Tanzania Journal of Science 44(4): 12-20, 2018 ISSN 0856-1761, e-ISSN 2507-7961

Effects of Substrate Radial-Position Relative to the Sputter-Gun Axis on the Electrical, Optical and Structural Properties of ZnO Thin Films Deposited by Reactive Direct Current Magnetron Sputtering

John Paul Eneku[1], Tom Otiti[1], Julius Mwakondo Mwabora[2]and David Horwat[3]
[1]*Department of Physics, Makerere University, Kampala, Uganda*
[2]*Department of Physics, University of Nairobi, Nairobi, Kenya*
[3]*University of Lorraine, Jean Lamour Institute, UMR & 198, Nancy F-54011, France*
E-mail: johnpauleneku@gmail.com; jpeneku@cns.mak.ac.ug

Abstract

ZnO thin films were deposited using reactive direct current (dc) magnetron sputtering on glass substrates placed at seven variable radial positions (-1, 0, 1, 2, 3, 4 and 5 cm) relative to the sputter-gun (target) axis. A pure zinc target was used and sputtering carried out in argon and oxygen atmosphere with flow rates of 50 sccm and 6 sccm, respectively. XRD characterization showed that, all films crystallized homogeneously in the wurtzite phase with a strong (002) and a weak (004) orientations. Film crystallinity was very low at substrate positions located less than or equal to 1 cm from the target axis but rapidly improved as substrate position increased beyond 1 cm. Film thickness decreased steadily (from 320 to 160 nm) with increase in substrate position from 1 to 5 cm. Film resistivity was much higher (over $\sim 10^4$ Ω cm) at substrate positions located less than 2 cm from the target axis and rapidly decreased with increase in substrate position reaching the order $\sim 10^{-3}$ Ω cm at 3 cm and leveled out. Optical transmittance was homogeneous with 86% in the wavelength range 380 – 2500 nm. Band gap increased dramatically (from 3.15 eV to 3.28 eV) with increase in substrate position.

Keywords: Magnetron sputtering, substrate radial position, properties of ZnO thin films

Introduction

Zinc oxide thin-films have emerged as potential materials for the fabrication of transparent electrodes for solar cells (Li and Gao 2004, Minami 2005). The utilization of ZnO thin film in this application originates from its ability to conduct charge and at the same time transmit light (Calderon et al. 2005). ZnO is also relatively cheaper than other competing transparent and conducting oxide materials such as indium tin oxide (Li and Gao 2004, Furuta et al. 2007, Ohmukai et al. 2015).

Pure ZnO thin films with high transparency (above 80%) in the visible region and low electrical resistance (resistivity $\sim 10^{-4}$ to $\sim 10^{-2}$ Ω-cm) have been reported (Minami 2000, Calderon et al. 2005). These results are realized for thin films deposited on small area substrates. However, large substrates are often used in the industrial fabrication of solar cells (Calderon et al. 2005). Hardly any studies considered the issue of lateral heterogeneity of material properties of ZnO thin-films deposited on large area substrates, which is crucial for practical device production (Horwat et al. 2010). Therefore, it is imperative to study the lateral heterogeneity in the properties of ZnO thin-films deposited on large area substrates.

Magnetron sputtering is the commonly used advanced deposition technique for ZnO thin films and besides, it is suitable for scaling up to large area substrates (Zhang et al. 2009, Zendehnam et al. 2010, Baek et al. 2012). Direct current (dc) reactive sputtering from zinc (Zn) target was preferred because it is an excellent method for deposition from a metallic target (Ohmukai et al. 2016). This investigation focused on the effect of substrate radial-position relative to the sputter-gun (sputter target) axis on the structural, electrical and optical properties of ZnO thin films deposited by dc reactive magnetron sputtering.

