

INVESTIGATION OF STRUCTURAL, OPTICAL, AND ELECTRICAL PROPERTIES OF ZnO THIN FILMS FOR ELECTRO-OPTICAL DEVICES

Sasimonton Moungsrijun and Sutthipoj Wongrerkdee*

Received: August 17, 2021; Revised: March 07, 2022; Accepted: March 18, 2022

Abstract

ZnO thin films were successfully deposited on fluorine-doped tin oxide substrates using a two-electrode homemade electrochemical deposition system. First, a zinc metal layer was deposited on the substrate via an electrochemical process, from aqueous solutions of zinc nitrate for various deposition times. Afterward, the Zn metal layer was transformed into multiple ZnO thin films through thermal oxidation under ambient air. Finally, a post-treatment was performed on the ZnO thin films by calcination. The morphology of the ZnO thin films, when observed under a scanning electron microscope, exhibited rough surfaces and porous characteristics. The X-ray diffraction patterns and the Raman shifts indicated hexagonal wurtzite structures. Moreover, the Fourier-transform infrared spectroscopy results confirmed the chemical structure of the films to be ZnO without a residue. The average optical transmittance values in the visible region were greater than 80%. The band gap energy was in the range of 3.13 to 3.43 eV. The four-point probe measurement revealed various sheet resistance values in the range of 167.21 to 1,066.28 Ω/sq . Concerning the electro-optical property evaluation, the optical transmittance and sheet resistance values were considered for calculating the figure of merit. It was found that the highest value reached $3.08 \times 10^{-3} \Omega^{-1}$, indicating that ZnO thin films have a potential application in electro-optical devices.

Keywords: ZnO, Electrochemical deposition, Thermal oxidation, Electro-optical devices

Introduction

ZnO thin films have been investigated for thin film-based devices because of their unique characteristics, including wide band gap energy (E_g), high exciton binding energy, and high mobility (Wongrat *et al.*, 2021; Wongrerkdee *et al.*, 2021). Furthermore, ZnO can be prepared in different nanostructures, such as nanoparticles, nanorods, nanowires, nanofilms, etc (Gonçalves *et al.*, 2021; Shahzad *et al.*, 2021). The nanofilm structure is important for thin film-based electro-optical devices

such as touch-screen monitors, light-emitting diodes (LEDs), solar cells, etc (Shahzad *et al.*, 2021). Thus, the deposition of ZnO thin films was demonstrated using different techniques, including atomic layer deposition (ALD), sputtering, and electrochemical deposition (ECD) (Pecharapa *et al.*, 2019; Rong *et al.*, 2019). Among these, ECD is an interesting technique for thin film deposition because it can be operated at low temperatures and does not require a vacuum system. The ECD technique is easily

Department of Physics, Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus, Kamphaengsaen, Nakhon Pathom 73140, Thailand. E-mail: sutthipoj.s@gmail.com

* Corresponding author

operated by applying a voltage or current between electrodes that are immersed in electrolytes. For ZnO thin film deposition, zinc compound materials, such as ZnCl_2 (Rosas-Laverde *et al.*, 2019), $\text{Zn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (Salman *et al.*, 2017), and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Shirvani and Naji, 2021), are commonly used as electrolytes and transferred as metallic films during the deposition.

