https://doi.org/10.48048/tis.2023.6372

Effect of Thickness on Electrical and Optical Properties of ZnO:Al Films

Thawatchai Chanthong[1], Weerawat Intaratat[1,*] and Thanate Na Wichean[2]

[1]Department of Physics, Faculty of Science and Technology, Phuket Rajabhat University, Phuket 83000, Thailand
[2]Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

([*]Corresponding author's e-mail: weerawat.i@pkru.ac.th)

Received: 19 November 2022, Revised: 23 December 2022, Accepted: 10 January 2023, Published: 18 January 2023

Abstract

Zinc oxide (ZnO:Al) films were prepared on a substrate of different thicknesses by sputtering at 1×10^{-2} mbar argon gas pressure and 200 W power. The effect of film thickness on the structural, electrical, and optical properties was investigated by X-ray diffraction (XRD), 4-point probe technique, and ultraviolet-visible spectroscopy. The XRD film crystal structure study revealed that all sample films at thicknesses of 66, 106, 150 and 193 nm, respectively, exhibited planar Hexagonal wurtzite crystal structure (002), and ZnO crystals were grown along the c-axis. The ZnO:Al film at a thickness of 66 nm had the highest strain and the smallest crystal size compared to other films. The electrical resistivity decreases with increasing film thickness. The sample at 193 nm has the lowest resistivity (1.37 Ω.m). The results showed that light transmission revealed that all sample films had high transparency in the white and near-UV region at a wavelength of 350 to 800 nm, with an average light transmittance shift of 85 - 95 %. The energy band gap increased with the film thickness of 3.49(66 nm), 3.55(106 nm), and 3.59(150 nm) eV, and decreased to 3.57 eV at 193 nm, respectively.

Keywords: ZnO films, Electrical resistivity, Optical properties

Introduction

Over the years, materials science technology has synthesized many new materials and has widespread applications. Among metal oxide nanomaterials, zinc oxide (ZnO) compounds have received great attention. Due to the vastly different electronic, optical, mechanical, magnetic, and chemical properties. Similar particle zinc oxide compounds have many advantages, such as non-interactive structural defects and high light transmittance. It has a high refractive index in the white light range, a wide power band gap at room temperature (3.37 eV) [1-3], and high binding energy (60 meV) [3-5]. It also has high electrical conductivity, high piezoelectric interaction coefficient, and is chemically and thermally stable [6]. Nowadays, nanotechnology is applied in various fields of science. Nanostructured materials and devices use different techniques because zinc oxide has unique physical and chemical properties as a versatile material, zinc oxide nanostructured materials have gained wide attention. It has found application in various devices such as sensor systems, light-emitting diodes, and other devices, nanogenerator, solar cells, transistors, piezoelectrics, transducers, etc [7,8].

Many different methods can be used to create zinc oxide into a nanoscale structure, including chemical vapor deposition (CVD) [3], metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD) [9], molecular beam epitaxy (MBE), reaction e-beam evaporation, DC magnetron sputtering [10], RF magnetron sputtering [11], sol-gel [6,12,13], successive ionic layer absorption and reaction (SIALR) [14], etc. Because of its scalability, effectiveness, and film uniformity, sputtering is one of the most popular methods for preparing thin films.

This research was to study the substrate material prepared zinc oxide film by RF sputtering technique and the effect of zinc oxide thickness changes on electrical and optical properties.

Materials and methods

Preparation of zinc oxide film

Zinc oxide film was prepared by RF sputtering technique using a high purity zinc oxide (ZnO:Al) target with a diameter of 7.6 cm. The glass slides were a kind of substrate measuring 2.52×7.6 cm^2. The glass substrate was cleaned in acetone and rinsed with deionized water using an ultrasonic bath for 10 min and dried in a hot air oven. Place the glass substrate in a vacuum chamber with a target-to-substrate distance of 3.8 cm. A rotary pump, coupled with a turbo pump was used to achieve 4×10^{-5} mbar pressure before introducing high-purity argon gas (99.99 %) 1×10^{-2} mbar pressure. The surface of the glass substrate was cleaned before the zinc oxide film coating process. The glass substrate was again fired by ion beams of argon gas in the sputtering process for 2 min. After that, a zinc oxide film was coated with different thicknesses, and controlled by film coating time in the range of 25 - 55 min at a constant power of 200 watts.