Materials and Methods

ZnO thin films were deposited using 99.995% pure zinc metal target by reactive direct current magnetron sputtering method onto unheated glass substrates mounted on a rotating substrate holder to ensure a homogeneous deposition. The target–substrate distance was set to 5 cm and the target of diameter 5 cm was fixed on a magnetron placed eccentric to the rotation axis of the substrate holder at a horizontal distance of 8 cm in order to reach good lateral homogeneity of the chemical composition (Mickan et al. 2016). The substrates were placed at seven variable radial-positions relative to the sputter-gun (target) axis (-1, 0, 1, 2, 3, 4 and 5 cm) on the rotating substrate holder. A schematic representation of the chamber is shown in Figure 1. The glass substrates were cleaned with liquid soap, water and etched with radio frequency (RF) plasma for 2 minutes prior to deposition. The base pressure in the chamber was 4.5×10^{-5} mbars and a mixture of argon and oxygen was introduced into the chamber with flow rates of 50 sccm and 6 sccm, respectively. Deposition was performed with direct current power of 24 W and working pressure of 4×10^{-3} mbars for 60 minutes.

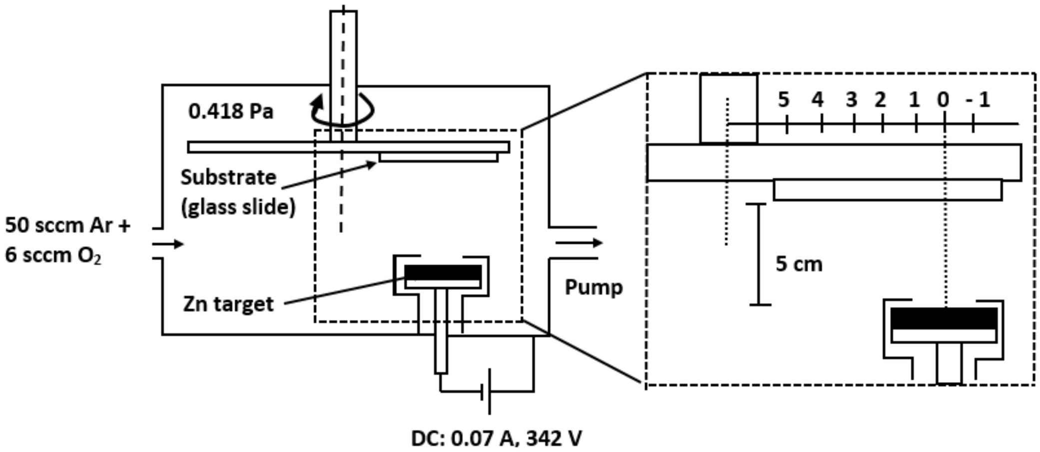

Figure 1: Experimental setup.

The structural properties were measured using θ/2θ x-ray diffraction (XRD) with an AXS Bruker Advance diffractometer with a Cu anode (Cu Kα = 0.154 nm). Electrical properties were measured using both a four-point probe and HMS 5000 Hall effect measurement setup in the van der Pauw geometry (Van der Pauw 1958). Transmittance measurements were performed using a Cary 5000 UV-Vis-NIR spectrophotometer in the ultraviolet, visible and near infrared ranges. The film thickness was measured using a Taylor Hobson Talysurf 10 surface profiler.

Results and Discussion

Structural properties

Figure 2 shows the XRD patterns of the ZnO thin films deposited at different substrate radial positions. All the films exhibited an intense peak centered at 34.39° – 34.50° and a less intense peak centered at 72.6°, corresponding to (002) and (004) planes of wurtzite cell of ZnO, respectively. Thus, the films had preferential growth along (002) crystallographic direction over (004) because the former has lower surface energy, making it easier to obtain (Kumar and Rao, 2011). 2θ values for the (002) peak deviated from the standard value of 34.45° for strain free-free bulk ZnO, indicating existence of stress between ZnO film and the glass substrate (Jeong et al. 2003, Lee et al. 2007, Ma et al. 2007, Kim et al. 2008). Generally, a significant shift in 2θ results from changes in the interplanar spacing that may arise from stress within the film (Zhang et al. 2009).

