# Influence of sputtering deposition parameters on electrical and optical properties of aluminium-doped zinc oxide thin films for photovoltaic applications

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**Abstract.** Transparent Conductive Oxides (TCOs) characterized by high visible transmittance and low electrical resistivity play an important role in photovoltaic technology. Aluminum doped zinc oxide (AZO) is one of the TCOs that can find its application in thin film solar cells (CIGS or CdTe PV technology) as well as in other microelectronic applications. In this paper some optical and electrical properties of ZnO:Al thin films deposited by RF magnetron sputtering method have been investigated. AZO layers have been deposited on the soda lime glass substrates with use of variable technological parameters such as pressure in the deposition chamber, power applied and temperature during the process. The composition of AZO films has been investigated by EDS method. Thickness and refraction index of the deposited layers in dependence on certain technological parameters of sputtering process have been determined by spectroscopic ellipsometry. The measurements of transmittance and sheet resistance were also performed.

## 1 Introduction

Transparent Conductive Oxides (TCO) films play a significant role as an transparent electrode in the optoelectronic and photovoltaic devices, especially in thin films solar cells [1–6]. The most widely used TCO, both in research and industry, are Indium Tin Oxide (ITO) films, because they are characterized by a good electrical and optical properties. However, future availability and cost issues require to replace it by another TCO. The main goal of the studies on TCO structures is to obtain high transmittance of the material, above 80% over a large spectral range, with resistivity below $10^{-3}$ $\Omega \cdot cm$ and wide band gap [6, 7]. In order to improve the efficiency in some optoelectronic applications the optical transparency of TCO films should be extended to the ultraviolet and infrared spectral ranges. One of the TCO materials that is widely investigated in recent years is zinc-oxide ZnO, which is non-toxic,

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abundant and relatively cheap material. Modified ZnO material, for example aluminum doped zinc oxide (AZO, ZnO:Al) can be a substitute of ITO in the top electrode or can be a part of double layer back contact in the thin film solar cell. It is also of high importance to obtain ZnO structures doped with the third group element, such as B, Ga, In or Al, since it leads to improvement of electrical conductivity of the layer [8].

Apart from magnetron sputtering belonging to physical vapour deposition methods (PVD), variety of techniques used for ZnO:Al production can be distinguished: sol-gel deposition, spray coating, pulsed laser deposition (PLD) and aerosol-assisted MOCVD technique [9-14]. In order to achieve aluminum doped zinc oxide layers with good electro-optical properties on inflexible or flexible substrate [15], RF and DC magnetron deposition or co-sputtering deposition can be used [16–21]. Numerous of technological parameters have the influence on the quality of the obtained thin films such as: power applied to the cathode, the pressure in the chamber during deposition process, target-substrate distance, type and flow of the process gases, substrate temperature or even positioning of the substrate relative to the target.

In the present study ZnO:Al layers were obtained by RF magnetron sputtering method on clean soda lime glass substrates and their composition was determined by EDS (Energy Dispersive Spectroscopy) method. Ellipsometry measurements provided information on the thickness of the films produced under different conditions of the deposition process. Basing on these data the rate of growth was estimated and the influence of AZO thickness on index of refraction was studied. The refractive index (*n*) of semiconducting material like AZO is one of the optical constants that is essential in optoelectronic studies and applications. In design of thin film photovoltaic devices determination of *n* for an outer transparent electrode is of high importance since it influences the amount of light that propagates into the p-n junction and can be potentially utilized. Spectroscopic transmittance measurement confirmed very good transparency of ZnO:Al films. Resistivity of the obtained layers, also determined in this work, plays an important role especially if they are meant to be applied as an electrode in thin film devices.