Properties analysis of zinc oxide film

The zinc oxide film thickness and surface were investigated using a scanning electron microscope (SEM) (APREO, FEI, USA) was used to analyze the nanostructures of the films at an accelerating voltage of 20 kV. The X-ray diffractometer (XRD) (Philips X'pert Pro MPD) was used to study structural properties with Cu $k\alpha_1$radiation (λ = 0.154065 nm) (40 kV, 35 mA) in the region from an angle of $30° < 2\theta < 80°$. The 4 - point Van der Pauw technique was used to study electrical properties. The optical transmission spectra of films were recorded by a UV-VIS spectrophotometer between wavelengths 300 - 900 nm. The band gap energy was calculated by inference from the graph between $(\alpha h\nu)^2$ and $(h\nu)$.

Results and discussion

Surface properties of the zinc oxide film

Figure 1(a) shows the average zinc oxide film thickness using SEM technique at 45 min with the different thickness of 150.6, 148.1 and 150.6 nm. Using the difference thickness at difference coating time as show in **Figure 1(b)** the number of atoms was removed from the target depending on the sputtering time.

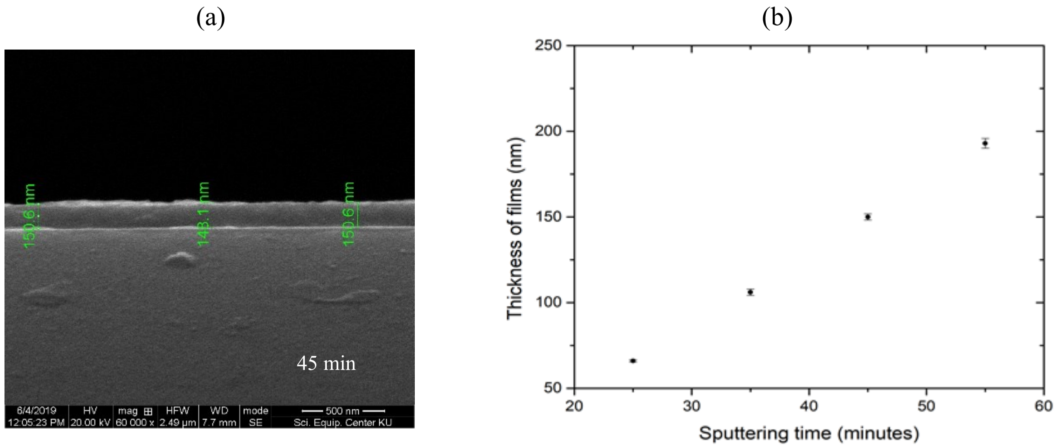
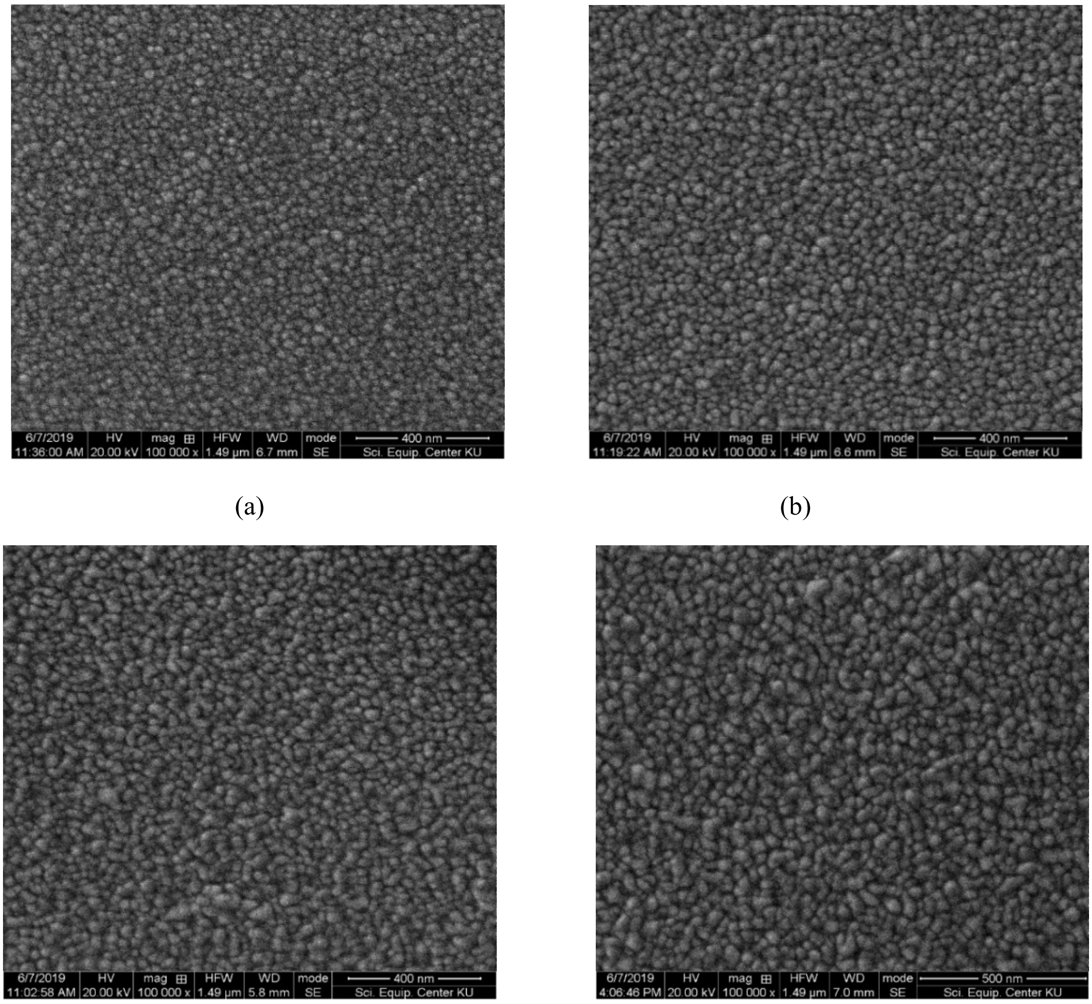