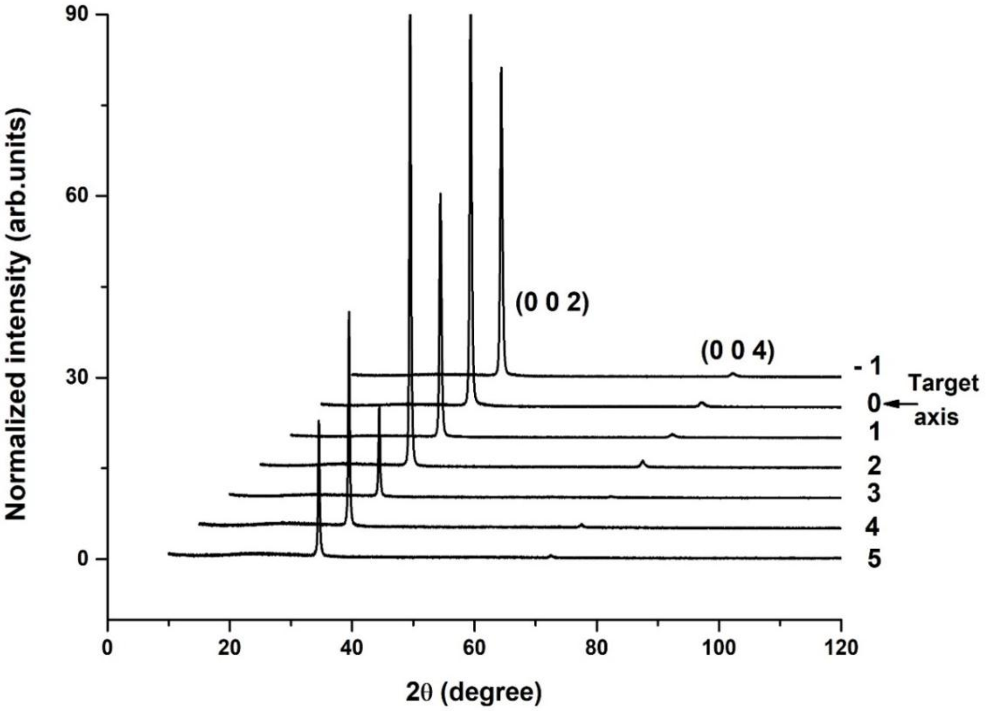

Figure 2: XRD patterns of ZnO thin films deposited at different substrate radial positions.

From the (002) peak of the films, average vertical grain size (D) was estimated using the Debye-Scherrer's equation: $D = 0.9\lambda/\beta cos\theta$ with β being the broadening of the diffraction line measured at its half maximum intensity in radians, λ is wavelength of the x-ray, θ is the Bragg angle and 0.9 is the shape factor of the average crystallite (Cullity and Stock 2001). Figure 3 shows the variation of estimated grain size with substrate radial position. Grain size is much smaller at substrate position located less than or equal to 1 cm from the target axis. However, it rapidly increased with further increase of substrate position beyond 1 cm, reaching a maximum at 3 cm before gradually decreasing. Thus, there was better crystallinity for films deposited at substrate positions greater than

1 cm. The low crystallinity closer to the target axis may be ascribed to bombardment of the film surface by excess oxygen ions accelerated by dc sputter voltage (Nomoto et al. 2011).