For example, preparation of ZnO films on an indium-doped tin oxide (ITO) substrate using constant current ECD has been reported by Timuda and Waki (Timuda and Waki, 2020). The preparation was performed using a standard three-electrode system at 60°C for three different current densities of -1, -2, and -5 mA/cm². The ITO substrate was used as the working electrode, and a mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and CH_3COOH was used as the electrolyte. Finally, the deposited sample was annealed at 400°C. X-ray diffraction (XRD) patterns showed that the crystalline structures of all samples were hexagonal wurtzite structures. Some composite structures, however, were obtained. The deposited ZnO films featured nanosheet structures. The film's thickness varied according to the current density and deposition time. Note that the deposited films were dense-like structures for a high applied current density and a long deposition time, which caused better attachment to the substrates. This finding is an interesting result for thin film-based applications. Battas *et al.* presented the growth mechanism of ZnO and Al-doped ZnO (AZO) nanostructures using ECD (Battas *et al.*, 2021). The ECD was performed in a three-electrode system on a fluorine-doped tin oxide (FTO) substrate without seed layer preparation. The ECD process was operated in an electrolyte of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or a mixture ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) under a constant voltage of -1.0 V and a temperature of 80°C. After the ECD, the ZnO-coated FTO substrate was thermally treated at 350°C in air to ensure the complete ZnO transformation. XRD patterns confirmed the hexagonal wurtzite structure for the ZnO and AZO samples. However, lateral growth was observed for AZO due to the addition of Al^{3+} . The nanorod structure was obtained for the ZnO sample, while the nanorod with large-size and nanosheet structures were observed for the AZO samples. This investigation gives a better understanding of ZnO crystallization using ECD with and without Al^{3+} , which can be applied to control the shape or crystallization rate of ZnO-based thin film. In a similar work, Shirvani and Naji presented a deposition of ZnO nanorod films using an electrochemical process for application as an electron transport layer in polymer solar cells (Shirvani and Naji, 2021). The deposition was performed within two steps of the seed layer and

nanorod preparation. The ZnO seed layer preparing step was carried out by spin-coating zinc acetate dihydrate solutions onto a cleaned ITO substrate. The ZnO nanorods were then grown using a three electrode ECD system in a zinc nitrate hexahydrate solution under a constant potential of -1.0 V. The nanorod structures showed hexagonal shapes and a wide range of nanorod lengths of around 90 to 250 nm. The deposited ZnO nanorods exhibited excellent crystallization alignment in the preferred orientation of (002) planes. The E_g of the nanorods was reduced to 3.39 eV compared with the ZnO seed layer of 3.7 eV. Interestingly, the nanorod structures were successfully used as an electron-transporting layer in polymer solar cells with a power conversion efficiency of around 2.51 to 3.65%. Therefore, ECDs can certainly be applied to prepare nanostructured ZnO thin films. Although the three-electrode system is frequently used for the ECD, it has some limitations for many users, including cost and complexity. Salman *et al.* demonstrated a two-electrode ECD system as a low-cost and flexible system (Salman *et al.*, 2017). The ZnO thin films deposited by the two-electrode system showed hexagonal wurtzite structures and high E_g . The grain size and roughness increased as the deposition time increased.

In this work, a two-electrode homemade ECD system was presented. The demonstration aims to prepare ZnO thin films using the low-cost and flexible ECD system, investigate the film's characteristics, and evaluate the film's performance for electro-optical device applications. For the ECD of ZnO thin films, Zn^{2+} electrolytes were first deposited onto the FTO substrate and transformed into Zn films under a constant applied current. Then, the deposited Zn films were thermally oxidized in ambient air to ensure the ZnO transformation. For characterization, the ZnO thin films were examined using various techniques, including scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) spectroscopy, ultraviolet-visible (UV-VIS) spectroscopy, and four-point probe measurement. The electro-optical property was determined to evaluate the film's performance for the electro-optical device application. The low-cost and flexible production in this work might be beneficial because it demonstrates an alternative technique for thin film-based deposition.

Materials and Methods

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in de-ionized (DI) water at a concentration of 0.1 M followed by stirring for 1 h to form a zinc nitrate aqueous

solution for use as a Zn^{2+} ion source. Then, two pieces of FTO substrate were immersed in the zinc nitrate solution. The distance between substrates was kept at around 1 mm. The ECD was performed by applying a constant current of 1 mA between the substrates to deposit Zn films on the cathode for various deposition times of 100, 200, 300, and 400 s, followed by rinsing with DI water several times. Then, the Zn films were thermally oxidized at 450°C on a hotplate under ambient air for 1 h to transform them into ZnO thin films. Finally, a post-treatment was performed by calcination at 500°C for 1 h.

ZnO thin films were characterized using several techniques. The morphology was observed by a scanning electron microscope (SEM). The chemical structure was examined by a Fourier-transform infrared (FT-IR) spectrometer. The crystalline structure was investigated by an X-ray diffraction (XRD) spectrometer. Molecular vibration was investigated using Raman spectroscopy. Optical transmittance was monitored by an ultraviolet-visible (UV-VIS) spectrophotometer. The sheet resistance was measured using a four-point probe measurement system.