Figure 1 (a) The example of average measuring film thickness at 45 min, (b) zinc oxide film thickness at different coating times with SEM technique.

The sputtering time at 25, 35, 45 and 55 min. The average thickness films are 66, 106, 150 and 193 nm respectively. The surface analysis of ZnO:Al films using SEM technique revealed the film's thickness depends on grain size. The average size of grain measured from images by ImageJ program in **Figure 2** about 23.55, 31.58, 39.74 and 54.69 nm respectively. The increasing concentration of zinc oxide causes complete crystallization of the compound and enlarges the grain size. The 66 nm thickness in Figure 2 (a) indicates that the smallest grains, those with comparable sizes, and those with the lowest densities between grains are regularly distributed. In the 106 nm film thickness illustrated in **Figure 2(b)**, the grain distribution was regular, slightly larger, and there were further obvious gaps between the grains. While the various sizes of grain in **Figures 2(c)** - **2(d)** at thicknesses of 150 and 193 nm, respectively. Particularly, the broad variety of grain sizes and creation of columns in the 193 nm thickness. The results show that the film thickness of Zinc oxide affects the structure and surface characteristics of zinc oxide films. Due to the initial coating process, initially formed by a small grain zinc oxide structure, and the thickness and regularly distributed of zinc oxide increases then the grain size becomes larger.



(a) (b)

(c) (d)

Figure 2 The results of surface analysis of ZnO:Al film by SEM technique at different thicknesses (a) 66 nm, (b) 106 nm, (c) 150 nm, and (d) 193 nm.

Structural properties of zinc oxide films

The structural analysis results of ZnO:Al films with different thicknesses (66 - 215 nm) using the XRD technique are shown in **Figure 3**. All ZnO:Al films exhibited the same diffraction pattern and the highest diffraction angle at 2Θ (≈34.4 degrees) [15]. The crystallinity increases with increasing the film thickness by observing the X-ray diffraction turn intensity at an angle of 34.4 degrees. All ZnO:Al films have a hexagonal crystalline phase structure called the plane of wurtzite (002) [7]. The XRD spectra were not found in the other phase diffraction pattern when compared to the other planes showing the apparent monocrystalline characteristic of zinc oxide. Zinc oxide was high along the c-axis and indicating that the crystalline quality of the ZnO:Al film could be improved with film thickness.