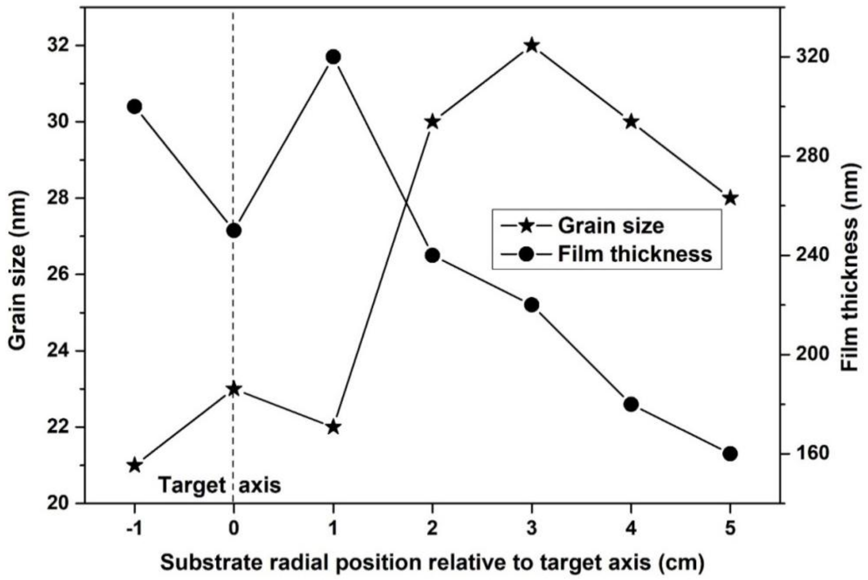

Figure 3: The variation of film thickness and estimated grain size of ZnO (002) diffraction peak at different substrate radial positions.

Figure 3 also shows film thickness variation with substrate radial position. Film thickness is maximum at1 cm distance from the target axis and decreased almost linearly with increase in substrate position relative to the 1 cm position. The occurrence of maximum film thickness at 1 cm may be attributed to its location right above the erosion track of the target which ensures it receives the highest deposition rate during film formation.

Electrical properties

Figure 4 shows the variation of resistivity (ρ), charge carrier concentration (n) and mobility (μ) with substrate radial position. Films obtained at substrate positions –1 and 0 cm had a much higher resistivity that it was not measurable by a four-point probe (over ~10^4 Ω cm). Consequently, it was impossible to measure charge carrier concentration and mobility by Hall Effect method. All effective measurements showed that the films had n-type conductivity due to the n-type background carrier concentrations unintentionally introduced during film formation. Resistivity ranged from a minimum of ~10^{-3} Ω cm at substrate positions at least 3 cm away from the target axis, to over ~10^4 Ω cm at substrate positions less than 2 cm from the axis. Generally, resistivity showed a rapid decrease with increase of substrate position and leveled out at 3 to 5 cm. Minimum resistivity of 1.14×10^{-3} Ω-cm was obtained at 4 cm. The decrease in resistivity with increase in substrate position is consistent with increase in carrier concentration as well as the increase in the product of carrier concentration and mobility ($n\mu$) as shown in Figure 4. Minimum resistivity is obtained at 4 cm because it has the highest $n\mu$ value, since resistivity is inversely proportional to $n\mu$. The increase of n and $n\mu$ with increase of substrate position may be due to increase of crystallinity of the films as shown in Figure 3 by the increase in grain size.

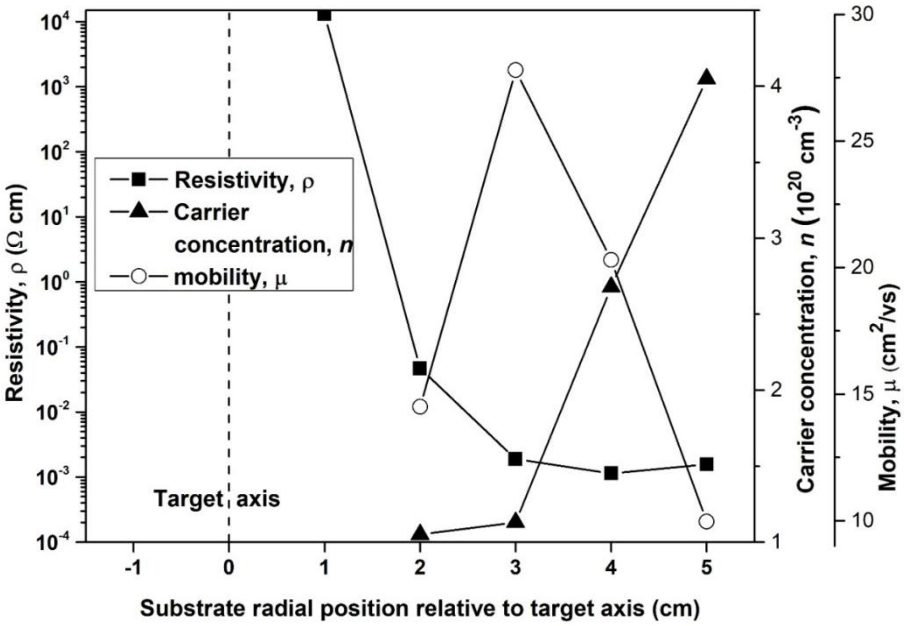

Figure 4: The variation of resistivity, carrier concentration and mobility of ZnO thin films with substrate radial position.

