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# Residual stress and texture in Aluminum doped Zinc Oxide layers deposited by reactive radio frequency magnetron sputtering

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ABSTRACT

Aluminum doped Zinc Oxide thin films were deposited on standard soda-lime substrates by reactive radio frequency magnetron sputtering. Residual stress and texture were studied by X-ray diffraction, while X-ray Absorption Near Edge Spectroscopy provided information on the Al environment in the best performing thin films. The influence of deposition parameters on structural and microstructural properties is discussed. A correlation between microstructure and residual stress state with electrical and optical properties is proposed.



## 1. Introduction

ZnO is a semiconducting material extensively used in photoelectronic devices for its wide band gap (3.37 eV), high exciting binding energy (60 meV), non-toxicity, low cost and availability [1]. A rich literature can be found on different applications, like light-emitting devices [2], gas sensors [3], piezoelectric transducers [4] and ultrasonic oscillators [5], just to cite a few.

Different dopants from group III of the periodic table have been used so far to produce conducting ZnO thin films, Al being the most promising one in terms of performance and low cost; in fact, Aluminum doped Zinc Oxide (AZO) is one of the most commonly used alternative to ITO (indium tin oxide).

Even though several techniques can be used to produce high quality thin films, controlling the growth mechanism is still the key to achieve optimal results. In this, Physical Vapor Deposition (PVD) methods provide a good compromise between overall production cost and final thin-film quality. This makes magnetron sputtering one of the most convenient choices for producing window layers in photovoltaic applications. While much has been done to study non-reactive and/or DC-magnetron sputtering setup, less has been reported on reactive RF-magnetron sputtering. In this paper we present a study on AZO thin layers deposited by this techniques, showing the correlation between the content of reacting oxygen (relative to the sputtering gas) and the resulting structural, microstructural, electrical and optical properties.

## 2. Experimental

Samples were produced by RF-magnetron sputtering in a customized Leybold Z400 system based on a sputter down setup, using Ar as working gas and $O_2$ as reactive gas. The target (zinc alloyed with 2 wt.% Al, disc diameter of 75 mm, thickness 3 mm and purity of 99.99%), was positioned 70 mm above the substrates. Two sets of samples were obtained by changing the relative oxygen pressure with respect to the Argon pressure. In the first set of samples (**S1** in the following), modifications in electrical and optical properties, as well as in crystalline structure, were achieved by changing the relative oxygen pressure (by modifying the absolute Ar pressure and keeping constant the $O_2$ pressure) in a wide range of values; the second set of samples (**S2**) was obtained in a much narrower range of low relative pressures (see Table 1 for details). It is important to note that in the **S2** group, for two samples, also the absolute oxygen pressure was changed. For all produced samples, film thickness was measured with a Dektak III stylus profilometer, leading to values ranging from 0.69 μm to 0.90 μm in the **S1** set, while it was stable at 1.00 μm in the **S2** set.

X-ray diffraction (XRD) data were collected in pseudo-parallel beam geometry using CuK$\alpha$ radiation on a four-circle PANalytical X'Pert MRD diffractometer. The machine is equipped with a polycapillary lens (0.3 ° divergence) in the incident beam and a vertical slit collimator (0.27 ° divergence), with a graphite flat-crystal analyzer in the diffracted beam. This setup was chosen to improve the illumination under unfavorable conditions (such as low $2\theta$ angles and/or high $\psi$ tilts) while involving, at the same time, a sufficiently large specimen area to obtain good grain statistics [6]. Furthermore, instrumental contributions to peak position and/or intensity have been carefully taken into account in all calculations. Optical properties were investigated by transmittance measurements in

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**Table 1**
Sputtering conditions in the deposition of the AZO thin films. Highlighted samples (bold) were produced with different oxygen content.

| **S1** [$\Delta P_{O_2}(\%) = 14.10$] | | | **S2** [$\Delta P_{O_2}(\%) = 1.57$] | | |
|---|---|---|---|---|---|
| $P_{Ar}$ ($10^{-1}$ Pa) | $P_{O_2}$ ($10^{-1}$ Pa) | $P_{O_2}$ (%) | $P_{Ar}$ ($10^{-1}$ Pa) | $P_{O_2}$ ($10^{-1}$ Pa) | $P_{O_2}$ (%) |
| 3.77 | 0.27 | 7.16 | 6.33 | 0.27 | 4.09 |
| 3.27 | 0.27 | 8.26 | 6.00 | 0.27 | 4.31 |
| 2.77 | 0.27 | 9.75 | **5.25** | **0.25** | **4.55** |
| 2.27 | 0.27 | 11.89 | **5.00** | **0.25** | **4.76** |
| 1.77 | 0.27 | 15.25 | 5.00 | 0.27 | 5.12 |
| 1.27 | 0.27 | 21.26 | 4.50 | 0.27 | 5.66 |

the 250–2500 nm wavelength range, using a Perkin Elmer Lambda 750 spectrophotometer equipped with a 10 cm integrating sphere. X-ray Absorption Near Edge Spectroscopy (XANES) measurements were performed in the Spherical Grating Monochromator beamline (with an energy range between 200 and 2000 eV), at the Canadian Light Source synchrotron facility.

## 3. Results and discussion

Fig. 1 shows two different properties, thin film texture and electrical resistivity, as a function of the relative oxygen pressure during deposition. It is clearly visible the evolution of the microstructure, i.e., the dispersion of grain orientations about the main 00 h fiber texture axis, with the oxygen content: texture is quite sharp at high oxygen relative pressures and decreases steeply by lowering the oxygen partial pressure below ca. 10%.