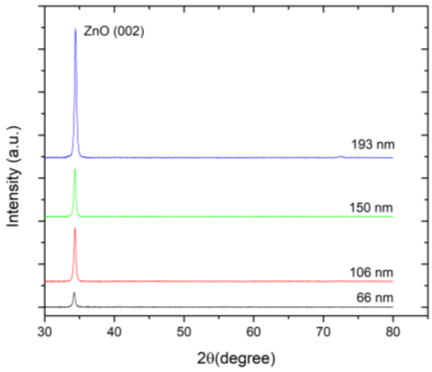


Figure 3 The XRD results of ZnO:Al film with different thicknesses.

The crystal size of the ZnO:Al film was calculated from the XRD spectra using the Scherrer formula [14,16,17].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ was the wavelengths of Cu $k\alpha_1$ (0.15406 nm), θ was the Bragg diffraction angle, and β was half peak amplitude (FWHM) of ZnO:Al in the plane (002). The internal strain film was calculated using the formula [16,18,19].

$$\varepsilon = \frac{\beta cos\theta}{4} \quad (2)$$

As a result, the crystal size and strain of the ZnO:Al film are shown in **Table 1**. The film thickness and crystal size increased when the peak FWHM value (002) decreased. However, if the thickness was more than 150 nm, the FWHM value was increased, causing the crystal size to decrease. The increasing proportion of the thickness and grain size from 66 - 150 nm slightly decreases when reaching the thickness at 193 nm. The ZnO:Al thin films crystal (66 nm) was growth incomplete because the atoms were randomly distributed, and then the nanocrystalline atomic layers disorganized the homogeneous film. As the film thickness increases, the crystal growth between atoms is close to each other, and fast-growing crystals grow above the nucleus. However, the thickness of ZnO:Al film was 193 nm, and the crystal size decreased because it was the arrangement for height along the c-axis and led to vertical growth consistent with the XRD effect. Furthermore, the crystalline mechanism was growth between nanocrystals, and nanocrystals ended when arranged to form the same crystalline [17]. In addition, it was also found the c-axis strain of the ZnO:Al film was dependent on the ZnO:Al thickness. All ZnO:Al films were low strain values because of high homogeneity and film quality results from the preparation condition. Therefore, the preparation condition was important in this research due to reducing the ZnO:Al film strain and improving the film's crystallinity.

On the other hand, the strain decreases with film thickness (66 - 150 nm), and the strain value increases in ZnO:Al film (193 nm). Increasing strain in the thinner film has related to accumulating and growth occurring randomly on the substrate. The structure could provide a lot of strain if the direction of growth differs from the vertical direction; then, the stranger ZnO:Al film in the c-direction reduces the strain.

Table 1 The film thickness, FWHM, grain size, and lattice parameters of the ZnO:Al film calculated from the spectra of XRD.

Film thickness (nm)	2θ (∘)	FWHM (∘)	Micro strain (βcos θ/4)	Crystallites size (nm)	Lattice parameters	
					a (nm)	c (nm)
66	34.22944	0.38418	0.001602	21.64	0.3021	0.5233
106	34.33567	0.36263	0.001512	22.93	0.3012	0.5217
150	34.32919	0.33743	0.001407	24.64	0.3013	0.5218
193	34.43000	0.36385	0.001517	22.86	0.3004	0.5203

Electrical properties of the zinc oxide film

The electrical properties of ZnO:Al films were studied by the 4 - point Van der Pauw technique, and the electrical resistivity (ρ) of the ZnO:Al films could be calculated using the formula (3) [15,20].

$$\rho = 2\pi s\left(\frac{V}{I}\right) \tag{3}$$

where s is the distance between probes (meters), V is the electric potential difference between the 2 inner probes (volts), and I is the current flowing through the 2 outer probes (amperes).

