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Impact of the particles impingement on the electronic conductivity of Al doped ZnO films grown by reactive magnetron sputtering

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Abstract. Aluminium doped zinc oxide thin films (4 at.% Al) were deposited by reactive magnetron sputtering technique and characterized by X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), four point probe technique and optical spectrophotometry. High heterogeneities were observed as a function of sample position in the chamber. The chemical analyses did not reveal significant change in composition. Optical investigation showed a strong variation of the density of free carriers, through the Burstein-Moss effect, suggesting that Al dopants were partially inactivated.

1. Introduction

Investigations about new transparent conductive oxide materials have dramatically increased over the last decade in order to elucidate their behaviour and concretize new solutions for crucial energy issues of nowadays. Al doped zinc oxide (AZO), which possesses high conductivity and transparency in the visible range, is probably the most promising candidate for transparent electrodes. For this reason, hundreds of recent studies have reported on various aspects of this transparent electrode material.
An important issue, rarely highlighted, is the lateral variation of the electrical conductivity along AZO thin films deposited by reactive magnetron sputtering. The degradation in electrical properties remains a significant problem for applications on large surfaces as for smart windows, solar cells contacts or antiglare mirrors. Indeed, strong degradations in film conductivity were observed depending on the position of the substrate in the deposition chamber. As Horwat and co-worker reported in 2007, the conductivity of 1.5 at.% Al doped films decreases when the film position approaches the position in front of the target axis and is not related to the variation in grain size [1]. The present paper reports on the lateral variations in the electrical properties of AZO thin films (4 at.% Al) synthesized by reactive magnetron sputtering. Several characterizations are presented here in order to emphasize the

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relationship between structural, chemical, optical parameters and the electrical conductivity behaviour. The issue of activated or inactivated dopants is discussed.

2. Experimental

ZnO:Al thin films were sputter deposited on soda lime glass and silicon wafers substrates in a reactive argon-oxygen atmosphere, with a 2 inches in diameter Al/Zn (4/96 at.%) target as described in figure 1. The deposition chamber is a 40L volume pumped down to 10^{-4} Pa and filled by an argon-oxygen mixture (20/5,5sccm) to reach 0.4 Pa (0.34 Pa Ar and 0.06 Pa O_2) as deposition pressure. This composition of the gas mixture was carefully determined to synthesize a stoichiometric material providing the high transparency required. The target is powered by dissipating 0.1 A with an Advanced Energy pulsed DC Pinnacle+. The distance between the target and the substrate holder was set to 50 mm. The surface of the substrate-holder was parallel to the target surface and put in rotation in order to ensure thickness homogeneity. The target was 50 mm off-axis relatively to the substrates-holder axis of rotation. Samples were placed at different distances (*d*) from the target axis. The thickness of our films was measured to be 140 nm by tactile profilometry with an accuracy of 10 nm. Structural properties were determined using a θ/2θ configuration D500 diffractometer with a $K_{\alpha 1}$Co radiation (λ=0.178897 nm). Electrical characterizations were performed using the four probe method. The optical behaviour was investigated thanks to transmittance measurements from 200 nm to 800 nm on a Carry 5000 Varian spectrophotometer.

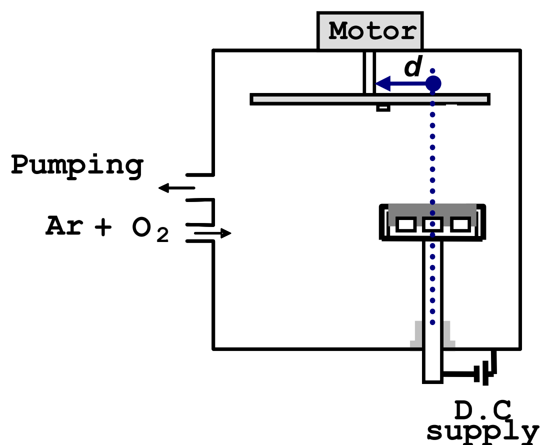

Figure 1. Schematic representation of the magnetron sputtering deposition chamber.

The optical band gaps were calculated from the transmittance curves by the Tauc's plot in extrapolating the $(\alpha h\nu)^2$=B(hν-Eg) curves. The chemical composition was determined by Rutherford backscattering spectrometry (RBS) with a 5 MV HVEE Tandetron accelerator sited at Universidad Autónoma de Madrid.
RBS spectra were collected using a 2 MeV He^+ beam. Experiments near the resonance were performed at energies of 3.028, 3.055 and 3.072 MeV to ensure the homogenous oxygen content. The data were acquired simultaneously with two silicon surface barrier detectors located at scattering angles of 170° with an energy resolution of 14 keV and an ion dose of 5 µC per detector, then, fitted using the programs RBX and SIMNRA.