Results and Discussion

Figure 1 shows the morphology of the ZnO thin films prepared for various deposition times. The films exhibit rough surfaces with porous characteristics. This formation might be due to non-homogeneous Zn films or the effect of rapid thermal oxidation. Note that the films deposited for the deposition time of 300 s present smoother surfaces than for the other conditions, according to comparative observation in lower porous surfaces and larger grain boundary. It is believed that this effect is caused by the optimum accumulation of Zn^{2+} ions on FTO substrates during the chemical process. The optimum Zn^{2+} ions can properly interact with oxygen during the thermal oxidation with low excess Zn^{2+} ions for smooth surface formation. This result indicates that the deposition time of 300 s should be the appropriate condition for thin film-based device applications.

Figure 2 reveals the chemical structures of the ZnO thin films deposited on the FTO substrate using an FT-IR spectrophotometer. All films are ZnO according to the presence

of the Zn-O vibration at the wavenumber of 474 to 502 cm^{-1} (Rahman *et al.*, 2021). Moreover, any vibration peaks of residues were not detected, indicating the high purity of the obtained ZnO films.

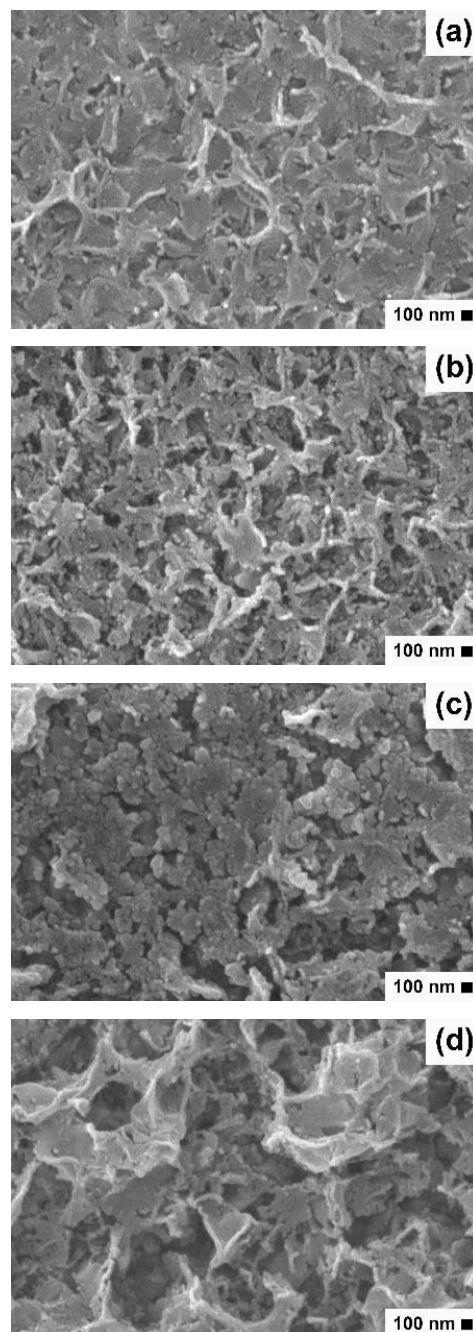


Figure 1. Morphology of ZnO thin films prepared at various deposition times of (a) 100, (b) 200, (c) 300, and (d) 400 s.

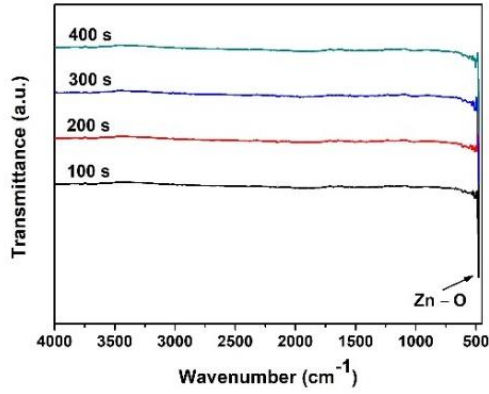


Figure 2. FT-IR of ZnO thin films deposited on FTO substrates at various deposition times

