbon lattice [41].

Most importantly, the moderate magnetoresistance in the high field limit (up to fields of not less than 45 T) seems to be conventional in nature; positive in sign and between linear and quadratic in the strength of the external magnetic field.

4 Conclusions In this article, we reported on a comparative study on the morphological and electronic transport properties of Al-substituted ZnO films prepared by DC sputtering. The nominal substitution ratio was 1.0 at. % Al on the Zn sites, while TEM-based EDX mapping points to the incorporation of 1.4 at. % Al. There is no indication for enrichment of Al at, for example, grain boundaries or for the presence of any other metallic phases. Although all samples were prepared at the same low deposition temperature (250 °C) and a constant background pressure of argon (2.00 hPa), we observed remarkably different resistivity and carrier-mobility values. This depends on the presence or absence of a minute addition of oxygen (<0.01 hPa) to the process gas: Type I films were deposited with oxygen addition while type II films were grown in the absence of oxygen. Films of type III were grown in a sequential mode with stopping the oxygen addition after the first 30 min of deposition time. Oxygen-free deposited films exhibit resistivity and mobility values according to the state-of-the-art for AZO samples subjected to a post-deposition reducing treatment in hydrogen. The carrier density in this case is four times higher than the value expected from the Al substitution ratio, suggesting that oxygen vacancies and possibly also interstitial zinc atoms contribute in the generation of free charge carriers. As a drawback, oxygen-free deposited films show a corrugated surface morphology and reduced optical transparency. Samples deposited in the presence of oxygen exhibit an outstanding transparency and well defined crystallites at the expense of rather low mobility and high resistivity values. Oxygen vacancies can be excluded in this case and the carrier density is in very close agreement with the Al-substitution ratio between 1.0 and 1.4 at. %. In order to achieve samples combining a high optical transparency with low resistivity and high carrier mobility, we finally developed a layered deposition technique: First, a seed layer is deposited in the presence of oxygen, followed by a capping layer deposited in a pure argon atmosphere. Although the room temperature resistivity is enhanced as compared to samples grown fully in argon, the resistivity shows metallic-like behaviour in the entire temperature range. Moreover, the resistivity values are 10-fold lower as compared to samples deposited in the presence of oxygen.
Finally, we analysed the temperature and field dependence of the magnetoresistance in these layered samples: In the limit of low fields, there is a weak negative magnetoresistance following a scaling law proposed originally by Koski and Fisher for carrier scattering at magnetic impurities in degenerate semiconductors. For fields exceeding 10 T, the magnetoresistance becomes weakly positive and resistivity increases according to a power law with the strength of the magnetic field. This agrees with the classical Kohler rule while the exponent is between $\alpha = 1$ (expected for ferromagnetic conductors) and $\alpha = 2$ (expected for non- or paramagnetic materials). This may point to the presence of ferromagnetic correlations in our AZO samples, which requires further experimental confirmation for the sample types under study. Defect-related ferromagnetism in ZnO has already been reported in previous literature. The existence of a distinguishable positive magnetoresistance as such can be seen as a confirmation of the high crystalline quality and low defect density of the thin-film samples studied within this article. Furthermore, this is corroborated by the fact that these AZO films can fully compete with the low resistivity and high transparency values documented in literature for indium-tin oxide ITO.

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