



Full Length Article

Suppression of grain boundary contributions on carrier mobility in thin Al-doped ZnO epitaxial films

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ABSTRACT

Realizing very thin transparent conductive (TCO) films is a key aspect of many applications, but often the film quality tends to worsen at very small thicknesses. In this work we demonstrate that Al-doped ZnO (AZO) thin films grown epitaxially on SrTiO₃ retain their optimal properties even at thicknesses as low as 30 nm. We deposit by radio frequency magnetron sputtering and investigate the film morphology, structure, crystallinity, electrical and optical properties. We prove that the Hall mobility of epitaxial films is limited mostly by ionized impurity scattering, with a negligible contribution of grain boundary scattering, leading to comparably high mobility in thin epitaxial films. On the contrary, in polycrystalline films the properties of AZO films strongly deteriorate at reduced film thickness, due to grain boundary contributions. The optical carrier density and mobility do not change significantly between epitaxial and polycrystalline films, suggesting that the different electrical properties are indeed mainly due to grain boundary scattering and not to a reduction of carriers and intrinsic mobility. In this way we obtain an epitaxial thin TCO film with the optimal properties of a bulk by a scalable technique, paving the way to applications in plasmonic devices and in thin films solar cells.

1. Introduction

Recently, a great challenge among researchers has been to find a class of materials that combines high optical transparency, typical of insulators, with good electrical conductivity, typical of metals. Materials displaying these properties offer a plethora of applications in fields like photovoltaics, infrared plasmonics and catalysis, optoelectronics, and photonics. One possible answer to this issue is represented by the family of Transparent Conductive Oxides (TCOs), which are highly-doped wide-bandgap semiconductors with electrical and optical properties that can be extensively tuned through doping [1–4].

ZnO is a wide-bandgap semiconductor and when it is doped with Al, it shows a marked *n*-type conductivity, retaining high transparency in the visible range [5,6]. For these reasons and its earth abundance with respect to other TCOs like indium tin oxide (ITO), Al-doped ZnO (AZO) is one of the most interesting and promising materials among TCOs.

For most applications, TCO films are grown as polycrystalline films. It is well known that polycrystalline thin films display lower

performances with respect to single crystal materials because they are characterized by far higher concentrations of defects. From an electrical point of view, for instance, a high density of grain boundaries and deep-level defects can trap charge carriers, with a significant detrimental effect on conductivity. In contrast, the control of the interfacial quality between film and support improves the properties of thin films, as in the case of epitaxy or buffer layers [7–9]. In order to fabricate robust and performing optoelectronic devices such as photovoltaic cells [10] or plasmonic devices [11] and in architectures for the modulation of the optical properties of AZO films by external bias [11,12], the epitaxial growth of each layer can be a route to improve efficiency. In these cases the use of a suitable perovskite supporting layer with small lattice mismatch and high dielectric constant is particularly envisaged and could foster epitaxy in AZO, increasing the carrier mobility in the electrode. The effect is particularly important in thin films, where the typical granular composition is constituted by very little grains and the presence of interfaces and grain boundaries dramatically reduces the electrical quality [13,14]. This happens mostly at very low thicknesses,

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where the electrical quality of TCO films, and AZO in particular, degrades [15–18]. For instance, the fabrication of high-quality ultra-thin TCO films would be very important to improve the efficiency of plasmonic-enhanced thin film solar cells, to minimize the parasitic ohmic losses [15,19].

Epitaxial ZnO and AZO films have been grown via various techniques, among which Pulsed Laser Deposition (PLD) [9,20,21] and Laser Molecular Beam Epitaxy (LMBE) [22,23], but very few works about AZO epitaxial growth employing Radio Frequency (RF) magnetron sputtering have been published [8,24,25]. These studies are devoted to the investigation of structural properties of ZnO or AZO on different substrates with a suitable lattice mismatch for epitaxy, like perovskites [20,22,23], sapphire [24,26] and GaN [25], or through a buffer layer [8,9], while in the case of pure ZnO the relation between epitaxy and mobility has been investigated on thick films [27–29].

While thin films grown by RF magnetron sputtering often display a lower quality with respect to films grown by PLD or LMBE, the latter suffer of very low deposition rates and higher costs compared to RF magnetron sputtering, whose scalability is appealing also for industrial applications.

In this work, we present a comprehensive study of the morphological, structural and electrical properties of epitaxial AZO thin films on SrTiO₃(110) grown by RF magnetron sputtering. We show that the improved structural order leads to electrical properties independent on film thickness, being limited only by ionized impurity scattering in very thin epitaxial films. On the contrary, in polycrystalline AZO films grown in the same conditions the electrical properties deteriorate with decreasing thickness.

2. Experimental

AZO films have been deposited by RF magnetron sputtering from an undoped ZnO 3'' target (ZnO purity 99.99 %) about 15 cm far from the substrate in 3×10^{-6} mbar base pressure. 60 W RF power has been applied to the oxide target, corresponding to a final rate of around 0.45 Å/s in an Argon pressure of 5 mTorr. At the same time Al doping was provided by DC magnetron co-sputtering from an Al target, to obtain the optimal doping concentration of ≈ 4 at. % [30]. The Al concentration was checked by Energy Dispersive X-ray Spectroscopy (EDX), performed at film surface with a FEI Quanta-200 ESEM. Film thickness is varied between 30 and 300 nm and it has been controlled during deposition by a calibrated quartz microbalance and subsequently by means of a stylus profilometer. The deposition temperature was set to 400 °C by resistive heating and measured with a calibrated thermocouple on the sample

stage.

The AZO films have been deposited on SrTiO₃(110) substrates (STO) annealed in vacuum for 3 h at the deposition temperature for degassing before growth. The deposition of AZO on this crystalline plane should be driven by the good matching of the $[\bar{1}10]$ direction of STO ($\sqrt{2}a_{STO} = 5.5225$ Å) with the $[1\bar{1}00]$ direction of ZnO ($\sqrt{2}a_{ZnO} = 5.6288$ Å), resulting in a lattice mismatch of 1.9 % [31,32], as shown in Fig. 1. As a reference, we grew polycrystalline AZO films with the same deposition conditions on thermal SiO₂ on Si(001) substrates.

We investigated the surface morphology of the films with Atomic Force Microscopy (AFM), utilizing an ambient pressure NT-MDT NTEGRA Aura AFM in tapping mode with Si cantilevers. The AFM images have been analyzed with the software *Gwyddion*.

