Sigma J Eng & Nat Sci 38 (2), 2020, 955-960

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article

SOME PHYSICAL PROPERTIES OF CZO THIN FILMS PRODUCED BY A NOVEL MAGNETIC SPIN COATING TECHNIQUE

M. Fatih GÖZÜKIZIL*[1], Sinan TEMEL[2], Nurgül ÖZBAY[3]

[1] *Bilecik Seyh Edebali University, Sogut Vocational School, BILECIK;* ORCID: 0000-0003-1719-959X
[2] *Bilecik Seyh Edebali University, Central Research Laboratory, BILECIK;* ORCID: 0000-0002-0889-9490
[3] *Bilecik Seyh Edebali University, Chemical Engineering Dept., BILECIK;* ORCID: 0000-0002-0666-3417

Received: 04.10.2019 Revised: 23.04.2020 Accepted: 27.04.2020

ABSTRACT

Semiconductor ZnO thin films, whose physical properties can be modified by doping various metals are used in many current technological areas, from antimicrobial structures to photodedectors, to photovoltaic attacks, to sensors with various uses. The crystal structures of the ZnO thin films can be modified by changing their properties such as band gaps and optical permeability by doping with Cd, and fine films can be produced in different properties suitable for the field of use. In this study, CZO (Cd-doped ZnO) thin films were produced using a novel magnetic spin coating technique, which was developed as an alternative to production techniques carried by complex and expensive device technology. The Cd doping process was increased by 1%, 3% and 5%, and by increasing the doping to 5%, the peaks of the hexagonal CdZn structure were observed in addition to the peaks of the ZnO series. When the surface properties of the produced films were examined, it was seen that the coating was distributed homogeneously on the surface, the particle size values increased as the amount of Cd doping increased and the voids disappeared on the surface, and thus formed of nanoparticles which were held better to each other. When the optical properties of Cd doped ZnO thin films were examined, it was seen that the band gap values decreased with increasing amount of doping.
Keywords: Thin films, ZnO, sol-gel, magnetic spin coating.

1. INTRODUCTION

ZnO thin films, which have unique physical properties such as optical permeability [1] and whose electrical properties can be enhanced by doping with different metal elements [2], are frequently used in technological applications such as acoustic sensors [3], high photocatalytic performance materials [4-5], antimicrobial activities [6], photodedectors [7], spintronic devices [8] photovoltaic cells [9] and various electronic and optoelectronic devices [10]. By doping Cd element to ZnO thin films, structural, electrical [15] and optical properties [16] can be improved such as improving crystal structure quality [11], improving light absorption coefficient [12], reducing band gap [13-14].

As an alternative to partially costly and complex techniques used in ZnO thin film production today, sol-gel magnetic spin coating technique were developed, and more economical, simple and convenient Cd doped ZnO thin films was produced with sol-gel magnetic spin coating technique.

* Corresponding Author: e-mail: fatih.gozukizil@bilecik.edu.tr, tel: (228) 214 16 53

1%, 3%, 5% Cd doped ZnO thin films wer e produced and their structural, morphological and optical properties were examined.

2. EXPERIMENTAL METHOD

In this study, ISOLAB microscope slides, which were cleaned and made suitable for thin film production, were used as a substrate to produce thin films.

ZnO sol-gel solution was prepared as 0.5 M. $Zn(CH_3COO)_2.2H_2O$ (zinc acetate dihydrate), 2-methoxyethanol and monoethanolamine was used to prepare the sol-gel solution. $Cd(CH_3CO_2)_2.2H_2O$ (cadmium acetate dihydrate) was used for Cd doping. By adding 1%, 3% and 5% cadmium acetate dihydrate to the ZnO solution, the doping process was carried out. The prepared solutions were stirred at room temperature for 2 hours and kept at room temperature for 2 days.

The thin film solutions to be produced by magnetic spin coating technique with optimum experimental parameters, were dripped by means of a micro pipette in a determined amount to the exact centre to ensure its uniform distribution all over the substrate placed on the magnetic platform, which can rotate at high speeds, and magnetically rotated at 3000 rpm. The glass substrates, which had finished spinning, were heat treated in the oven at 150 ° C for 10 minutes to evaporate the solution retained on the surface and to remove the organic compounds from the surface. The processes for each layer were repeated to obtain 9 layer films. The obtained thin films were annealed at 500° C for 120 minutes. Structural, morphological and optical characterizations of thin films were obtained by using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-Vis Spectroscopy respectively, and the effects of doping were examined by comparing with the undoped ZnO series. The naming of the compared series is shown in Table 1.