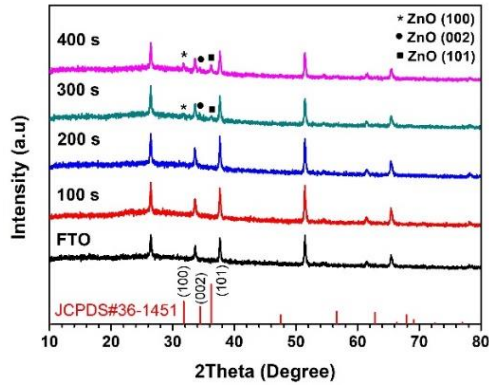


Figure 3. XRD patterns of ZnO thin films deposited on FTO substrates at various deposition times in comparison with FTO and JCPDS card no. 36-1451.

To investigate the crystalline structures of the ZnO thin films, the XRD patterns were recorded, as shown in Figure 3. It was found that only the XRD patterns of FTO are primarily observed for the deposition times of 50, 100, and 200 s, while the XRD patterns that correspond to ZnO are not detected. This behavior can be explained due to obscuring by FTO for the short deposition time, which was further investigation. For the long deposition times of 300 and 400 s, the XRD patterns of the ZnO hexagonal wurtzite structure, in accordance with JCPDS card no. 36-1451 (Krobthong *et al.*, 2020; Krobthong and Wongrerkdee, 2020), were observed. For the ZnO structure validation, the Raman shift of ZnO deposited on FTO at 400 s (FTO/ZnO) was measured as a representative ZnO film in comparison with FTO as shown in Figure 4. It was found that the hexagonal wurtzite structure of ZnO is observed according to the peak at 435 cm^{-1} . The peak corresponds to the non-optical phonon E_{2H}

mode, attributable to the hexagonal wurtzite phase of ZnO (Krobthong *et al.*, 2020). These results indicate the crystallization of the ZnO thin films on the FTO substrates.

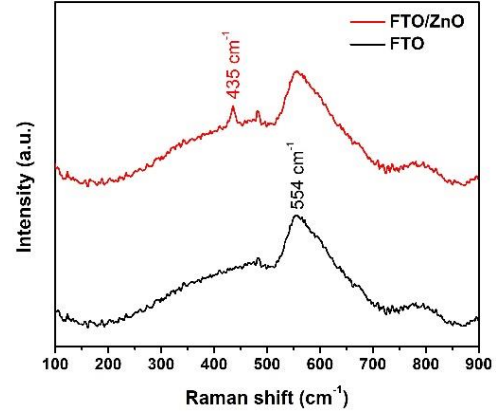


Figure 4. Raman shifts of ZnO thin films deposited on FTO substrates at a deposition time of 400 s (FTO/ZnO) in comparison with FTO

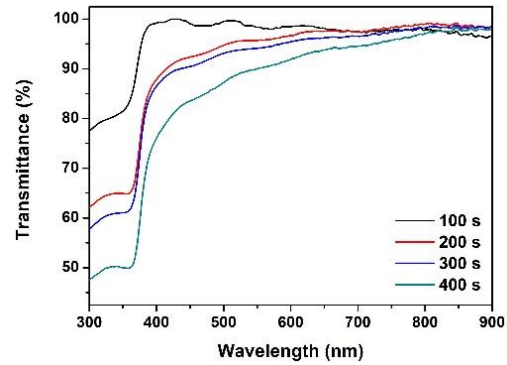


Figure 5. Optical transmittance spectra of ZnO thin films deposited on FTO substrates at various deposition times

Table 1. Average transmittance and energy gap of ZnO thin films

Deposition time (s)	T_{avg} (%)	E_g (eV)
100	98.67	3.30
200	95.07	3.25
300	93.59	3.18
400	88.77	3.13

Figure 5 shows the optical transmittance of ZnO thin films. The transmittance slightly decreases as the deposition time increases, which indicates the increase in the thickness of the ZnO thin films. To estimate the transmittance values, the average transmittance (T_{avg}) in the visible region was calculated, as summarized in Table 1. All ZnO thin

films have high transmittance values, which could be suitable for electro-optical device applications.