This behavior correlates with the resistivity, showing a qualitatively similar trend: actually the resistivity drops exponentially by lowering the oxygen relative pressure. The $P_{O_2}$ also affects sample homogeneity: at high oxygen pressure the resistivity varies across the surface of the deposited thin film (measurement points labeled as left, center and right) whereas, at low $P_{O_2}$ resistivity values become increasingly more uniform, converging to a single value. To better visualize this feature, results for set **S2** are shown in the inset of the figure.

As stated before, XRD was used for structural characterization as well as for texture and residual stress analysis. According to the XRD all samples present the hexagonal wurtzite phase only, whereas residual stress has a peculiar trend related to the specific microstructure developed by the different deposition conditions. Actually, in general, thin films obtained by physical vapor deposition methods (such as magnetron sputtering technique), are subjected to intrinsic compressive residual stresses, in particular when dealing with relatively dense films [7]. Fig. 2 shows the so-called $\sin^2\psi$ plots [8] for two crystalline reflections ((002) and (101)) of the first set of AZO samples (**S1**). In both pictures, the insets show separately the first and the last samples of the series, as well as the three most homogeneous samples. Independently

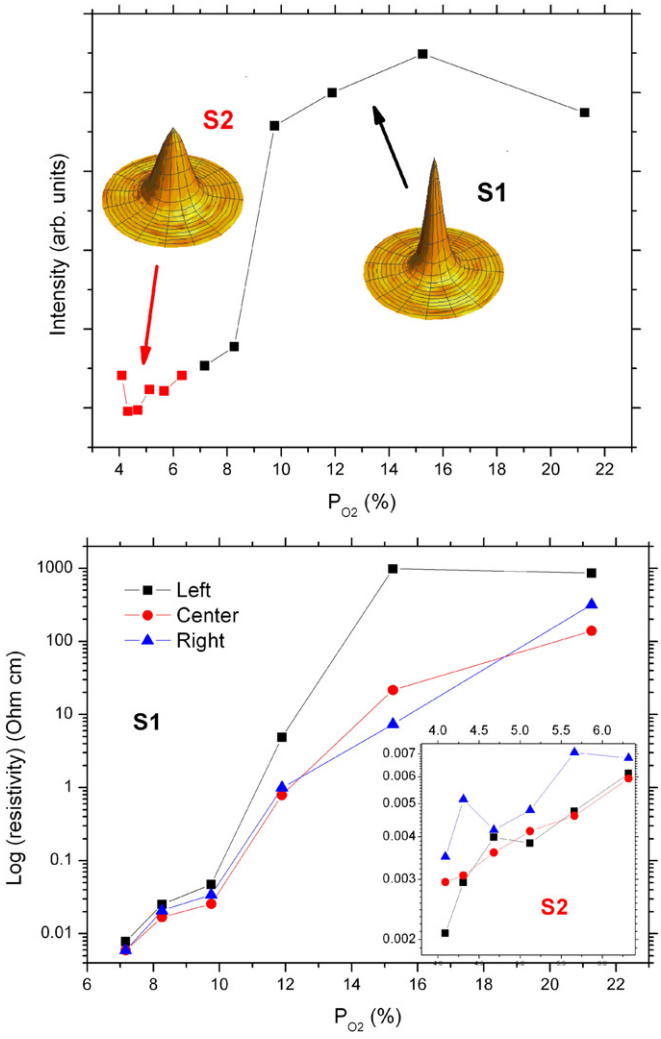


**Fig. 1.** Variation of the intensity diffracted by the principal ZnO reflection (002) (top) and resistivity (bottom) with respect to the relative oxygen pressure, $P_{O_2}$. See text for details.

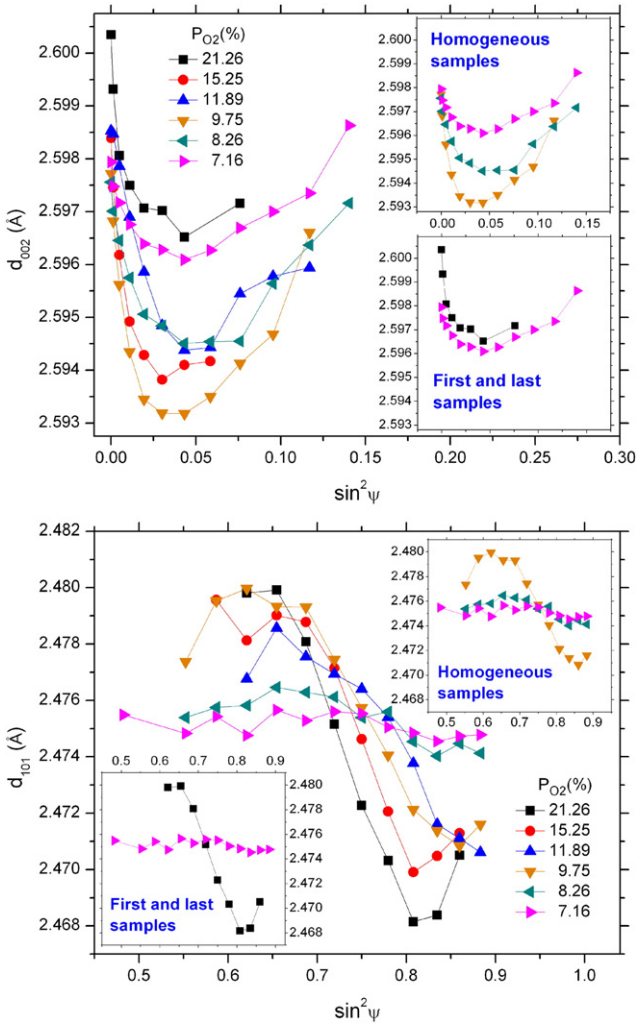


**Fig. 2. S1** set of AZO thin films: $\sin^2\psi$ plots for the (002) (top) and the (101) reflections (bottom).