Structural, electrical and optical characteristics of Al-doped zinc oxide thin films deposited by reactive magnetron sputtering

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Abstract. ZnO:Al (AZO) thin films on glass were deposited by DC reactive magnetron sputtering at approximately 300°C substrate temperature. Structural, electrical and optical properties were investigated as a function of oxygen flow. XRD data shows that AZO thin films are polycrystalline with pronounced c-axis orientation and the grain size increasing with the oxygen flow. The lowest achieved resistivity within the deposited set of samples was $7.6 \cdot 10^{-4} \Omega \text{cm}$. The transmittance of AZO films was above 80% at 550 nm with the optical band gap between 3.4 and 3.8 eV.

1. Introduction
ZnO is a direct wide band gap (3.4 eV) semiconductor with large exciton binding energy (60 meV) and wurtzite-type hexagonal structure [1-3]. As-grown ZnO films are n-type conductors due to sub-stoichiometric composition and omnipresent hydrogen impurity which acts like a shallow donor [3]. Al-Doped ZnO films are a lower cost alternative to expensive In$_2$O$_3$:Sn (ITO), because of virtually unlimited availability of source material. ZnO thin films are characterized by high chemical and thermal stability, and non-toxicity [4]. The most often used ZnO based composition is Al doped ZnO (AZO). However, industrially perspective technologies of DC reactive magnetron sputtered Al-doped ZnO films have not yet reached the performance of ITO in terms of the combination of electrical conductivity and optical transmittance, as well as stability of the process [4]. Therefore, the deposition techniques must still be developed as well [5].

Physical vapour deposition techniques such as sputtering, pulsed laser deposition, evaporation etc. are commonly used for ZnO thin films deposition.

This paper reports on characterisation of structural, electrical and optical properties of AZO thin films deposited by reactive magnetron sputtering upon varied amount of oxygen in the sputtering atmosphere.

2. Experimental details
AZO thin films were deposited on glass substrates by reactive magnetron sputtering from a metallic (Zn=98%, Al=2%) target in an Ar+O$_2$ atmosphere. The substrates were washed in acetone before deposition. The chamber was pumped to base pressure below $1 \cdot 10^{-5}$ Torr by a turbo-molecular pump. During the deposition the substrate was kept at about 300°C temperature, the sputtering was conducted at 20 mTorr working pressure and constant 100 W sputtering power. The target to substrate separation was 5 cm. Argon gas flow was kept constant at 50 sccm, oxygen gas flow was varied to cover the range from partly to fully oxidized target. The flows of both gases were controlled by MKS mass flow controller. Deposition time was 20 minutes. The process was controlled by Plasma emission monitoring (PEM), carried out by a high resolution spectrometer (Ocean Optics “HR4000”) connected to the chamber view port through a fibre optic cable. A set of samples was deposited in the oxygen flow range between 2 and 4.5 sccm. The setpoint was approached from the metallic (low-oxygen) side.

Films thickness was determined by profilometer (CART “Veeco Dektak 150”). Thicknesses for different films were in the range from 400 to 500 nm, with the corresponding deposition rate between 20 and 25 nm/min. Resistivity, electron concentration and Hall mobility were measured by Hall effect.
using van der Pauw configuration (HMS5000). Structural analysis was carried out by X-ray diffraction, XRD (X’Pert Pro MPD). Films transmittance in the range from 200 to 1100 nm was determined by a double-beam spectrophotometer (Analytik Jena AG “Specord 210”). All measurements were performed at room temperature.

3. Results and discussion

3.1 AZO structural analysis

XRD data shows typical textured polycrystalline hexagonal ZnO structure (Fig. 1). The (002) peak has the highest intensity indicating that AZO films are strongly oriented with the c-axis perpendicular to the substrate surface. The diffraction angles are slightly shifted compared to the standard (002) angle of 34.34° [6] due to non-stoichiometry and aluminium doping. For the films deposited at lower oxygen content, low intensity (101) peaks are present as well. No phases of Zn, Al, Al₂O₃ or ZnAlO₄ were detected. At oxygen flows below 2 sccm, the films were X-ray amorphous or nanocrystalline and therefore not presented in the paper. Based on the FWHM values, the crystal size (Fig. 2) increases from 20 to 55 nm with the increased oxygen flow.

![Figure 1. XRD spectra for the films deposited with different oxygen content in the sputtering atmosphere.](image)

![Figure 2. Grain size dependence on the oxygen content in the sputtering atmosphere.](image)

3.2. Electrical properties

Hall effect of AZO films was investigated as a function of oxygen flow in the sputtering atmosphere. The films exhibit n-type conductivity. Within the studied range, the lowest resistivity of 7.6·10⁻⁴ Ωcm was obtained for the film deposited at 2.3 sccm oxygen flow (Fig.3a). For this film, the carrier concentration and Hall mobility are 4.6·10²⁰ 1/cm³ and 18.8 cm²/(Vs), respectively.

Material resistivity is determined by the charge carrier concentration and mobility. For the studied set of films, the carrier concentration was found to decrease with the oxygen flow (Fig.3b). A similar trend has been observed for films of pure ZnO [7], Indium – Zinc oxide [8], and ITO [2], suggesting that the number of carriers is related to the deviation from stoichiometry. Interstitial oxygen may be present in ZnO [9], which would act as an acceptor in the films deposited at high oxygen content.

Based on the increased grain size, a higher Hall mobility could be expected for the films deposited at higher oxygen content. However, a mobility decrease with the oxygen flow is seen in Figure 3c, indicating that the grain boundary scattering is not the only mechanism affecting the mobility. It may not be ruled out that interstitial oxygen may contribute to charge carrier scattering as well. Oxygen acting as a scattering centre has been suggested for the mobility decrease observed for films deposited at different pressure [10]. Further research is needed to confirm the reason for the mobility decrease.
3.3. Optical properties

For the studied set of films, the optical transmittance is approximately 85% at 550 nm. Transmittance curves shown in Fig. 4 are normalized with respect to the transmittance of bare glass substrate. Films deposited at lower oxygen content are less transparent in the NIR region, which can be caused by higher charge carrier concentration.

Figure 4. Transmittance of AZO films deposited at different oxygen flows: (a) 2.0 sccm, (b) 2.3 sccm, (c) 2.5 sccm.

Figure 5. Square of the AZO films absorption coefficient $\alpha$ as function of photon energy. Linear extrapolation of $\alpha^2$ shows that the optical gap depends on the oxygen flow.

The optical absorption coefficient was measured using transmittance data ($T$) and films thickness ($d$): $\alpha = \frac{1}{d} \ln \left( \frac{T_{air}}{T} \right)$. Fig. 5 shows $\alpha^2$ as a function of photon energy. The optical band gap can be obtained by extrapolating the linear part of the curve towards the $x$-axis. The optical band gap of the studied films was found to change from 3.4 to 3.8 eV depending on the oxygen flow.
Degenerate semiconductor absorption edge shift in the shorter wavelength direction with increasing electron concentration is known as Burstein-Moss effect. Since zinc oxide is heavily doped with aluminium, optical band gap increases as the lower conduction band states become occupied and unavailable for excitation.

4. Conclusions
AZO thin films were deposited by DC reactive magnetron sputtering technique with varied oxygen/argon content in the sputtering atmosphere. The lowest achieved resistivity was $7.6 \cdot 10^{-4} \ \Omega \cdot \text{cm}$ at approximately 85% optical transmittance and $E_g=3.78 \ \text{eV}$. Oxygen content in the sputtering atmosphere was found to significantly affect the films structure and thus the electrical and optical properties.

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