High-Resolution X-ray Diffraction (HRXRD) measurements have been performed with a PanAnalytical X'Pert Pro four-circle diffractometer (Cu-K α_1 , wavelength 1.5406 Å), equipped with a Göbel mirror in the incidence optics in order to obtain a parallel X-ray beam. The detection optics was comprised of a 0.27° parallel plates collimator, a flat graphite monochromator and a single point gas proportional detector. The goniometer can perform both 2θ - ω scans, where the ω axis follows 2θ at half speed and θ - ω (offset angle) remains constant during the scan, and ω scans, also known as rocking curves, where ω is scanned with 2θ kept constant. The sample was mounted on an Euler cradle that allows independent tilt (ψ) and azimuthal (ϕ) rotations of the sample with respect to the goniometer plane, as shown in Fig. 2. This configuration allows the acquisition of pole figures of selected crystal planes, i.e. the intensity of a given Bragg reflection (constant 2θ) recorded as a function of sample tilt and rotation angles (ψ , ϕ) varied in a large number of orientations.

The electrical properties of the films have been investigated by Van der Pauw and Hall measurements, exploiting aluminum contacts produced via Electron Beam Lithography. The optical response of AZO films was measured by means of variable-angle Spectroscopic Ellipsometry (SE), performed through a J.A. Woollam V-VASE ellipsometer (190–2500 nm spectral range) and a J.A. Woollam M–2000 ellipsometer (245–1700 nm). SE measures the variation of the state of polarization of light reflected off the samples, quantified by the so-called ellipsometric angles Ψ and Δ , defined according to Eq. (1)

$$\frac{r_p}{r_s} = \tan(\psi)e^{i\Delta} \quad (1)$$

where r_p and r_s are the complex Fresnel reflection coefficients of the system for p(s)-polarized radiation. The spectra were measured at 60°

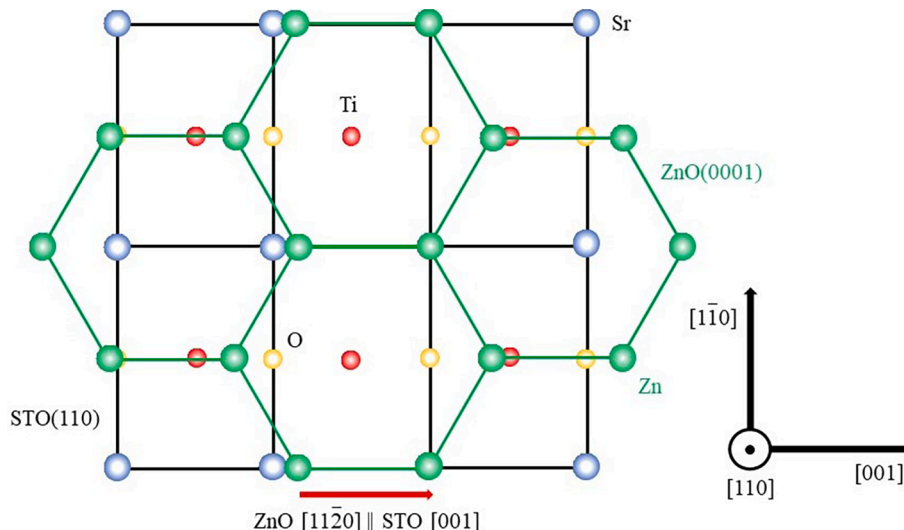


Fig. 1. Expected epitaxial relationship of AZO growth on STO(110).

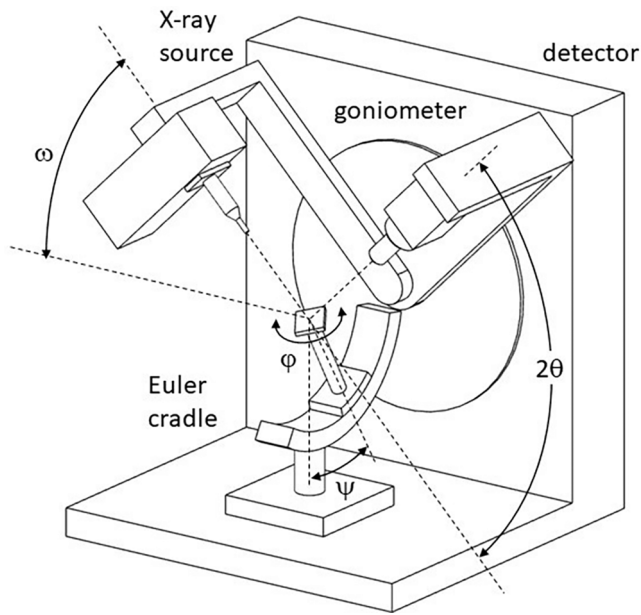


Fig. 2. Scheme of the four-circle diffractometer.

angle of incidence, in the 190–2500 nm range.

3. Results

3.1. Morphology

Fig. 3(a)–(d) shows the AFM surface images of AZO thin films grown on STO(110). The surface is characterized by uniform grains that are densely packed, implying a three-dimensional island growth mode, consistent with previous literature [27,33]. The surface morphology is not particularly influenced by the substrate: images of the AZO/SiO₂ films can be seen in Figure S1 of the Supporting Information (SI). The results of the grain analysis and surface roughness are summarized in Fig. 3(e). We observe that surface roughness and mean radius of grains increase with thickness almost linearly. The results are similar for AZO films grown on SiO₂, with the 50 nm and 100 nm thick films having a slightly smaller roughness and mean radius of grains.

3.2. Crystalline structure

Fig. 4(a) reports the 2θ–ω scans for the 300 nm film of AZO on STO (110). The scans have been recorded at a small (<0.1°) but not zero offset angle (θ–ω), in order to reduce the intensity of the substrate peaks, i.e. STO(110) and STO(220). The lack of any ZnO peak apart from ZnO (0002) and ZnO(0004) (please note the logarithmic intensity scale, spanning four orders of magnitude) demonstrate the strong preferential c-axis orientation of the AZO grains, already observed on other substrates [30,34].

The epitaxial relationship between the substrate and the film has been assessed by measuring pole figures of substrate and film Bragg reflections from planes that cut the STO(110) plane at an angle, namely STO(200) and ZnO ($\bar{1}101$) (and symmetry equivalent planes). The substrate reflections ($2\theta = 46.485^\circ$, PDF 00–035–0734, [35]) are expected at tilt $\psi = 45^\circ$ (angle between the [110] and the [200] directions in a cubic structure), with a periodicity in ϕ of 180° , corresponding to the two-symmetry equivalent STO(200) and STO(020) crystal planes. The pole figure in Fig. 4(b) shows such two substrate reflections at $\psi = 45^\circ$ with the expected ϕ periodicity. We used these two reflections to set the azimuthal ϕ axis of the substrate to zero. The substrate spots are elongated in the tilt direction due to the asymmetric X-ray beam cross section that emerges from the Göbel mirror. The reflections from ZnO

($\bar{1}101$) and symmetry equivalent planes ($2\theta = 36.253^\circ$) are expected at tilt $\psi = 61.6^\circ$, i.e. the angle between the [0001] and the normal to the ($\bar{1}101$) plane of the hexagonal structure, which can be calculated as $\cos(\psi) = (1 + 4c^2/3a^2)^{1/2}$, where $a = 3.2498 \text{ \AA}$ and $c = 5.2066 \text{ \AA}$ are the lattice constants of the ZnO structure (PDF 00–036–1451, [36]). The pole figure shows that the ZnO ($\bar{1}101$) and symmetry equivalent reflections are found at the expected tilt angle and with the expected 60° periodicity in ϕ , indicating that AZO forms a single hexagonal and epitaxial phase. Furthermore, the occurrence at the same value of ϕ of STO(200) and ZnO ($\bar{1}101$) indicates that the in-plane directions STO [001] and ZnO [$\bar{1}120$] are collinear, as confirmed by the literature [31,32].