Optical Properties

Figure 5 shows the variation of optical transmittance as a function of substrate radial position. All the films have uniform average transmittance of 86% in the wavelength range 380 – 2500 nm. The high transmittance may be associated with good structural homogeneity of the films.

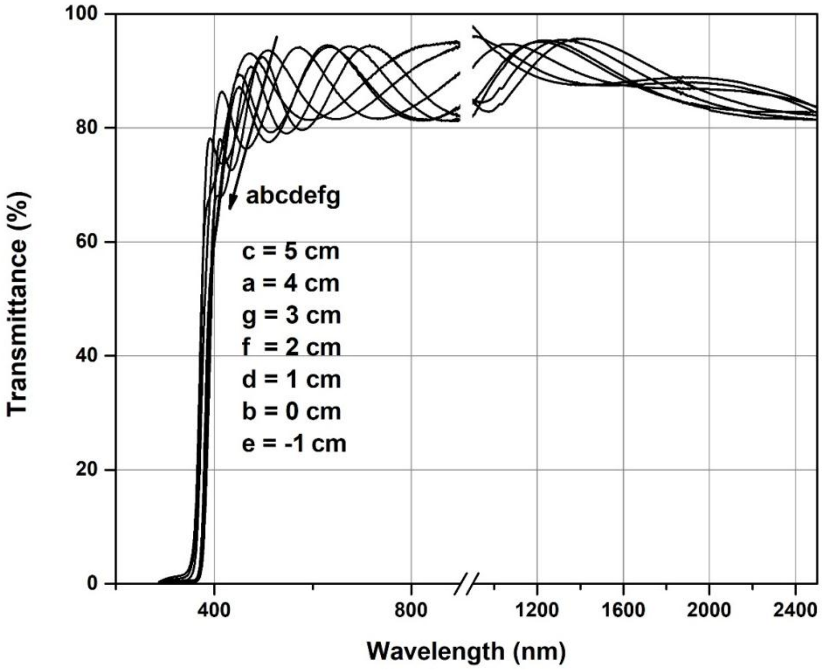

Figure 5: Optical transmittance spectra of ZnO films as a function of substrate radial position.

The optical band gap (E_g) of the ZnO films was determined from the dependence of absorption coefficient values (α on the photon energy (*hv*), using the Tauc's equation (Lin et al. 2007):

$$(\alpha h v)^2 = A(hv - E_g)$$

where A is a constant dependent on the electron-hole mobility. The optical band gap was estimated from the Tauc's plot of $(\alpha h v)^2$ versus hv shown in Figure 6a and the values obtained are shown in Figure 6b. The band gap increased steadily with increase of substrate position away from the target axis (from 3.15 eV to 3.28 eV). The band gap values are lower than the standard value of 3.37 eV for bulk ZnO at room temperature but are consistent with previously reported data on ZnO films (Gumus et al. 2006, Wang et al. 2009). The increase of band gap is consistent with increase of carrier concentration shown in Figure 4. This behaviour is in conformity with Burstein-Moss shift, which considers that a shift to higher energies of band gap is due to increase in carrier concentration (Nunes et al. 2002).