## 2  Experimental

The transparent conductive Al doped ZnO films were deposited onto soda lime glass (SLG) substrate using RF (Radio Frequency) magnetron sputtering method. Alliance Concept AC450 magnetron sputtering system was used in the experiment in order to find optimum parameters of the sputtering process. The radio frequency (RF) power was applied to 4 inches in diameter and 6 mm thick ceramic target composed by 98 wt.% ZnO and 2 wt.% Al with purity of 99.99%, purchased from BIMO Tech. Before the process soda lime glass substrates were ultrasonically and chemically cleaned in detergent, isopropyl alcohol, ethanol, deionized water and then dried in a nitrogen gas. The clean substrate was immediately mounted in the magnetron deposition chamber. Substrates were placed under the target directly onto unheated work holder, which is presented in Fig. 1. The static mode of substrate holder was used. The target – substrate distance was equal to 90 mm. In this work AZO films were obtained at room temperature. The substrate holder temperature was kept at constant level during the deposition process due to water cooling system.
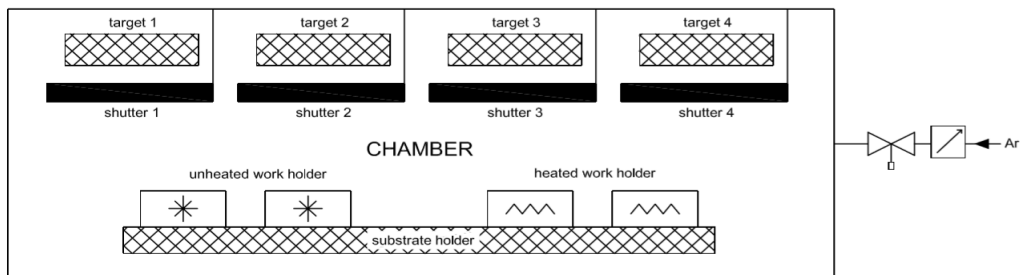
**Fig. 1.** The inside of the magnetron sputtering system chamber.

The magnetron chamber was evacuated to the base pressure of 1.0 x $10^{-2}$ Pa and then presputtering process was carried out to clean the target surface and remove encountered impurities. Stability improvement of sputtering conditions was also achieved at the beginning. The RF power during the films deposition process varied in the range of 120–200 W (1.5–2.5 W/cm²). The working pressure was stabilized at 1.57 Pa by flow of the pure Ar gas, which was set at 20 sccm. EDS detector was applied to achieve EDS profile and analyze energy spectra of the layers. Film thickness and refractive index were measured by spectroscopic ellipsometer Jobin-Yvon Horiba UVISEL model, working between 1.5 and 5 eV (around 830 to 250 nm wavelength) with use of new amorphous model. The sheet resistance of the obtained samples was measured at room temperature using RM3000+ four point probe equipment from Jandel Engineering Limited.

## 3 Results

Figure 2 shows the example of EDS diagram of the ZnO:Al deposited film. The qualitative analysis was made to obtain the mass and weight fractions of the elements existing in the prepared film. The composition of elements was as follows: Zn w.% – 68.06, O w.% – 29.65, Al w.% – 2.29. It should be noticed that all prepared samples revealed the similar composition and irregularities were not detected.
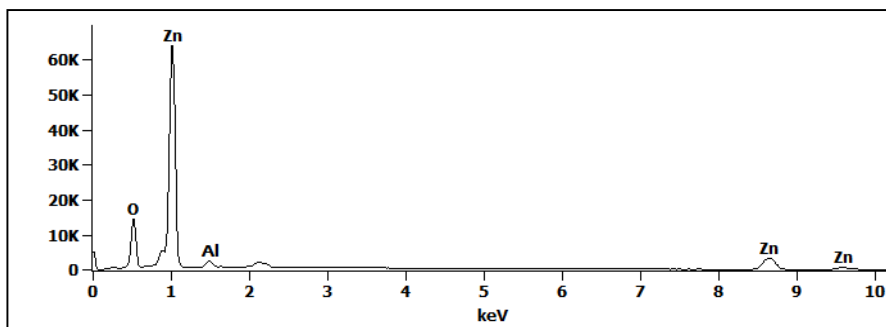