In order to obtain information about the microstructure of the AZO thin films, we performed 2θ – ω and ω scans of the ZnO(0002) peak. We analyzed them using the single line method, following the approach of De Keijser [37,38], which is based upon the fitting of a single diffraction peak with the Voigt function, in order to separate the Lorentzian contribution from the Gaussian one. The Lorentzian broadening is associated with the coherence length of the films, which is defined as the average extension of the crystal lattice regions which scatter coherently, i.e. those regions which are free of macroscopical defects like grain boundaries. Instead, the Gaussian component is linked to the broadening due to microstrain, i.e. lattice strain from displacements of the unit cells about their lattice positions due to defects, and tilt, that is out-of-plane rotation of the grains perpendicular to the surface normal [39,40]. Analyzing the broadening of the 2θ – ω peaks, the vertical coherence length L_z and the microstrain ε can be retrieved, while the ω peaks give the lateral coherence length L_x and the tilt α . The terms vertical and lateral are related to the directions perpendicular and parallel to the film surface, respectively. The approach is based on the Scherrer formula for the coherence lengths (Equations (2) and (3))

$$L_z = \frac{K\lambda}{\beta_{2\theta-\omega}^L \cos(\theta)} \quad (2)$$

$$L_x = \frac{K\lambda}{\beta_{\omega}^L \sin(\theta)} \quad (3)$$

where K is the shape factor, which is usually taken to be 0.9, λ is the X-ray wavelength and β is the integral breadth, marked by a G when it is the Gaussian integral breadth and by a L when it is the Lorentzian one. The microstrain ε is obtained via the Wilson-Stokes formula (Eq. (4))

$$\varepsilon = \frac{\beta_{2\theta-\omega}^G}{4\tan(\theta)} \quad (4)$$

and the tilt α is directly measured from β_{ω}^G . The scans are shown in Fig. 5 (a) and (b), all normalized and aligned to the most intense peak which is the one of the 300 nm thick sample to better underline their different widths. The instrumental Gaussian broadening has been evaluated from the broadening of a peak of the substrate, in our case the STO(110) peak, which is close to the (0002) peak of ZnO, to minimize its dependence from the angle. The exploitation of the substrate peak allows to determine it in the same measurement run of the film, minimizing the errors in this minor correction. The results of the analysis are shown in Fig. 5(c) and (d). The numerical values are included in Table 1 of the SI. (0002) peaks in the 2θ – ω scans are all shifted at higher angles with respect to the (0002) ZnO bulk peak (34.422° , PDF 00–036–1451, [36]), from 34.502° at 30 nm to 34.486° at 300 nm (values are reported in Table 1 in the SI). This means that we have compressive strain along the c-axis, in accordance with an expected in-plane expansion to accommodate lattice mismatch (Fig. 1). The vertical coherence length is instead comparable with the film thickness, as expected for materials characterized by columnar growth like ZnO [27,33]. An exception is the 300 nm thick film. We want to evidence that the Scherrer equation is accurate up to coherence lengths of around 100–200 nm [41]. As a

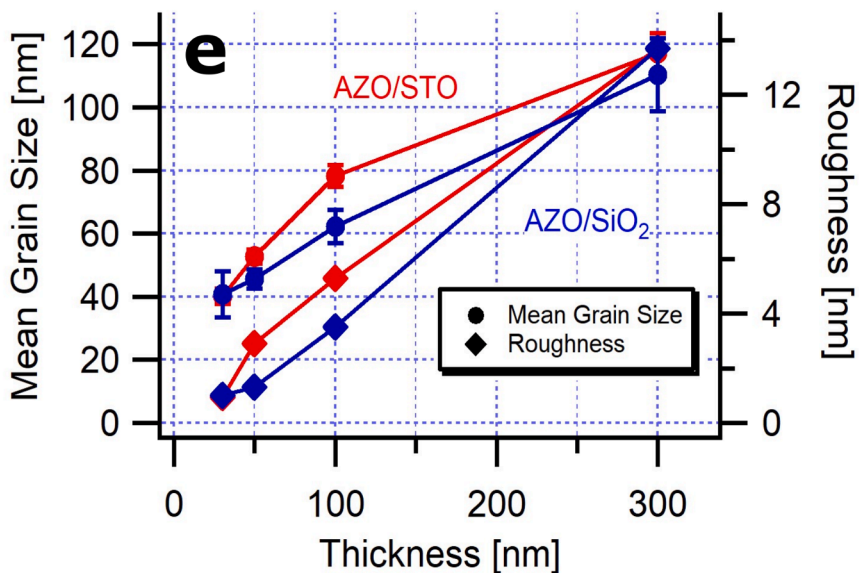
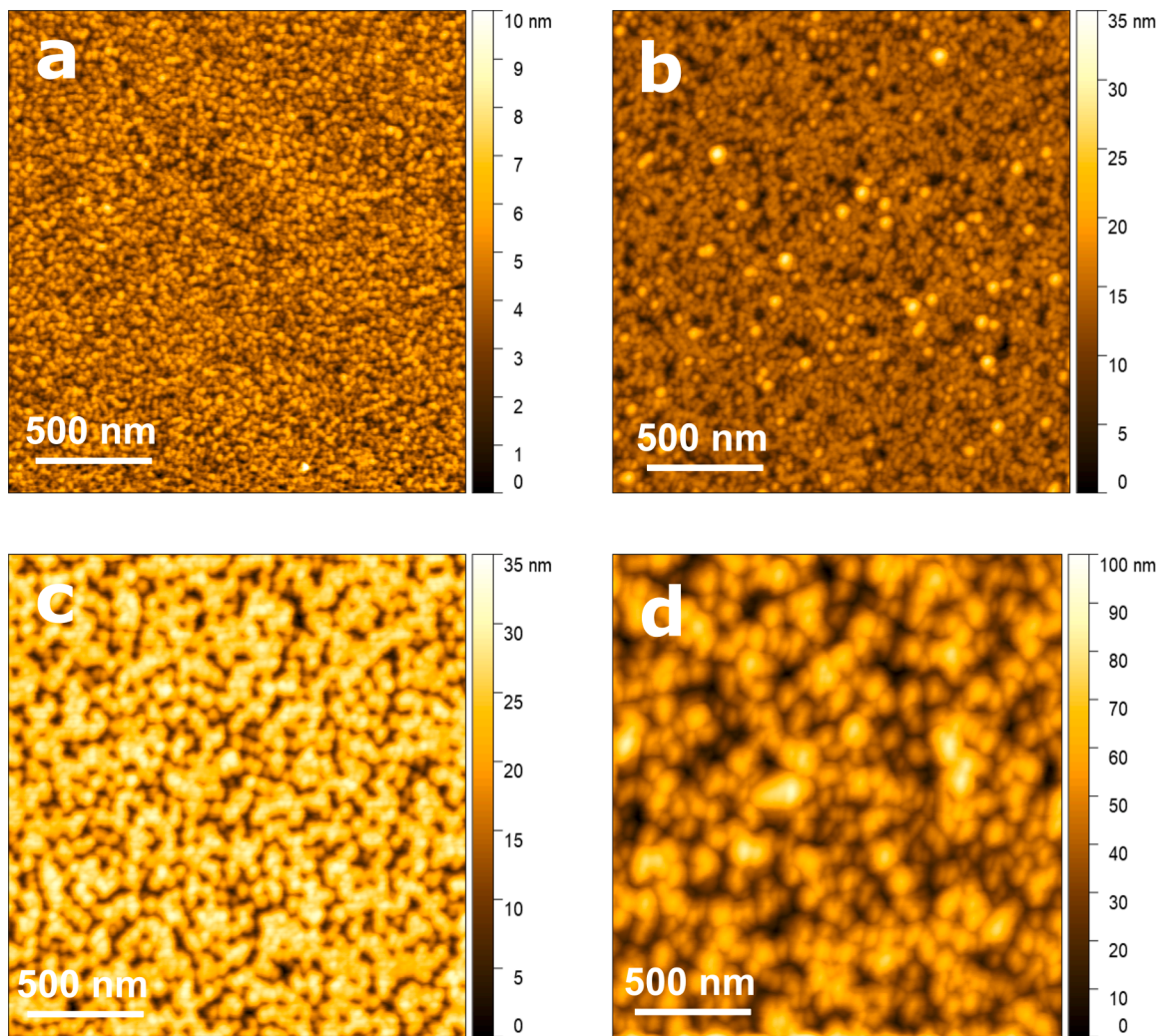