For E_g estimation of the ZnO thin films, the Tauc plot was performed based on the transmittance following Equation (1). (Rodwihok *et al.*, 2019; Sujinnapram *et al.*, 2021).

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where α , A , h , and ν are the optical absorbance coefficient, constant, Planck's constant, and frequency, respectively. Figure 6 shows the Tauc plots of ZnO thin films, which depict $(\alpha h\nu)^2$ versus $h\nu$. The extrapolation of the straight line was drawn to the $h\nu$ -axis. Then, the E_g can be estimated from the interception of the $h\nu$ -axis as listed in Table 1. The E_g slightly decreases as deposition time increases. This behavior might occur due to numerous defects or disorders in the ZnO thin films for the long deposition time, which is in agreement with previous reports (Iqbal *et al.*, 2016; Muchuweni *et al.*, 2017). This effect potentially leaves excess electrons in the ZnO films, which increases the density of states of electrons in the conduction band and thus pulls down the conduction band edge near to the valence band edge. Thus, E_g is found to have a decreasing trend over a long deposition time (Tang *et al.*, 2013).

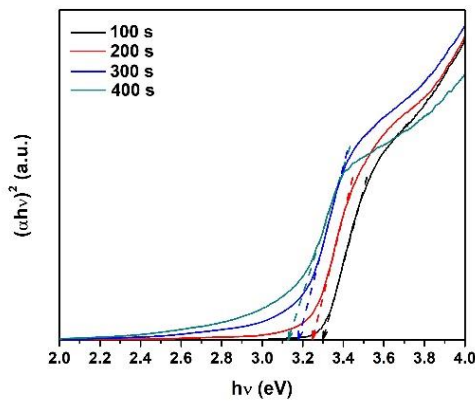


Figure 6. The tauc's plots of ZnO thin films deposited on FTO substrates at various deposition times

To investigate the electrical property, a four-point probe measurement was used to measure the sheet resistance (R_s) of the ZnO thin films, as shown in Figure 7. The measurement was performed for at least three positions within a square area of $1 \times 1 \text{ cm}^2$ for each sample. The measured R_s value of the FTO, $7.59 \pm 0.03 \text{ } \Omega/\text{sq}$, is used as a reference. To estimate

othe R_s of ZnO thin films, a calculation of R_s was performed using a parallel resistance model following Equation (2). (Liu *et al.*, 2021).

$$\frac{1}{R_{total}} = \frac{1}{R_{FTO}} + \frac{1}{R_{ZnO}} \quad (2)$$

where R_{total} is the total R_s measured from ZnO films coated on FTO substrates, R_{FTO} is the R_s of FTO substrates, and R_{ZnO} is the R_s of ZnO films, respectively. The R_s values of the ZnO thin films decrease as deposition time increases from 100 to 300 s. However, the R_s reaches the maximum value at the deposition time of 400s. This effect is believed to be due to the non-uniformity of the films, which is caused by the over-accumulation of Zn metal for the long deposition time. Thus, it can be assumed that the deposition time of 300 s is the optimum condition for minimizing R_s .

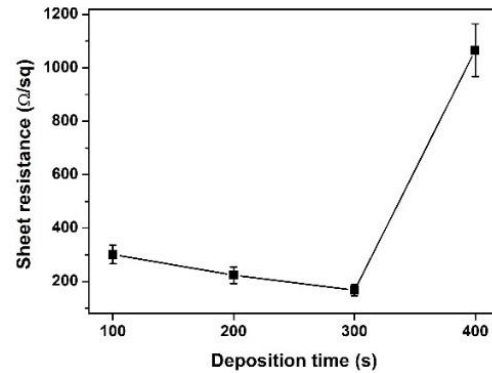


Figure 7. Sheet resistance of ZnO thin films deposited on FTO substrates at various deposition times

In order to evaluate the ZnO thin film performance for the possible application in electro-optical devices, the figure of merit (FOM) is calculated, from the average transmittance and R_s values, according to Equation (2). (Liu *et al.*, 2019).