3. Results and discussion

The main features of the films deposited at different distances from the target axis (*d*), are summarized in table 1.

Table 1. Synthesis parameters, conductivity, stoichiometry and optical band gap of AZO films.

Sample	d (mm)	σ (S cm^{-1})	Al (at.%)	Al/Zn	Eg (eV)
1	**0**	**0.019**	**4**	**0.100**	**3.409**
2	**10**	**0.530**	**4**	**0.098**	**3.418**
3	**20**	**25.21**	**4**	**0.098**	**3.566**
4	**30**	**35.21**	**4**	**0.098**	**3.639**

3.1. Structural and chemical analyses
The Xray diffractogramm of figure 2 (left) is consistent with the wurtzite structure of ZnO (JCPDS 01-070-8070). Nevertheless, as usually observed for sputtered thin film, a strong preferential growth appears along the *c* axis. A quasi linear correlation between X-ray diffracted intensity, normalized by the thickness, and the conductivity is found. The closer is the position of the sample from the magnetron axis; the higher is the intensity of the XRD peak and the lower is the conductivity. This behaviour that we already noticed for films with lower Al content [1] is quite surprising since previous studies on films deposited at fixed position but various thickness [2] and oxygen partial pressure [3] showed a positive correlation between the conductivity and the film texture. For practical application, the Al content is usually ranging from 1.5 to 4 at.% Al. The overall aluminium concentration measured was around 4 at.% (see table 1) for all the deposited film. Around this upper limit, partial segregation of Al dopants may occur. It is not clear whether this could sensitively affect the structural signature and it was not possible to point out the origin of the correlation between the XRD intensity and the conductivity behaviour. For instance, Yoshioka et al [4] evidenced, with Al-K edge X-ray absorption near edge structure (XANES) measurement, such a segregation of Al in heavily doped ZnO (>20 at.% Al) but could not link it to changes in the XRD spectra. Figure 2 (right) shows the RBS spectra for the four deposited samples. As can be noticed, the curves are quasi perfectly overlapped. Nevertheless software fitting evidenced very little variations of the Al/Zn ratio as reported in table 1. Thus, the chemical composition is stable along parameter *d*. From these observations one may be tempted to conclude on the inactivation of part of the dopants as the origin of the observed electrical heterogeneity. The next section will provide further evidence of such an effect.

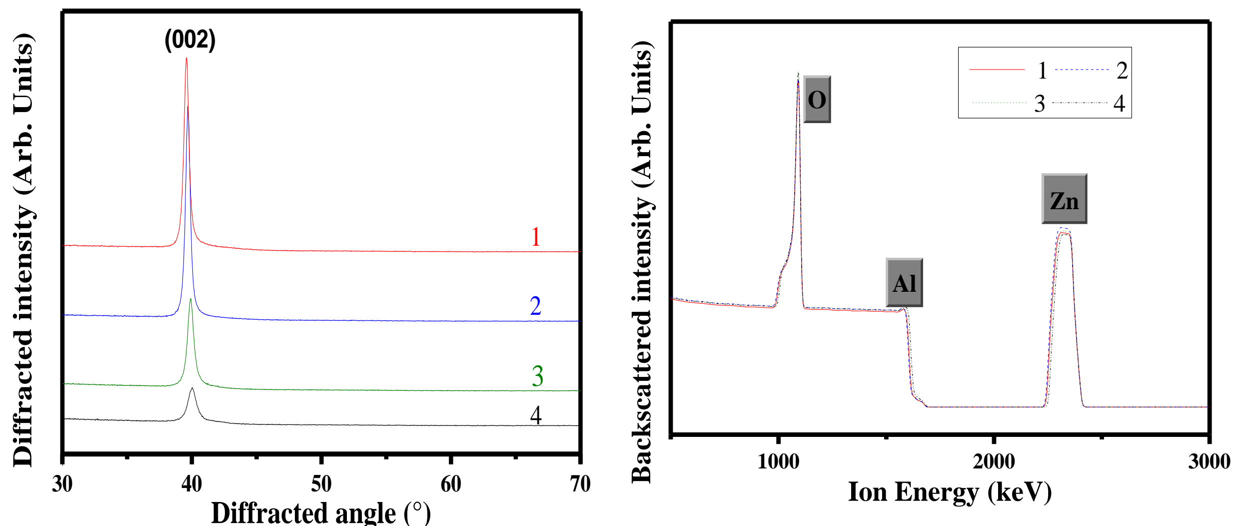

Figure 2. X-ray diffractograms of wurtzite structure (left) and RBS spectra(right)