Fig. 3. AFM images ($2 \times 2 \mu\text{m}^2$) of the AZO/STO films of thickness (a) 30 nm, (b) 50 nm, (c) 100 nm and (d) 300 nm. (e) Mean grain radius and roughness of AZO films. If the bar is not present, the marker size indicates the error.

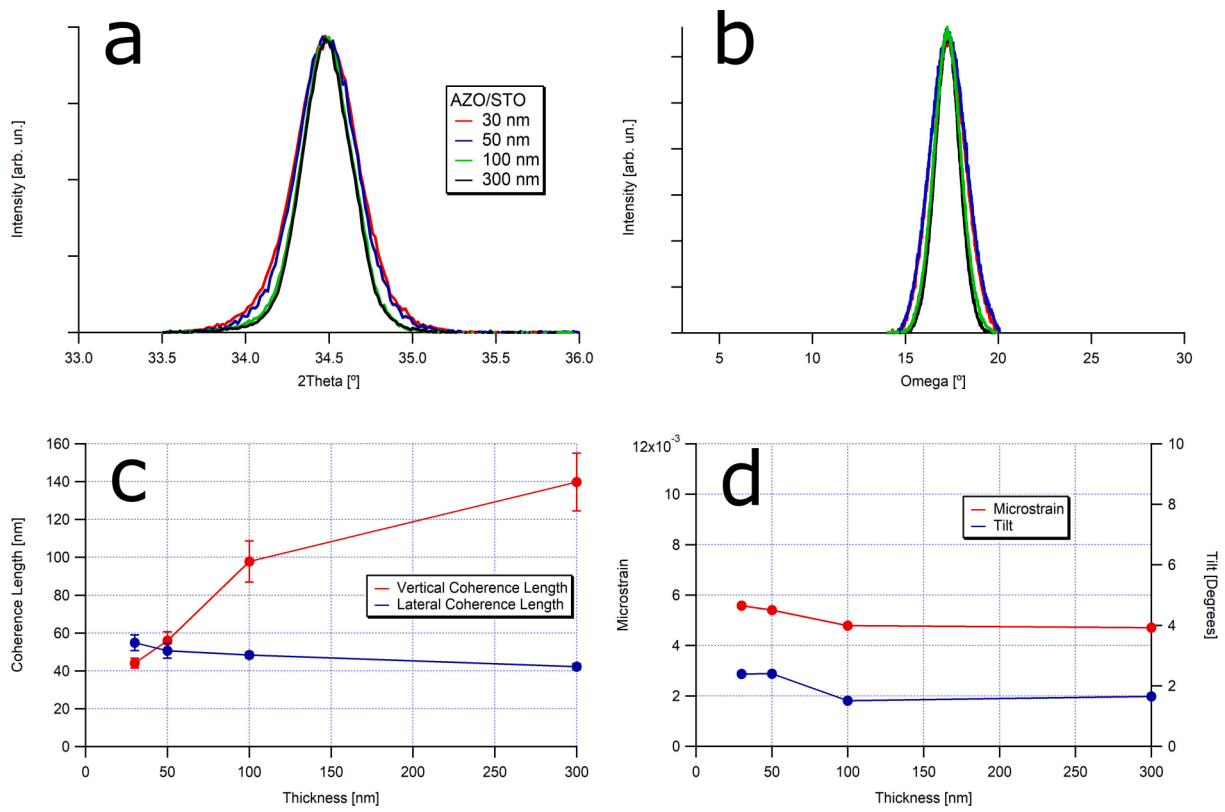


Fig. 5. (a) 2θ-ω and (b) ω scans of the (0002) ZnO peak, (c) coherence lengths, (d) microstrain and tilt for AZO/STO films. Peaks have been normalized and aligned to the most intense one, which is the one of the 300 nm thick film. If the bar is not present, the marker size indicates the error.