$$FOM = \frac{T_{avg}^{10}}{R_s} \quad (2)$$

The plot of FOM in Figure 8 shows that the FOM values are 2.90×10^{-3} and $2.70 \times 10^{-3} \text{ } \Omega^{-1}$ for deposition times of 100 and 200 s, respectively. The FOM reach the maximum value of $3.08 \times 10^{-3} \text{ } \Omega^{-1}$ for the deposition time of 300 s. After that, the FOM value decreases to $2.85 \times 10^{-4} \text{ } \Omega^{-1}$ for the deposition time of 400 s. This result suggests that the ZnO thin films prepared with the optimum deposition time of 300 s could be applied to electro-optical devices.

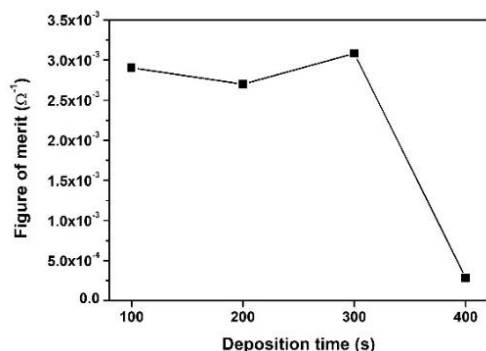


Figure 8. Figure of merit of ZnO thin films deposited on FTO substrates at various deposition times

Conclusions

ZnO thin films were successfully deposited on FTO substrates using a two-electrode homemade ECD system. The morphology of the ZnO thin films exhibited rough and porous surfaces. The crystalline structure features hexagonal wurtzite structures. The chemical structure of all the films was ZnO without residue. The average optical transmittance values in the visible region decrease from 98.67% to 88.77% as the deposition time increases. The band gap energy slightly decreases for longer deposition times, which is caused by defects or disorders. The sheet resistance values are 167.21 to 1,066.28 Ω/sq . For evaluation of the electro-optical property of the ZnO thin films, the FOM was considered. The highest FOM value of $3.08 \times 10^{-3} \Omega^{-1}$ is obtained for the appropriate deposition time of 300 s, which indicates that the ZnO thin films have a potential application for electro-optical devices.

Acknowledgements

This work was supported by the Research Promotion and Technology Transfer Center (RPTTC), Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus (grant number 206/2564); and the Department of Physics, Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus (grant number PHY-2021/07). The authors gratefully thank the Department of Physics, Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus for facility support.