Figure 4 shows the properties of ZnO:Al film was determined by analyzing the effect of film thickness on the electrical resistivity of ZnO:Al films. The change in resistivity of ZnO:Al film depends on the film thickness. It was found that the film thickness increased when the resistivity of the sample decreased. The thickness ZnO:Al film at 66 nm had the highest resistivity (24.3 Ω.m). At 193 nm had the lowest electrical resistivity (1.37 Ω.m). Also, the thickness range of 66 to 106 nm has the resistivity decreases rapidly, after which it gradually decreases. According to carrier movement (electron) reception that is impacted by crystallization and nanostructure, the electrical resistance reduces as coated thickness increases. As a result, better crystallization causes carrier movement to rise with increasing thickness and grain size and electrical resistance to decrease [12].

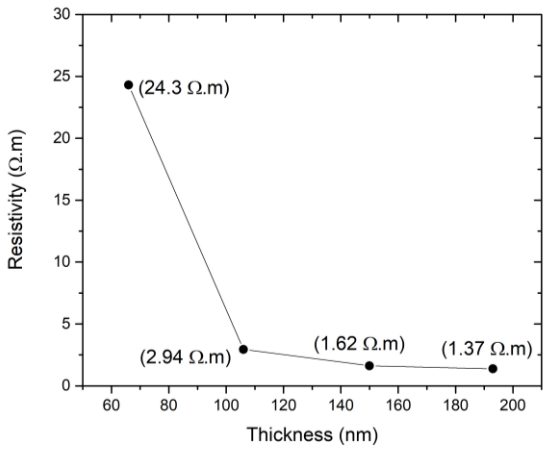


Figure 4 The relationship between the electrical resistivity of ZnO:Al films at different thicknesses.

Optical properties of the zinc oxide film

The analysis of light transmission through ZnO:Al films of various thicknesses at room temperature is shown in **Figure 5** using UV-vis spectroscopy. It was found that all samples of ZnO:Al films had high transparency in the visible light region and near UV at a wavelength of 350 to 800 nm. In this research, the average light transmittance of all ZnO:Al films was changed from 85 - 95 % in the wavelength range of 350 to 800 nm, clearly indicating that the ZnO:Al films used as oxides transparent in solar cells.

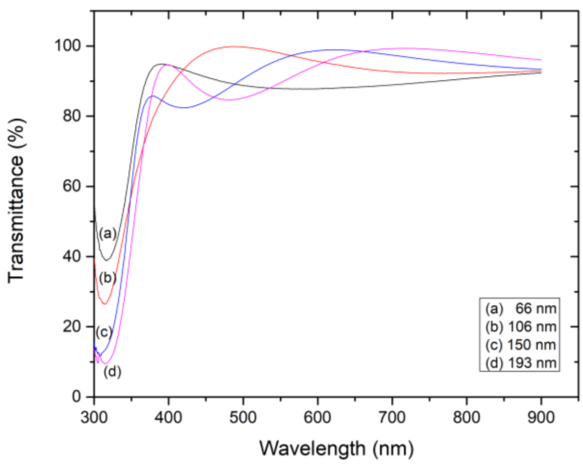


Figure 5 Light transmittance spectra of ZnO:Al thin films at different thicknesses.

The graph represents the light transmittance as a function of the wavelength, can represent the change of $(\alpha h v)^2$ with (hv), and the energy band gap calculated from the equation [16,17,21].

$$(\alpha h v)^2 = A(hv - E_g) = f(hv) \quad (4)$$

where A is the constant, hv is the energy of the incident photon, α is the absorbance coefficient, and E_g is the energy band gap.

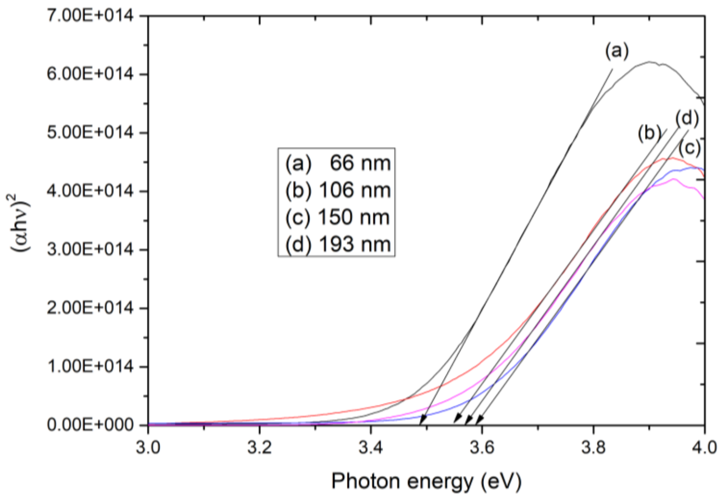


Figure 6 The relationship between $(\alpha h v)^2$ and the energy of the incident photon (h) on the ZnO:Al film at different thicknesses.