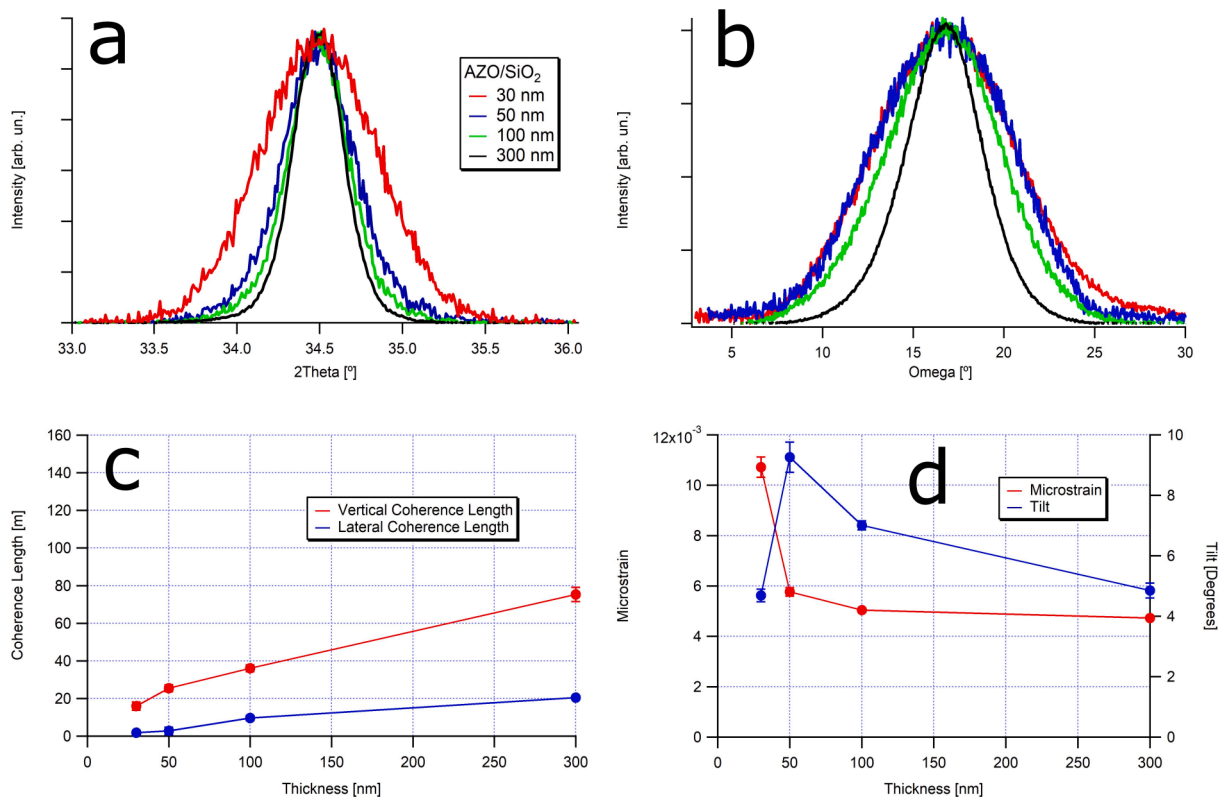


Fig. 6. (a) 2θ-ω and (b) ω scans of the (0002) ZnO peak, (c) coherence lengths and (d) microstrain and tilt for AZO/SiO₂ films. Peaks have been normalized and aligned to the most intense one, which is the one of the 300 nm thick film. If the bar is not present, the marker size indicates the error.

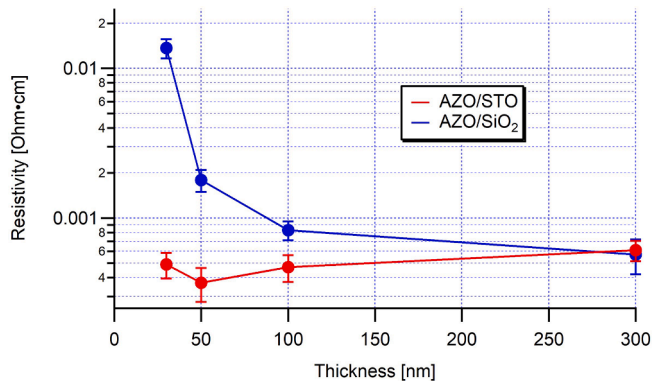


Fig. 7. Resistivity of the AZO/STO films (red) and of the AZO/SiO₂ films (blue).

μ_{lat} lattice vibration scattering mobility. The lattice vibration scattering is dominant in the high-temperature range and its contribution should be negligible at room temperature [47]. Nevertheless, it can be taken into account by considering the lattice mobility of pure ZnO, i.e. 210 cm²/(V·s) [49].

The resistivity due to surface scattering in thin films depends on thickness and it can be estimated via the Fuchs-Sondheimer model [51,52], but since the resistivity of AZO/STO films is independent on thickness, surface scattering cannot contribute significantly to the mobility, and the same should be true in AZO/SiO₂ films, since they have the same thicknesses.

The mobility due to ionized impurity scattering can be evaluated via the Pisarkiewicz model [49,53], that is a modified version of the classic Brooks–Herring–Dingle (BHD) theory for a degenerate semiconductor based on the screened Coulomb potential [54,55]. The Pisarkiewicz model, which takes into account the non-parabolicity of the conduction band that was shown to be important in highly doped AZO [56–58],

better fits the mobility data for degenerate semiconductors than the BHD model [49]. According to the Pisarkiewicz model, μ_{imp} can be written as

$$\mu_{imp} = \frac{3(\epsilon_r \epsilon_0)^2 h^3 n_e}{Z^2 m^* e^3 N_i F(\xi)} \frac{1}{N_i F(\xi)} \quad (6)$$

where ϵ_r is the relative dielectric constant, ϵ_0 is the vacuum permittivity, h is the Planck constant, e is the electron charge, Z is the charge state of the impurity (for Al atoms in ZnO is 1, but at very high dopant concentrations it has to be taken into account that the impurities assemble into clusters with a larger electronic charge Z greater than 1 and a reduced concentration of scattering centers $N_i = N_i / Z$ [49,50]), m^* is the electron effective mass, N_i is the impurity concentration, which may be assumed equal to the electron density n_e for an uncompensated fully ionized semiconductor (this can always be assumed at room temperature), and $F(\xi)$ is

$$F(\xi) = \left[1 + \frac{4\xi_{np}}{\xi} \left(1 - \frac{\xi_{np}}{8} \right) \right] \ln(1 + \xi) - \frac{\xi}{1 + \xi} - 2\xi_{np} \left(1 - \frac{5\xi_{np}}{16} \right) \quad (7)$$

where

$$\xi = (3\pi^2)^{\frac{1}{3}} \frac{\epsilon_r \epsilon_0 h^2 n_e^{\frac{1}{3}}}{m^* e^2} \quad (8)$$

and

$$\xi_{np} = 1 - \frac{m_0^*}{m^*} \quad (9)$$

where m_0^* is the effective mass at the conduction band minimum. The dependence of the effective mass on the electron energy E relative to the conduction band edge E_C in the conduction band can be in fact approximated by