**Fig. 2.** EDS profile of the Al doped ZnO sample prepared using magnetron sputtering system.

Several series of samples were prepared at three different values of deposition power under the same working pressure at room temperature during different sputtering time. The influence of the sputtering time on the thickness of the AZO films is presented in Fig. 3 for three different deposition powers: 1.5 W/cm², 2 W/cm², 2.5 W/cm². Ellipsometry measurements provided the following thickness values obtained for 30, 40 and 45 min deposition time, respectively: 286 nm, 413 nm, 463 nm (power 1.5 W/ cm²), 322 nm,

539 nm, 622 nm (power 2 W/cm$^2$), 490 nm, 823 nm, 1178 nm (power 2.5 W/cm$^2$). The dependence shows that the thickness of the deposited films increases for higher power values and longer deposition time. The estimated growth rate values change from average 8.8 nm·min$^{-1}$ for the power of 1.5 W/cm$^2$, 11 nm·min$^{-1}$ for 2 W/cm$^2$ to 18 nm·min$^{-1}$ for 2.5 W/cm$^2$. One can note that linearity is better for high power value. The highest sputtering ratio equal to 19.7 nm·min$^{-1}$ was obtained for the longest deposition time.
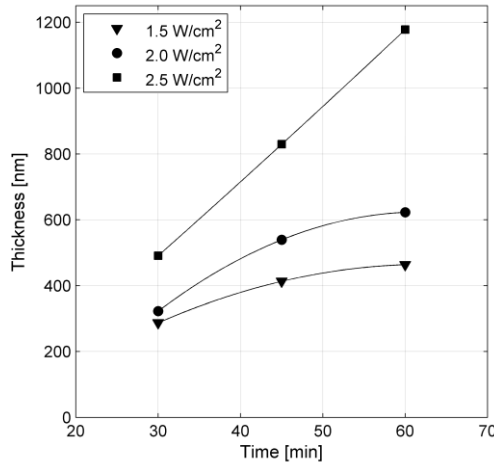


**Fig. 3.** The thickness of the obtained AZO films as the function of the deposition time for different magnetron power.
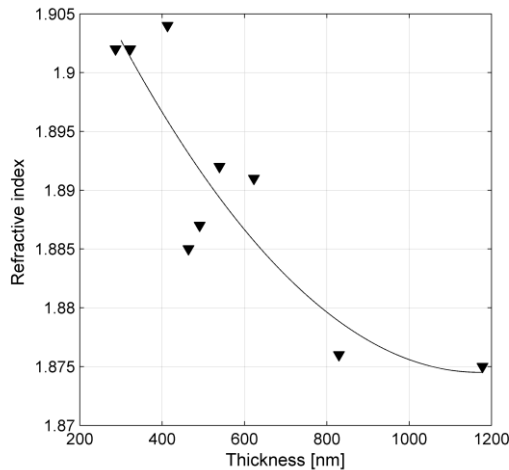


**Fig. 4.** The refractive index of ZnO:Al films as a function of the thickness, measured at λ = 633 nm.

The refractive index (*n*) was obtained from ellipsometry measurements for AZO films of different thickness. Index of refraction values are shown in Fig. 4 as a function of the thickness of the deposited layers at wavelength of 633 nm. The obtained *n* values decrease from 1.905 to 1.875 with increasing thickness of the films and are lower than those for ZnO i.e. 1.95–2.1 in visible range [22]. The observed relation corresponds to dependency reported in the literature [23]. Basing on the refractive index values transmittance and reflectance at normal incidence can be determined according to Fresnel formulas (Eq. 1, 2):

$$T = \frac{4n_1n_2}{(n_1+n_2)^{2,}},$$
(1)

$$R = \left(\frac{n_2 - n_1}{n_1 + n_2}\right)^2,$$
(2)