The energy band gap of the ZnO:Al films at different thicknesses is shown in **Figure 6**. When the linear part is separated and crosses the energy axis (hv) and $(\alpha h v)^2 = 0$ to form an empty gap energy bar (E_g) as shown in **Table 2**.

Table 2 The thickness, resistivity, and Energy band gap values.

Thickness (nm)	Resistivity (Ω.m)	Energy band gap (eV)
66	24.3	3.49
106	2.94	3.55
150	1.62	3.59
193	1.37	3.57

The energy band gap value for ZnO:Al film is shown in **Table 2** that the ZnO:Al film thickness increases from 66 to 150 nm, then the value of the energy band gap (E_g) slightly increased accordingly and decreased as the ZnO:Al film thickness increased to 193 nm. We investigated that when the thicknesses varied, the energy band gap grew larger [8]. Burstein-Moss shift describes the different thicknesses related to the properties of electronic film, which could be used to explain how the energy band gap for ZnO:Al films changed with thickness [22,23]. As a result, the state of valence band carrier concentration, n_e, is lower in a thin ZnO:Al film than in a thick one, where n_e becomes stable and E_g becomes stable.

Conclusions

In this research, the preparation of ZnO:Al films at different thicknesses studied the film structural, electrical, and optical properties. As a result, the XRD crystal structure showed an in-plane Hexagonal wurtzite crystal structure (002), with ZnO:Al crystals growing along the c-axis. Furthermore, 66 nm has the highest strain and the smallest crystal size compared with other thicknesses films. The resistivity of film decreased with the film thickness. The ZnO:Al film at a thickness of 193 nm had a minimum resistivity of 1.37 Ω.m. Studying the light transmittance properties emphasizes all samples of ZnO:Al films had high transparency in the white. The near-UV region at wavelengths 350 to 800 nm has the light transmittance average changed from 85 - 95 %. This ZnO:Al film used as a transparent oxide in solar cells, and the film energy band gap increased markedly as the thickness increased from 66 to 150 nm and decreased when the film thickness was 193 nm. Future research should concentrate on applications that make advantage of ZnO:Al film properties that might be applied in nanoscale semiconductor materials.

Acknowledgements

The author appreciates the support from Phuket Rajabhat University, Thailand (Grant number PKRU10/2562). Furthermore, we gratefully the Department of Physics, Faculty of Science and the Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Thailand for facilitating access.