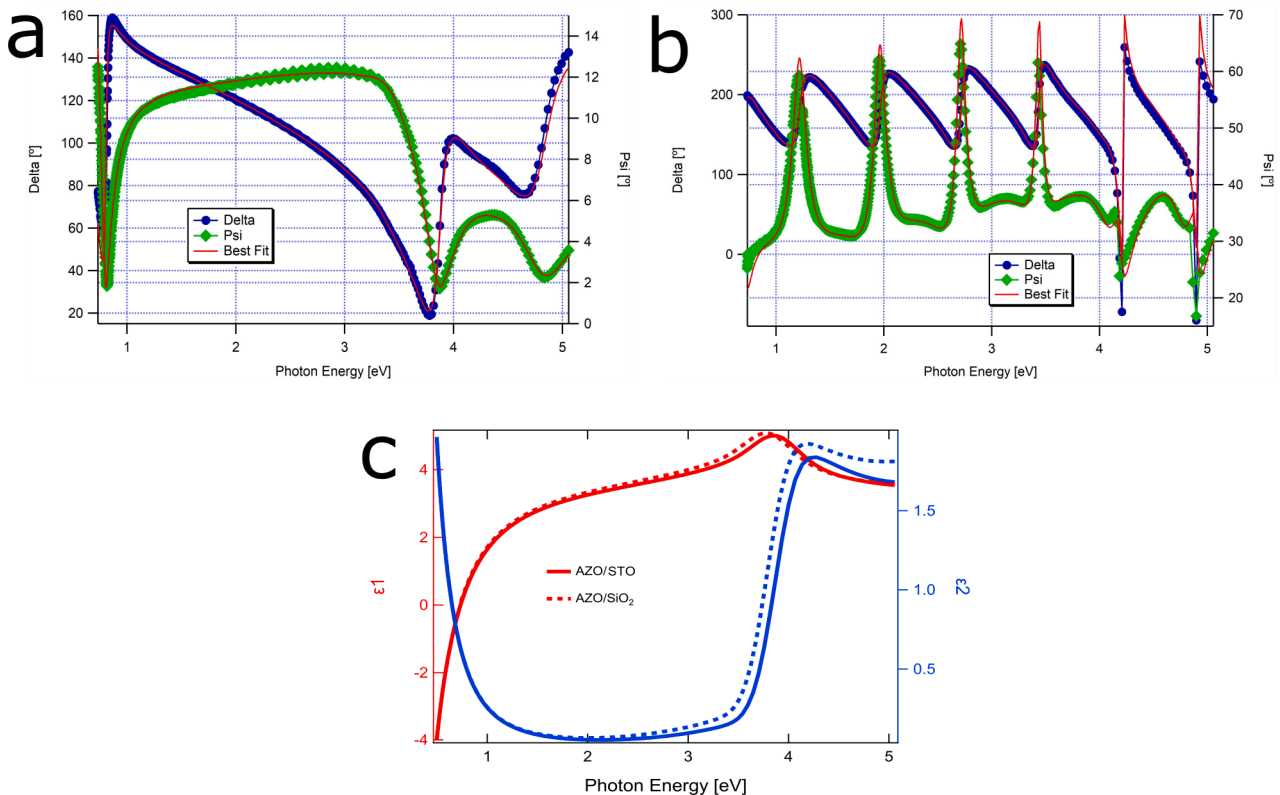


Fig. 8. (a) Ellipsometric angles for the 30 nm thick AZO/STO film with best fit. (b) Ellipsometric angles for the 30 nm thick AZO/SiO₂ film with best fit. (c) Real (ϵ_1) and imaginary part (ϵ_2) of the dielectric function of 30 nm thick AZO/STO film (full curve) and AZO/SiO₂ film (dashed curve).

$$m^* = m_0^*[1 + 2C(E - E_c)] \quad (10)$$

where C is called the non-parabolicity parameter. For the high dopant concentrations observed in this system, the electron gas is completely degenerated, and the Fermi energy is calculated as

$$E_F = \frac{1}{2C} \left[\sqrt{1 + 2C \frac{\hbar^2}{4\pi^2 m_0^*} (3\pi^2 n_e)^{\frac{2}{3}} - 1} \right] \quad (11)$$

Then, the effective mass dependence on the carrier density can be written as

$$m^* = m_0^* \sqrt{1 + 2C \frac{\hbar^2}{4\pi^2 m_0^*} (3\pi^2 n_e)^{\frac{2}{3}}} \quad (12)$$

The effective electron mass for AZO was reported to be in a range between $0.24m_e - 0.28m_e$, depending on the source [49,57,59–62], so we took $0.26m_e$. The relative dielectric constant of AZO thin films was taken to be 7.8 [60], which is the value of the static permittivity in the direction perpendicular to the c -axis, which is the direction along which conduction takes place since the films are c -axis oriented, while the non-parabolicity parameter was taken to be 0.56 eV^{-1} , which seems to be the most reasonable value looking at the literature [50,59]. Z has been set to 1.2, following the work of Ellmer and coworkers, and takes into account the fraction of donated electrons that are trapped due to the clustering of impurities and to the presence of oxygen vacancies and do not contribute to conductivity, together with the fact that the presence of clustering determines a reduction of the concentration of the scattering centers [50]. With our mean carrier density of $5.1 \cdot 10^{20} \text{ cm}^{-3}$ we obtain a μ_{imp} of around $44 \text{ cm}^2/(\text{V}\cdot\text{s})$ for epitaxial AZO/STO films. This contribution does not take into consideration the presence of compensating Zn vacancies, which are always present in AZO [63]. To account for them a compensating factor is typically included in the model [64]. However, this compensation does not significantly change this quantitative evaluation within the error of the considered approximations and is negligible compared to the other terms. Since we do not have a reliable estimation of the compensating vacancies in our films and because of the negligible correction, we decide to set the compensating factor to 0.

The last contribution to take into consideration is grain boundary scattering, that also accounts for the fraction of electrons trapped at these sites. A possible way to evaluate its contribution to mobility is the Seto model [65], where it is postulated that defects at grain boundaries induce trap states in the band gap with an areal concentration N_t . Upon occupation by electrons, these trap states form potential barriers, which have to be surmounted by the charge carriers during electron transport. Seto model can be extended to degenerate conditions [50], and μ_{grain} can be written as

$$\mu_{grain} = \frac{4\pi e m^* L_x k_B T}{n_e \hbar^3} \ln \left(1 + e^{\eta - \frac{E_B}{k_B T}} \right) \quad (13)$$

where L_x is the lateral grain size (our lateral coherence length), k_B is the Boltzmann's constant, T is the temperature, E_B is the potential barrier height and η is the reduced Fermi energy. For electron densities above $6 \cdot 10^{18} \text{ cm}^{-3}$, η can be approximated with an error smaller than 3 % by the following formula [66]

$$\eta = \sqrt{\left(\frac{3\sqrt{\pi}}{4} \frac{n_e}{N_C} \right)^{\frac{4}{3}} - \frac{\pi^2}{6}} \quad (14)$$

where N_C is the effective conduction band density of states, that is

$$N_C = \frac{2}{\hbar^3} (2\pi m^* k_B T)^{\frac{3}{2}} \quad (15)$$

The grain barrier height is given by

$$E_B = \frac{e^2 L_x^2 n_e}{8\epsilon_r \epsilon_0} \text{ for } L_x n_e < N_t \quad (16)$$

$$E_B = \frac{e^2 N_t}{8\epsilon_r \epsilon_0 n_e} \text{ for } L_x n_e > N_t \quad (17)$$

