Transparent and conductive ZnO:Al prepared by RF diode sputtering

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Abstract. High transparent and conductive, aluminium-doped zinc oxide thin films (ZnO:Al), were prepared by radio-frequency (RF) diode sputtering from ZnO+2 wt. % Al₂O₃ target on Corning glass 7059 substrates. The RF power and the substrate temperature modified their structure and surface morphology, electrical and optical parameters. The XRD patterns reveal only one sharp (002) diffraction line, providing a clear evidence for highly textured ZnO films, with a preferential c-axis orientation. Maximum intensity and the lowest full-width at half-maximum (FWHM) (3.26°) of the Ω-scan were obtained for ZnO:Al deposited at 800 W RF power and 200ºC substrate temperature. The developed ZnO:Al have a low electrical resistivity (2 × 10⁻³ Ω·cm) and high optical transmittance (> 82 %, including Corning glass substrate) in the visible region. The direct optical band gap (~ 3.3 eV) increases with the increasing carrier concentration.

1. Introduction
The unique material properties in combination with a great natural abundance and low cost, make ZnO a promising transparent conducting oxide (TCO) for application in thin film solar cells and various optoelectronic devices [1,2]. A matter of great importance for these industrial applications is the availability of a cost effective deposition technology. RF sputtering is such method that offers a deposition at low temperatures, safety advantages, and where the use of the toxic gases is avoided. This plasma assisted deposition method involves an energetic bombardment of neutral atoms, ions and electrons on the growing film. Our previous experiments showed that the total energy flux density and temperature are determining for the properties of sputtered ZnO films [3]. In this work we present experimental results for ZnO:Al thin films prepared at different RF powers and substrate temperatures in order to investigate the correlation structure↔surface morphology↔electrical↔optical parameters.

2. Experimental details
We prepared ZnO:Al thin films in a planar RF sputtering diode system Perkin Elmer 2400/8L, using a ceramic target (ZnO+2 wt. % Al₂O₃) in Ar working gas. Films with thicknesses from 560 nm to...
800 nm, depending on the sputtering power and time, were deposited on Corning glass 7059 substrates. The Ar pressure was maintained constant 1.3 Pa. Two variable sputter parameters, chosen to tailor the physical properties of the ZnO:Al films, were RF power (P) and the substrate temperature (T_s), and were changed from 200 to 1200 W, and from room temperature (RT) to 300°C respectively. The crystal orientation and microstrains of the films were investigated by X-ray diffractometer AXS Bruker D8 with 2D detector and CoKα (λ = 0.179 nm) radiation. The surface morphology was evaluated by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM). The electrical parameters of ZnO:Al thin films were obtained from Hall measurements. The optical transmittance was determined by spectrometer Specord 210.

3. Results and discussions

3.1. Structure characterization

The development and changes in crystalline structure with varying either RF power or substrate temperatures are displayed in the XRD patterns, figure 1 (a-b). Characteristic parameters of the (002) line: position of the diffraction angle (2θ), intensity and FWHM of the Ω-scan, provide information about the crystalline state, texture and lattice stresses of the films. The patterns are dominated from the strongest (002) diffraction line, which indicates a texture film growth, with a preferential c-axis crystallographic orientation.

XRD analysis of ZnO:Al thin films indicates that all investigated ZnO films are polycrystalline with a very strong texture in the [001] direction perpendicular to the substrate. Significant asymmetry of (002) diffraction line when room substrate temperature was used indicates that there is a region with heterogeneous structure at the substrate – film interface. The position of the (002) diffraction angels shifts from approximately 39.6° for ZnO:Al deposited with 200 W to 40.2° (reference position) for those deposited with 800 W.