References

[1] V Parihar, M Raja and R Paulose. A brief review of structural, electrical and electrochemical properties of zinc oxide nanoparticles. *Rev. Adv. Mater. Sci.* 2018; **53**, 119-30.
[2] A Moezzi, AM McDonagh and MB Cortie. Zinc oxide particles: Synthesis, properties and applications. *Chem. Eng. J.* 2012; **185-186**, 1-22.
[3] A Alarabi, Z Zeng, Y Gao, S Gao, S Jiao, D Wang and J Wang. Influence of different substrates on ZnO nanorod arrays properties. *Solid State Sci.* 2018; **85**, 21-5.
[4] A Deachana, PK Chu and D Boonyawan. ZnO nanorod synthesis via controlled ZnO seed layer by filtered pulse cathodic vacuum arc: Luminescence enhancement. *Adv. Mater. Res.* 2013; **802**, 1-6.
[5] BA Farsi, TM Souier, FA Marzouqi, MA Maashani, M Bououdina, HM Widatallah and MA Abri. Structural and optical properties of visible active photocatalytic Al doped ZnO nanostructured thin films prepared by dip coating. *Opt. Mater.* 2021; **113**, 110868.
[6] NH Erdogan, T Sedefoglu and H Kavak. Effect of Na doping on microstructures, optical and electrical properties of ZnO thin films grown by sol-gel method. *J. Alloys Compounds* 2021; **881**, 160554.
[7] Y Ammaih, A Lfakir, B Hartiti, A Ridah, P Thevenin and M Siadat. Structural, optical and electrical properties of ZnO:Al thin films for optoelectronic applications. *Opt. Quantum Electr.* 2014; **46**, 229-34.
[8] AH Hammad, MS Abdel-Wahab, S Vattamkandathil and AR Ansari. Structural and optical properties of ZnO thin films prepared by RF sputtering at different thicknesses. *Phys. B Cond. Matter* 2018; **540**, 1-8.
[9] LP Dai, H Deng, EY Mao and JD Zang. The recent advances of research on p-type ZnO thin film. *J. Mater. Sci. Mater. Electr*. 2008; **19**, 727-34.
[10] G Malik, S Mourya, J Jaiswal and R Chandra. Effect of annealing parameters on optoelectronic properties of highly ordered ZnO thin films. *Mater. Sci. Semiconduct. Proc.* 2019; **100**, 200-13.
[11] AK Jazmati and B Abdallah. Optical and structural study of ZnO thin films deposited by RF magnetron sputtering at different thickness: a comparison with single crystal. *Mater. Res.* 2018; **21**, 1-6.
[12] SS Shariffudin, M Salina and SH Herman. Effect of films thickness on structural, electrical and optical properties of sol-gel deposited layer-by-layer ZnO nanoparticles. *Tran. Ele. Electr. Mater.* 2012; **13**, 102-5.
[13] M Baradaran, FE Ghodsi, C Bittencourt and E llobet. The role of Al concentration on improving the photocatalytic performance of nanostructured ZnO/ZnO:Al/ZnO multilayer thin films. *J. Alloys Compounds* 2019; **788**, 289-301.
[14] G Yergaliuly, B Soltabayev, S Kalybekkyzy, Z Bakenov and A Mentbayeva. Effect of thickness and reaction media on properties of ZnO thin films by SILAR. *Sci. Rep.* 2022; **12**, 851.
[15] MR Islam, M Rahman, SFU Farhad and J Podder. Structural, optical and photocatalysis properties of sol-gel deposition Al-doped ZnO thin films. *Surfaces Inter.* 2019; **16**, 120-6.
[16] N Nagayasamy, S Gandhimathination and V Veerasamy. The effect of ZnO thin film and its structural and optical properties prepared by sol-gel spin coating method. *Open J. Met.* 2013; **3**, 8-11
[17] R Pérez-Cuapio, M Pacio, H Juárez, JA Alvarado, C Guarneros, C Bueno and A Pacio. Effect of ZnO film thickness on its optical and structural properties. *J. Nano Res.* 2018; **52**, 102-14.

[18] BA Anandh, AS Ganesh, R Thangarasu, R Sakthivel, R Kannusamy and K Tamilselvan. Structure, morphological and optical properties of aluminium doped ZnO thin films by dip-coating method. *Orient. J. Chem.* 2018; **3**, 1619-24.
[19] T Amakali, LS Daniel, V Uahengo, NY Dzade and NHD Leeuw. Structural and optical properties of ZnO thin films prepared by molecular precursor and sol-gel methods. *Crystals* 2020; **10**, 132.
[20] P Ghosh and Q Tran. Correlation between bulk and surface resistivity of concrete. *Int. J. Conc. Struct. Mater.* 2014; **9**, 119-32.
[21] A Ismail and MJ Abdullah. The structural and optical properties of ZnO thin films prepared at different RF sputtering power. *J. King Saud Univ. Sci.* 2013; **25**, 209-15.
[22] BZ Dong and GJ Fang. Effect of thickness on structural, electrical, and optical properties of ZnO:Al films deposited by pulsed laser deposition. *J. Appl. Phys.* 2007; **101**, 033713.
[23] KG Saw, NM Aznan, FK Yam, SS Ng and SY Pung. New insights on the burstein-moss shift and band gap narrowing in indium-doped zinc oxide thin films. *PLoS One* 2015; **10**, e0141180.