References

- Battas, M., Atourki, L., Bouabid, K., Ihlal, A., Abd-Lefdil, M., and Regragui, M. (2021). Investigations on the Growth Mechanism of Nanostructured ZnO: Shedding Light on the Effect of Al^{3+} Doping, *Surf. Eng. Appl. Electrochem.*, 57(1):1-9.
- Gonçalves, R.A., Toledo, R.P., Joshi, N., and Berengue, O.M. (2021). Green Synthesis and Applications of ZnO and TiO_2 Nanostructures, *Molecules.*, 26(8):2,236.
- Iqbal, J., Jilani, A., Hassan, P.M.Z., Rafique, S., Jafer, R., and Alghamdi, A.A. (2016). ALD grown nanostructured ZnO thin films: Effect of substrate temperature on thickness and energy band gap, *J. King Saud Univ. Sci.*, 28(4):347-354.
- Krobthong, S., Nilphai, S., Choopun, S., and Wongrerkdee, S. (2020). Synthesis and characterization of ZnO nanoparticle films its application in dye-sensitized solar cells, *Dig. J. Nanomater. Biostructures.*, 15(3):885-894.
- Krobthong, S. and Wongrerkdee, S. (2020). Incorporation of Fe and Cu for antibacterial performance enhancement of Fe-Cu-ZnO nanocomposites synthesized by a facile chemical precipitation. *J. Met. Mater. Miner.*, 30(3):38-45.
- Liu, L., Jiang, J., Xu, Z., Zhou, J., and Li, Y. (2021). Enhanced electrical conductivity of PEDOT-encapsulated silver nanowire film pretreated with surfactants. *Colloid Polym. Sci.*, 299:595-601.
- Liu, Y., Qiao, Y., Nie, C., Xiong, L., Zeng, Q., Wang, B., Lv, H., Yu, H., and Yang, G. (2019). High photoelectric performance of Cu-based AZO multilayer films deposited via TiO_2 barrier layer and oxygen-containing atmosphere. *Ceram. Int.*, 45(18):24,303-24,308.
- Muchuveni, E., Sathiaraj, T.S., and Nyakoty, H. (2017). Synthesis and characterization of zinc oxide thin films for optoelectronic applications. *Heliyon.*, 3(4):e00285.
- Pecharapa, W., Santibenchakul, S., Khamon, W., Ruangon, K., and Noonuruk, R. (2019). Effects of group-III dopants on the structural and optical properties of sol-gel derived ZnO thin films, *Suranaree J. Sci. Technol.*, 26(1):44-50.
- Rahman, A., Harunsani, M.H., Tan, A.L., Ahmad, N., Hojamberdiev, M., and Khan, M.M. (2021). Effect of Mg doping on ZnO fabricated using aqueous leaf extract of *Ziziphus mauritiana Lam.* for antioxidant and antibacterial studies, *Bioprocess Biosyst. Eng.*, 44(4):875-889.
- Rodwihok, C., Choopun, S., Ruankham, P., Gardchareon, A., Phadungthitidhada, S., and Wongratanaphisan, D. (2019). UV sensing properties of ZnO nanowires/nanorods. *Appl. Surf. Sci.*, 477:159-165.
- Rong, P., Ren, S., and Yu, Q. (2019). Fabrications and Applications of ZnO Nanomaterials in Flexible Functional Devices-A Review, *Crit. Rev. Anal. Chem.*, 49(4):336-349.
- Rosas-Laverde, N.M., Pruna, A., Cembrero, J., Orozco-Messana, J., and Manjón, F.J. (2019). Performance of graphene oxide-modified electrodeposited ZnO/Cu₂O heterojunction solar cells, *Bol. Soc. Esp. Ceram. V.*, 58(6):263-273.
- Salman, O.N., Dawood, M.O., Ali, A.K., Ahmed, D.S., and Hassoon, K.I. (2017). Low cost synthesis of ZnO nano thin films by electrochemical deposition, *Dig. J. Nanomater. Biostructures.*, 12(3):719-726.
- Shahzad, S., Javed, S., and Usman, M. (2021). A Review on Synthesis and Optoelectronic Applications of Nanostructured ZnO, *Front. Mater.*, 8:613,825.
- Shirvani, M. and Naji, L. (2021). Interface engineering of electrochemically deposited ZnO nanorods as electron transport layer in polymer solar cells using organic dyes. *Mater. Chem. Phys.*, 259:124,064.

- Sujinnapram, S., Nilphai, S., Moungsrijun, S., Krobthong, S., and Wongrerkdee, S. (2021). Clustered zno nanoparticles synthesized via precipitation for photocatalytic degradation of methyl orange and Glyphosate, Dig. J. Nanomater. Biostructures., 16(1):317-329.
- Tang, G., Liu, H., and Zhang, W. (2013). The Variation of Optical Band Gap for ZnO: In Films Prepared by Sol-Gel Technique, Adv. Mater. Sci. Eng., 2013:348,601.
- Timuda, G.E. and Waki, K. (2020). Galvanostatic electrodeposition of ZnO nanosheet: effect of different applied current densities and deposition times on the nanosheet morphology, Adv. Nat. Sci-Nanosci., 11(2):025,005.
- Wongrat, E., Nuengnit, T., Panyathip, P., Chanlek, N., Hongsith, N., and Choopun, S. (2021). Highly selective room temperature ammonia sensors based on ZnO nanostructures decorated with graphene quantum dots (GQDs), Sens. Actuators B. Chem., 326:128,983.
- Wongrerkdee, S., Moungsrijun, S., Pimpang, P., Hongsith, K., and Choopun, S. (2021). Linking bridge improvement of ZnO/N719 interfaces via ammonia treatment for efficiency enhancement of dye-sensitized solar cell, Surf. Interfaces, 23:100,991.