Further energy delivered to the growing film by heating the substrate from RT to 300°C improved the crystallinity of the films as can be seen in Figure 1 (b). The asymmetry of (002) line as well as heterogeneous regions completely diminished at higher substrate temperatures and small shifts from the reference line position were observed, which indicates only unimportant lattice strains. The widths of (002) lines became narrower and dimensions of crystallites growing from 60 to 120 nm for films deposited at RT and to more than 200 nm for those deposited at higher substrate temperatures. The widths of azimuthal line profiles also decreased from 15 to 3.5° with increasing energy delivered to the growing film during the deposition. This indicates lower declination of individual crystallites from
the normal to the substrate (stronger texture). At the highest substrate temperature (300°C) also the other diffraction lines appeared, which is caused by more randomly oriented crystallites of the film. The other authors report the same changes with the temperature [4]. In this case the film losing its anisotropy. The 2θ values remain constant (~ 40.2°) for all substrate temperatures. The only exception was the films grown at 200°C where the 2θ shifted to approximately 40.3°. The up shift of the 2θ with increasing RF powers and temperatures is a result of the increase of Al³⁺ substituents (Al³⁺ that substitute for Zn²⁺ in the ZnO lattice) and a reduction of the interplanar distance, which changes the lattice distortion in ZnO:Al films from compressive to tensile lattice stresses. The RF power and temperature growth, result in the larger grains (growth from 60 to more than 200 nm) and better crystalline structure (no line asymmetry).

The surface images of ZnO:Al prepared with 800 W RF power and 200°C substrate temperature obtained by means of SEM (Figure 2) and AFM (Figure 3), show a nanostructured surface.

![Figure 2. SEM image of ZnO:Al prepared at 200°C and 800 W RF power](image)

![Figure 3. AFM image of ZnO:Al prepared at 200°C and 800 W RF power](image)

### 3.2. Electrical properties

The n-type conductivity of ZnO is more often ascribed to the native donor defects, zinc interstitial (Zn_i), oxygen vacancies (V_O), or hydrogen acting as an unintentional donor impurity. The high carrier concentrations of ZnO:Al compared to undoped ZnO results from the contribution of the Al³⁺ substituents in addition to the native donor defects [5].

![Figure 4. Dependence of resistivity, carrier concentration and mobility on (a) RF power (b) on substrate temperature](image)

As the RF power increases (Figure 4 (a)), the carrier concentration and the mobility rise and their highest values (2 x 10²⁰ cm⁻³, 7.81 cm²/Vs) are obtained for ZnO:Al grown at 1200 W RF power and RT. The slight drop in mobility for RF power range 400÷600 W is caused from the crystallinity worsening. The resistivity decreases with increasing RF power as a result of the improved crystallinity
and the enhanced Al\textsuperscript{3+} substituents into the films. The carrier concentration goes straightforwardly up (to $2.4 \times 10^{20} \text{ cm}^{-3}$) with increasing temperatures as well, as a result of the increased Al\textsuperscript{3+} substituents (Figure 4 (b)). The mobility drop with the temperature mounting to 300ºC reflects the degradation of the crystallinity, which is observed in the XRD patterns (Figure 1 (b)). The resistivity reduces as the temperature changes from RT to 200ºC and then slightly increases following the mobility drop.

### 3.3. Optical properties

The average transmittance of a glass substrate coated with ZnO:Al varies from 82–86 % with increasing RF power (Figure 5). The sharp absorption edge appears at $\sim 380 \text{ nm}$ wavelength. The enlargement of the sputter power results in the blue shift of the cut-off wavelength which is clearly noticeable for 1000 W and 1200 W RF powers. We determined $E_g$ ($\sim 3.3 \text{ eV}$) of the ZnO:Al by determining the absorption coefficient $\alpha$ from the measured transmittance and plotting $\alpha^2(h\nu)$ versus photon energy. The $E_g$ widen with increasing RF power and temperature due to the increased carrier concentration [5].

![Figure 5. Dependence of optical transmittance on RF power](image)

### 4. Conclusions

The (002) diffraction line has a maximum intensity and minimum FWHM (3.26º) for ZnO:Al deposited at 200ºC, indicating highly orientated crystalline structure. The 2$\Theta$ shifts up with increasing RF powers and temperatures as a result of the increase of Al\textsuperscript{3+} substituents and a reduction of the lattice parameter, which changes the lattice distortion in ZnO:Al films from compressive to tensile lattice stresses. The lowest resistivity ($2 \times 10^{-3} \Omega\text{cm}$) and the highest mobility (12 cm\textsuperscript{2}/Vs), carrier concentration ($2 \times 10^{20} \text{ cm}^{-3}$) and transmittance (> 82% including the substrate) are obtained in highly orientated ZnO:Al films prepared at high RF powers and temperatures, which demonstrates their correlation with structural properties. The blue shift and $E_g$ widening due to the increased carrier concentrations gives the relation between electrical and optical parameters.

### References

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