where $n_1 = 1$ in the air, $n_2$ – index of refraction of the layer. Taking into account $n_2 = 1.905$ or $n_2 = 1.875$ the transmittance is equal to 90.3% and 90.7% and reflectance values to 9.7% and 9.3% respectively. Experimentally obtained transmittance spectra presented in Fig. 5 reveal mean values above 90% both for the lowest and highest film thickness. Very good transmittance and homogeneity of the ZnO:Al films were also exhibited before [24].
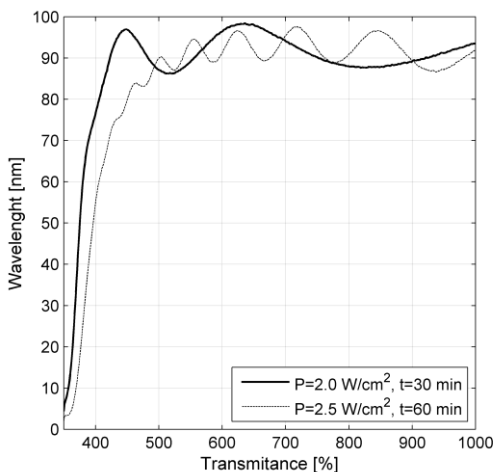


**Fig. 5.** Transmitance spectra of ZnO:Al layers of thickness 322 nm and 1178 nm (pure glass transmittance is subtracted).

Electrical properties of AZO films were also subject of our investigations. The correlation between sheet resistance and thickness of the deposited AZO layers is shown in Fig. 6. The sheet resistance decreases with increasing thickness of the layers. According to all obtained results these dependences are analogues for all RF powers used under the same pressure of the process. Here we considered the films obtained at the discharged power of 2.5 W/cm$^2$ since in this case we achieved the lowest range of the resistance value. As expected, the sheet resistance decreases very significantly as the thickness of AZO film increases from the 491 nm to 830 nm. Beyond this range of thickness the resistance drop is not so considerable with further AZO thickness increase. According to all obtained results these dependences are analogues for all RF powers used under the same pressure of the process. Taking into account prospect applications of ZnO:Al layers, the sheet resistance value is expected to lay below 50 $\Omega$/sq. The improvement of the results we obtained is probably possible by lowering the chamber pressure or heating of the samples.
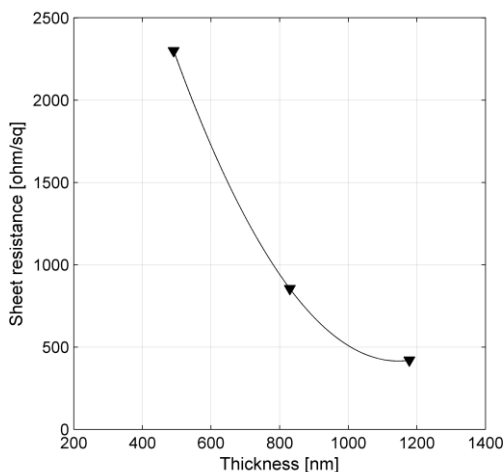
**Fig. 6.** Sheet resistance of ZnO:Al films as a function of the thickness.

## 4  Summary

ZnO layers doped with about 2.3 w.% Al were obtained in magnetron sputtering system and their properties were studied. The growth rate during deposition was estimated to be in the range of 8.8-18 nm/min depending on the magnetron power and time of the sputtering process. Refractive index of AZO films is directly related to deposited film thickness and changes from 1.905 to 1.875 for thicker layers. These values were used to calculate transmittance and reflectance according to Fresnel formula, which together with experimental data, allowed confirming good transparency of the layers. It has been also shown that higher power applied to the cathode material results in the lower resistivity of the thin film so the sheet resistance drops below 500 $\Omega$/sq for the power of 2.5 W/cm$^2$ used during deposition. Further conductivity improvements are necessary to make the produced AZO films useful in photovoltaic applications.

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