Since N_t is in the range $1 \cdot 10^{13} \text{ cm}^{-2} - 5 \cdot 10^{13} \text{ cm}^{-2}$ in doped ZnO [50,67–69] and L_x for the AZO/STO films is around 50 nm, we fall in the second case. Taking an average N_t of $3 \cdot 10^{13} \text{ cm}^{-2}$, we obtain a μ_{grain} of around $200 \text{ cm}^2/(\text{V}\cdot\text{s})$, which is a small contribution with respect to ionized impurity scattering in epitaxial AZO/STO films but can account for the decrease to about $25 \text{ cm}^2/(\text{V}\cdot\text{s})$, considering also the contribution from the lattice.

Via Matthiessen's rule, we can put all these contributions together to explain the measured mobilities of AZO/STO films. Fig. 9 shows the experimental electrical mobility compared to that evaluated from Pisarkiewicz and Seto models with the measured carrier densities and lateral coherence length, plus the contribution from the lattice. The error bar on the latter is calculated by propagating the error on the carrier density. The values are all compatible within the error bars: the good agreement between experiment and models proves that in our epitaxial AZO/STO films the electrical Hall mobility is mostly limited by ionized impurity scattering, while grain boundary scattering and lattice mobility are smaller contributions. For this reason no variation is evident with decreasing thickness and thinner films maintain the same electrical response of thicker bulk-like films.

As a comparison, AZO/SiO₂ polycrystalline films grown in the same conditions and with the same thickness show a decreasing resistivity as a function of thickness. Optical mobility and optical carrier density are very similar between AZO/STO and AZO/SiO₂ films. This means that the different crystalline quality does not affect too much the intrinsic properties of the material inside grains even at reduced thickness, but affects their ability to contribute to conduction, because of grain boundary scattering. During optical excitation, there is only a slight oscillation of carriers around their equilibrium positions, so that most of them do not have to overcome the potential barriers at grain boundaries. Hence, it is only from the electrical point of view that we observe a difference between epitaxial and polycrystalline films. In fact, as already noted by Bikowski and Ellmer [67], optical and electrical measurements show nearly the same mobility values when the electron transport is limited by ionized impurity scattering and not by grain boundary scattering. For this reason in AZO/SiO₂ polycrystalline films the increasing trend of the resistivity when the thickness is reduced is expected to be associated with grain boundary scattering, since the lateral coherence length follows an opposite trend and becomes extremely small in comparison to that of epitaxial films in the thinnest films.

We can apply the same model exploited for epitaxial AZO films with polycrystalline films, using the optical carrier density obtained by

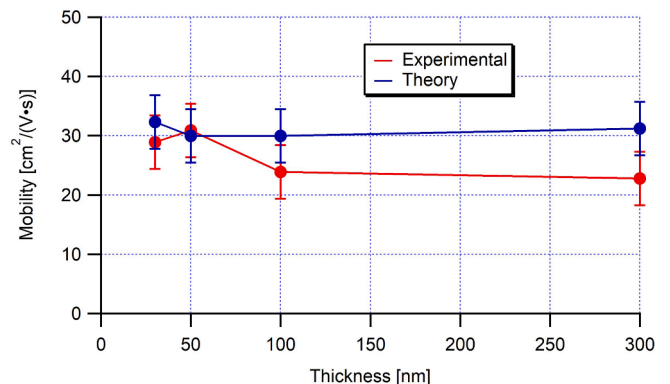


Fig. 9. Electrical Hall mobility of the AZO/STO films as measured (red) and calculated (blue).

spectroscopic ellipsometry modelling, including contributions from ionized impurity scattering via Pisarkiewicz model, from grain boundary scattering via Seto model and from lattice mobility. The similar behavior of optical and electrical carrier concentration has been demonstrated in previous studies on TCO [9,70] and recently on AZO [71], and assumed in several works on ellipsometry [72,73]. In principle one can easily switch from mobility μ to resistivity ρ by the simple relation

$$\rho = \frac{1}{ne\mu} \quad (18)$$

If we evaluate the resistivity in this way, we obtain values which are very close to the experimental ones, as shown in Fig. 10. Since the only contribution which is varying between films of different thicknesses and can justify a variation of resistivity is the lateral coherence length, this agreement is indicating that grain boundary scattering is the dominant contribution. The only point with a bad agreement is the one at 30 nm thickness. In this case however the lateral coherence length is affected by a big relative error because of its small value and thus it is at the resolution limit of XRD. This big relative error is reflected on a big uncertainty on the calculated resistivity value, that is however consistent with the experimental value.

The contribution to resistivity due solely to grain boundary scattering can be also modeled via the Mayadas-Shatzkes model [74,75]. According to the Mayadas-Shatzkes model, the resistivity ρ_{grain} of a polycrystalline film for which the influence of surface scattering can be neglected can be evaluated as

$$\frac{\rho_0}{\rho_{grain}} = 1 - \frac{3}{2}a + 3a^2 - 3a^3 \ln\left(1 + \frac{1}{a}\right) \quad (19)$$

where

$$a = \frac{l_0}{D} \frac{R}{1-R} \quad (20)$$

where ρ_0 and l_0 are the conductivity and the electron mean-free path inside a grain (i.e., the conductivity and mean-free path of a single

crystal of the same material, which has the same density of defects and impurities as a grain), R is the grain boundary reflection coefficient and D is the average grain size, which in our case is the lateral coherence length L_x . The electron mean-free path l_0 [46–48] can be evaluated via Eq. (21)

$$l_0 = \left(\frac{\hbar}{2e}\right) \left(\frac{3n_e}{\pi}\right)^{\frac{1}{2}} \mu_H \quad (21)$$