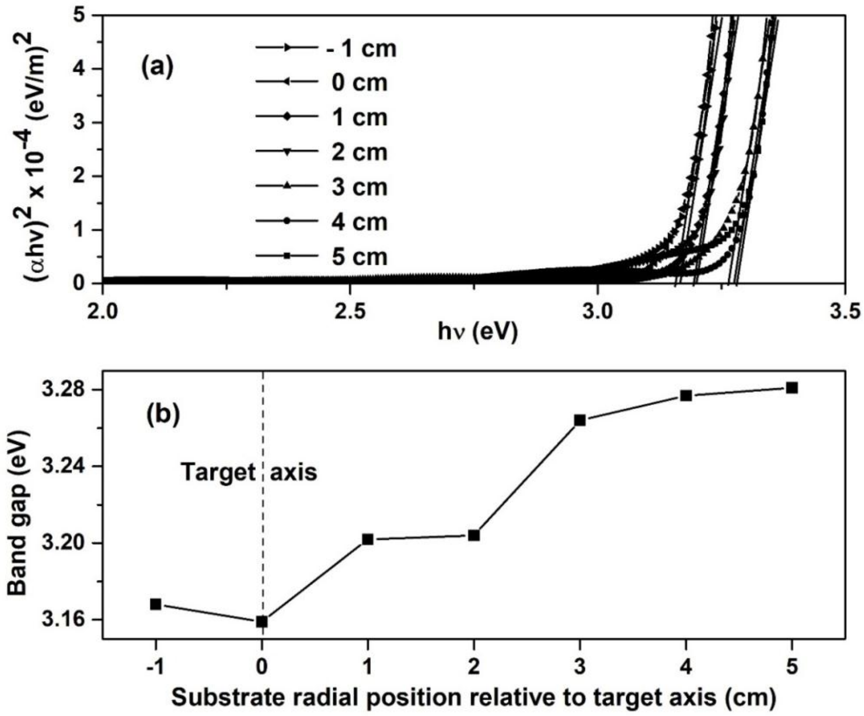

Figure 6: (a) Tauc's plot of $(\alpha h\nu)^2$ versus $h\nu$ (b) Optical band gap of ZnO thin films as a function of substrate radial position.

Conclusion

The effects of the substrate radial positions on the properties of ZnO films deposited by reactive dc magnetron sputtering have been investigated. The results clearly demonstrate that the structural and electrical properties of the ZnO thin films are closely related to the substrate radial positions while the optical transmittance is not. XRD characterization showed that all the films crystallized homogeneously in the wurtzite phase of ZnO with strong (002) and weak (004) orientations. Increasing substrate position beyond 1 cm from the target axis improved crystalline quality evidently and lowered film thickness. Film resistivity decreased rapidly, from over ~10^4 Ω cm at the target axis to ~10^{-3} Ω cm at 3 cm and leveled out. Optical transmittance was homogeneous with 86% in the wavelength range 380–2500 nm but the band gap increased dramatically with increase in substrate position (from 3.15 eV to 3.28 eV). To deposit ZnO thin films with homogeneity of both high transparency (86%) and low resistivity (1×10^{-3} Ω cm), it is essential to consider substrate positions 3 to 5 cm from the target axis.

Acknowledgements

The authors thank the Institute of Jean Lamour, University of Lorraine (France) for hosting the research experiments. This work was sponsored by the International Science Programme (ISP), Uppsala University, Sweden.

References

Baek CS, Kim DH, Kim HH and Lim KJ 2012 Effect of thickness on properties of ZnO film prepared by direct current reactive magnetron sputtering method. *J. Ceram. Proc. Res.* 13: S403-S406.

Calderon C, Gordillo G and Olarte J 2005 Study of electrical transport properties of ZnO films used as front contact of solar cells. *Phys. Stat. Sol.* 242: 1915-1919.

Cullity BD and Stock SR 2001 Elements of X-ray Diffraction. 3rd Ed., Prentice-Hall, New York.

Ellmer K 2001 Resistivity of polycrystalline zinc oxide films: current status and physical limit. *J. Phys. D: Appl. Phys.* 34: 3097-3108.

Furuta M, Hiramatsu T, Matsuda T, Furuta H and Hirao T 2007 Effect of energetic particle bombardment on microstructure of zinc oxide films deposited by RF magnetron sputtering. *Japan. J. Appl. Phys.* 46: 4038-4041.

Gumus C, Ozkendir OM, Havak H and Ufuktepe 2006 Structural and optical properties of zinc oxide thin films prepared by spray pyrolysis method. *J. Optoelectron. Adv. Mater*. 8: 299-303.