3.2. Optical characterization
Figure 3 plots the optical transmittance from 200 nm to 800 nm for the deposited films. A spectrum of an undoped ZnO film is indicated as a reference. This reference spectrum is characterized by a band gap of 370 nm (3.35 eV). The curves for Al doped films are shifted towards lower wavelengths comparatively to the ZnO reference. This shift (ΔEg) all the more marked as the conductivity is high, can be related to the Burstein-Moss effect [5] and this shift is representative of a change in the density of free carriers (electron, n_e) trough the following expression [6]:

$$-\Delta Eg \; \alpha \; n_e^{2/3}$$

These observations support the hypothesis that the inactivation of the Al dopants significantly impacts on the conductivity of the 4 at.% Al doped ZnO sputtered thin films.

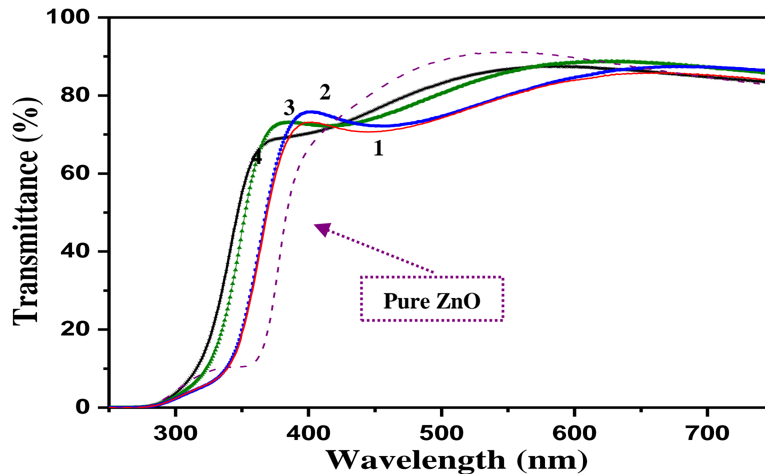

Figure 3. Transmittance curves of the four samples placed at different positions from the sputtered target axis.

4. Discussion

Using a radiofrequency sputtering process with fixed position, Tominaga et al [7] highlighted the influence of energetic oxygen atoms backscattered from the erosion track of the target on the formation of Al-O bonds in the films. We believe that this effect is also at the origin of the inactivation of the dopants for DC reactive deposited AZO films which rules the lateral electrical heterogeneity. Effectively, in our experiments the higher flux originating from the erosion track is received by the sample placed on a circumference facing the target axis. The energetic bombardment can have positive impact on the quality of the crystals but partially inactivate the dopants. Thus, the use of AZO thin films for large applications will request further understandings of the inactivation mechanisms and the knowledge of the local coordination of Al.

5. Conclusions

4 at.% Al doped zinc oxide thin films deposited by magnetron sputtering deposition technique, were grown on soda lime glass and silicon substrates. Structural and chemical analysis did not directly explain the observed electrical heterogeneities along the films. The optical spectroscopy analysis evidenced a Burstein Moss shift of the optical band gap which implies a carrier concentration change. These observations support the partial deactivation of Al dopants. This phenomenon may originate from the variations in the flux energetic oxygen atoms of backscattered from the target surface and triggering the formation of Al-O bonds.

Acknowledgements
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[1] Horwat D and Billard A 2006 *Thin Solid Films* **515** 5444-5448
[2] Birkholz M, Selle B, Fenske F Nad Fuhs W 2003 *Phys. Rev* B **68** 205414
[3] Ellmer K, Diesner K, Wendt R and Fiechter S 1996 *Solid State Phenomena* **51-52** 541-546
[4] Yoshioka S, Oba F, Huang R and Tanaka I 2008 *J. Appl. Phys.* **103** 014309
[5] Burstein E *Phys Rev* **93**, 632-633
[6] Hamberg I, Granqvist C G, Berggren K F, Sernelius B E and Engström L 1984 *Phys. Rev* B **30** 3240
[7] Tominaga K, Kuroda K and Tada O 1988 *Jpn. J. Appl. Phys.* **27** 1176-1180