We took ρ_0 and l_0 respectively as $4.9 \cdot 10^{-4} \Omega \cdot \text{cm}$ and 6 nm, that are the mean values of resistivity and electron mean-free path for AZO/STO films, where grain boundary scattering can be neglected in first approximation, and thus we can take these values as the intragrain characteristics of the films. We fitted the resistivity experimental values of AZO/SiO₂ films as a function of their lateral coherence length with the Mayadas-Shatzkes model, letting the grain boundary reflection coefficient R free. The best fit is shown in Fig. 10, together with the calculated resistivity via Pisarkiewicz and Seto models. We observe a good agreement of the model considering a grain boundary reflection coefficient of approximately 0.5, which is in accordance with the literature [76]. Also, the only point for which the fit is not very close to the measure (but still in the error bar) is the one referring to the 30 nm thick AZO/SiO₂ film, because of the aforementioned resolution limit of XRD. The Mayadas-Shatzkes curve is also consistent with the previously calculated resistivity, proving once more that grain boundary scattering is the dominant contribution to resistivity for polycrystalline AZO films. These results are consistent with previous studies, where thin polycrystalline TCO films show lower crystalline quality and smaller grain sizes with respect to thicker ones, enhancing grain boundary scattering and resistivity [77]. It was reported for instance that electrical properties of Ta:TiO₂ film degrades very fast below 50 nm of thickness, with resistivity of the order of 10^{-1} - $10^{-2} \Omega \cdot \text{cm}$ and mobilities of few $\text{cm}^2/(\text{V} \cdot \text{s})$ for 20 nm thick films [14], and a similar behavior was observed also for ultrathin ITO films [15]. On the contrary, when a buffer layer is introduced or the interfacial quality is controlled and optimized, the mobility of charge carriers remains higher than $20 \text{ cm}^2/(\text{V} \cdot \text{s})$ and constant down to 20 nm thickness, comparable to our results [7].

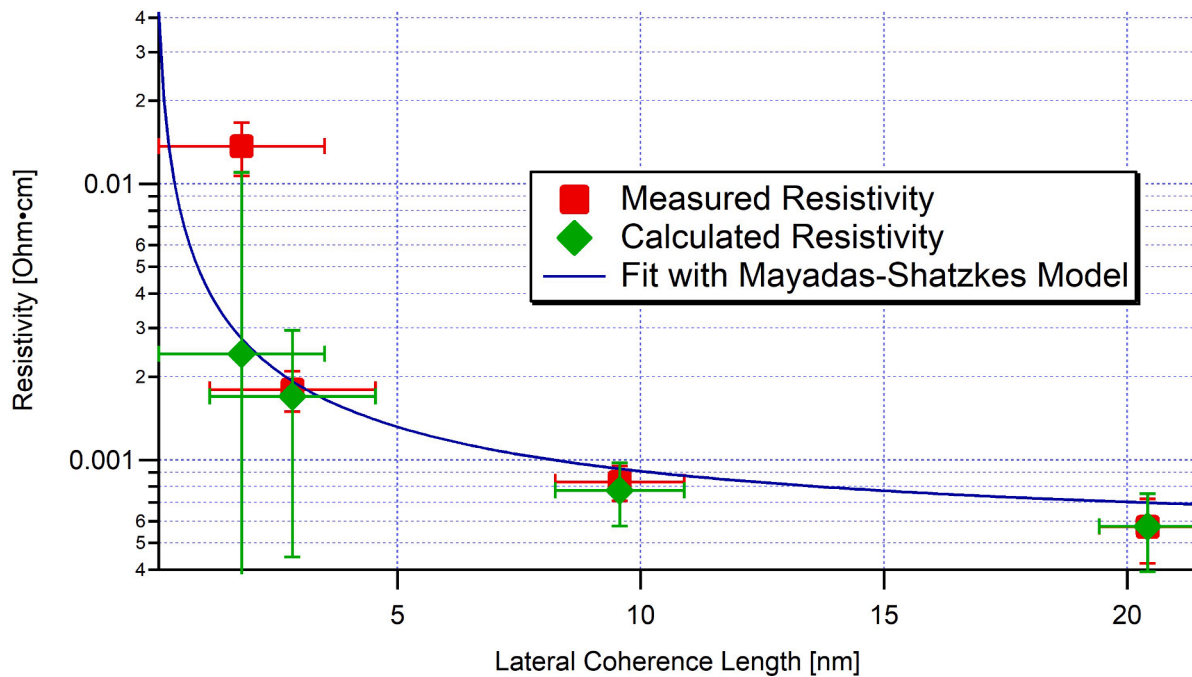


Fig. 10. Measured resistivity (red markers) of the AZO/SiO₂ films vs lateral coherence length, fitted with the Mayadas-Shatzkes model. Green markers represent the resistivity calculated via the combination of Pisarkiewicz and Seto models plus the contribution from the lattice, considering the corresponding measured lateral coherence lengths.

5. Conclusions

In conclusion, we reported an exhaustive study about RF magnetron sputtering growth of epitaxial 4 at. % AZO films as a function of thickness on STO (110) substrates and their comparison with polycrystalline films grown in the same conditions on thermal SiO₂ on Si (001) substrates. We grew films in a thickness range from 30 to 300 nm.

While the surface morphology of the films is similar, as underlined by AFM, XRD measurements proved that AZO/STO films grow epitaxial, and they display far higher crystalline quality with respect to polycrystalline films. In particular, epitaxial films show a constant lateral coherence length with respect to thickness, while polycrystalline ones show a monotonous decrease with decreasing thickness, as well as higher values of microstrain and tilt.

Electrical measurements point out that epitaxial films retain their optical properties down to thicknesses as low as 30 nm, while polycrystalline films are considerably more resistive at low thicknesses. In contrast, no evident differences were found from an optical point of view.

These features were explained by acknowledging that, in epitaxial AZO films, grain boundary scattering is a far lesser contribution to mobility with respect to ionized impurity scattering, because of their large lateral coherence length. Hence, their electrical Hall mobility is limited mostly by ionized impurity scattering, and that copes with their constant resistivity as a function of thickness. This conclusion is corroborated by the fact that the mobility evaluated thanks to a combination of Pisarkiewicz and Seto models, where the most important contribution comes from ionized impurity scattering, and Matthiessen's rule is consistent with the measured one.

In polycrystalline films, instead, grain boundary scattering is dominant at low thicknesses and this enhances resistivity, whose trend was successfully fitted by the Mayadas-Shatzkes model. Optical properties do not show significant differences between epitaxial and polycrystalline films neither as a function of thickness, confirming that the intrinsic properties of the material inside the grains is not affected by crystal quality and grain boundary scattering is the main reason behind the degradation of the electrical properties in thinner polycrystalline films.

These considerations led us to conclude that epitaxy is a viable root to obtain high performing TCO thin films below 50 nm of thickness. These results could be very interesting for future applications where high-quality ultra-thin TCO films are needed or growth of AZO thin films on perovskite substrates is involved.

CRedit authorship contribution statement

Riccardo Magrin Maffei: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Alessandro di Bona:** Conceptualization, Methodology, Resources, Data curation, Writing – review & editing. **Maria Sygletou:** Formal analysis, Investigation, Data curation. **Francesco Bisio:** Writing – review & editing, Supervision, Funding acquisition. **Sergio D'Addato:** Writing – review & editing, Supervision, Funding acquisition. **Stefania Benedetti:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2023.157133>.

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