Horwat D, Jullien M, Capon F, Pierson J-F, Andersson J and Endrino JL 2010 On the deactivation of the dopant and electronic structure in reactively sputtered transparent Al-doped ZnO thin films. *J. Phys. D: Appl. Phys.* 43: 132003.

Jeong SH, Lee JW, Lee SB and Boo JH 2003 Deposition of aluminium-doped zinc oxide films by RF magnetron sputtering and study of their structural, electrical and optical properties. *Thin Solid Films* 435: 78-82.

Kim DH, Jeon H, Kim G, Hwangboe S, Verma VP, Choi W and M. Jeon 2008 *Optics Communicat*. 281: 2120-2125.

Kumar BR and Rao TS 2011 Effect of substrate temperature on structural and optical properties of zinc aluminium oxide thin film prepared by dc reactive magnetron sputtering technique. *J. Ovon. Res.* 7: 115-123.

Lee YC, Hu SY, Water W, Huang YS, Yang MD, Shen JL, Tiong KK and Huang CC 2007 Improved optical and structural properties of ZnO thin films by rapid thermal annealing. *Solid State Communicat*. 143: 250-254.

Li Z and Gao W 2004 ZnO thin films with DC and RF reactive sputtering. *Mater. Lett.* 58: 1363-1370.

Lin W, Ma R, Shao W and Liu B 2007 Structural, electrical and optical properties of Gd doped and undoped ZnO:Al (ZAO) thin films prepared by RF magnetron sputtering. *Appl. Surf. Sci*. 253: 5179-5183.

Ma QB, Ye ZZ, He HP, Hu SH, Wang JR, Zhu LP, Zhang YZ and Zhao BH 2007 Structural, electrical and optical properties of transparent conductive ZnO:Ga films prepared by DC reactive magnetron sputtering. *J. Cryst. Growth* 304: 64-68.

Mickan M, Helmerson U, Rinnert H, Ghanbaja J, Muller D and Horwat D 2016 Room temperature deposition of homogeneous, highly transparent and conductive Al-doped ZnO films by reactive high power impulse magnetron sputtering. *Solar Energy Mater. Solar Cel.* 157: 742-749.

Minami T 2005 Transparent conducting oxide semiconductors for transparent electrodes. *Semiconduct. Sci. Technol*. 20: S35-S44.

Minami T 2000 New n-type transparent conducting oxides. *MRS Bull.* 8: 38-44.

Nomoto J, Miyata T and Minami T 2011 Optical and electrical properties of transparent conducting B-doped ZnO thin films prepared by various deposition methods. *J. Vac. Sci. Technol. A: Vac. Surf. Films* 29: 041504.

Nunes P, Fortunato E, Tonello P, BrazFernandes F, Vilarinho P and Martins R 2002 Effects of different elements on the properties of ZnO thin films. *Vacuum* 64: 281-285.

Ohmukai M, Nakagawa T and Matsumoto A 2015 Oxygen surplus to Zn in ZnO films deposited by means of direct current sputtering. *J. Nanoelectron. Optoelectron.* 10: 65-68.

Ohmukai M, Nakagawa T and Matsumoto A 2016 ZnO films deposited on glass by means of dc sputtering. *J. Mater. Sci. Chem. Engin.* 4: 1-7.

Van der Pauw LJ 1958 A method of measuring specific resistivity and Hall Effect of discs of arbitrary shape. *Philips Res. Rep.* 13: 1-9.

Wang S, Li X and Zhang J 2009 Effect of substrate temperature on the properties of Heavy Ga-doped ZnO transparent conductive film by RF magnetron sputtering. *J. Phys.: Conf. Ser*. 188: 012017.

Zendehnam A, Shirazi M, Doulatshah S and Sadat M 2010 Effect of temperature and period of post-annealing on the optical properties of ZnO thin films. *Armen. J. Phys.* 3(4): 305-311.

Zhang D, Fan P, Cai X, Huang J, Ru L, Zheng Z, Liang G and Huang Y 2009 Properties of ZnO thin films deposited by DC reactive magnetron sputtering under different plasma power. *Appl. Phys. A.* 97: 437-441.