Table 1. Naming of Cd doped ZnO Series

Rotating Speed (rpm)	Number of Layers	Annealing Temperature (^oC)	Cd Doping Amount (%)	Series
3000	9	500	-	ZnO
3000	9	500	1	CZO1
3000	9	500	3	CZO3
3000	9	500	5	CZO5

3. RESULTS AND DISCUSSION

PANALYTICAL Empyrean X-Ray Diffractometer (XRD) was used to investigate the structural properties of the films. Samples were examined at $30° \leq 2\theta \leq 60°$ limit values, using a CuK_α beam with a scanning speed of 2 degrees/minute and a wavelength of 1,5406 Å, at 45 kV voltage and 40 mA current. The structures found were compared with ICDD (International Centre for Diffraction Data): 98-003-1052 for ZnO in hexagonal structure and 98-010-2090 cards for CdZn in hexagonal structure. XRD analysis spectra of doped CZO thin films are compared with undoped ZnO in Figure 1.

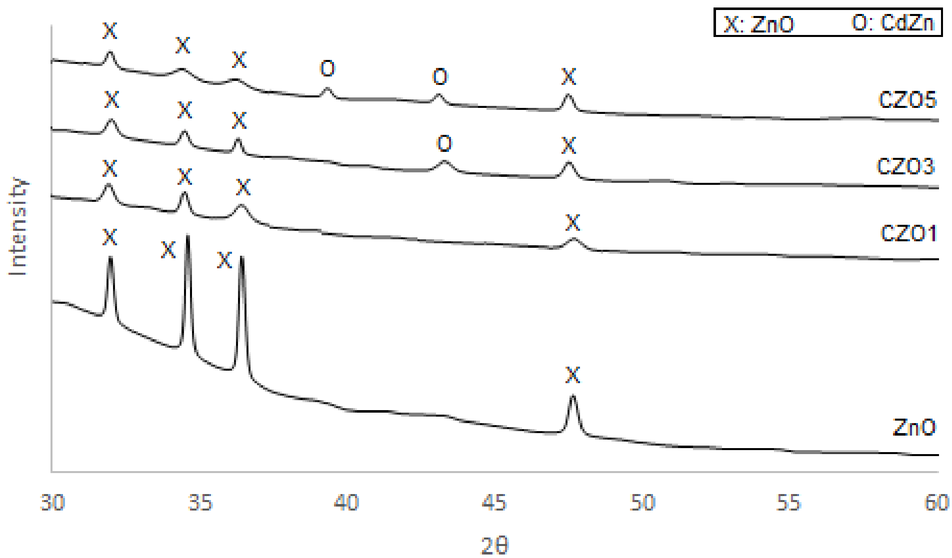

Figure 1. Comparative XRD analysis spectrum of undoped and Cd doped ZnO thin films.

All series were observed to be polycrystalline in XRD spectra. In the undoped ZnO series films, 4 peaks of the hexagonal ZnO structure are observed as (010), (002), (011) and (012) respectively. Although no peaks of the Cd structure were observed with the effect of 1% doped Cd, the intensity of the peaks of the ZnO structure with doped Cd decreased. With the increase of the doping amount, the peak belonging to hexagonal CdZn structure (011) was observed in CZO3 series alongside the peaks belonging to ZnO series. In CZO5 series, by increasing the doping amount to 5%, the peaks (010) and (011) of hexagonal CdZn structure were observed in addition to the peaks of ZnO series. It is also clear from the comparative XRD spectrum that peak intensities decreased significantly as the doping ratio increased. From these results, it is understood that the level of crystallization decreases as the ratio of Cd contributed to ZnO structure increases.

The average particle size (D) values can be calculated by using Scherrer Formula with the information obtained from XRD spectra;

$$D = \frac{0{,}9\lambda}{\beta\cos\theta_B} \qquad (1)$$

Here λ; is the wavelength of X-rays, β; is the half-peak width in radians [17]. In Table 2, the grain size values of the undoped ZnO and doped CZO thin films calculated by Scherrer Formula are given. As can be seen from the table, the average grain size values increase as the amount of doping increases.

Table 2. Grain size values of undoped ZnO and doped CZO

Seri	**D (nm)**
ZnO	112
CZO1	113
CZO3	130
CZO5	154

Surface properties of thin films were studied using ZEISS Supra 40VP field emission scanning electron microscope (FESEM). FESEM images of undoped ZnO and doped CZO thin films with 50kx magnification are given in Figure 2.

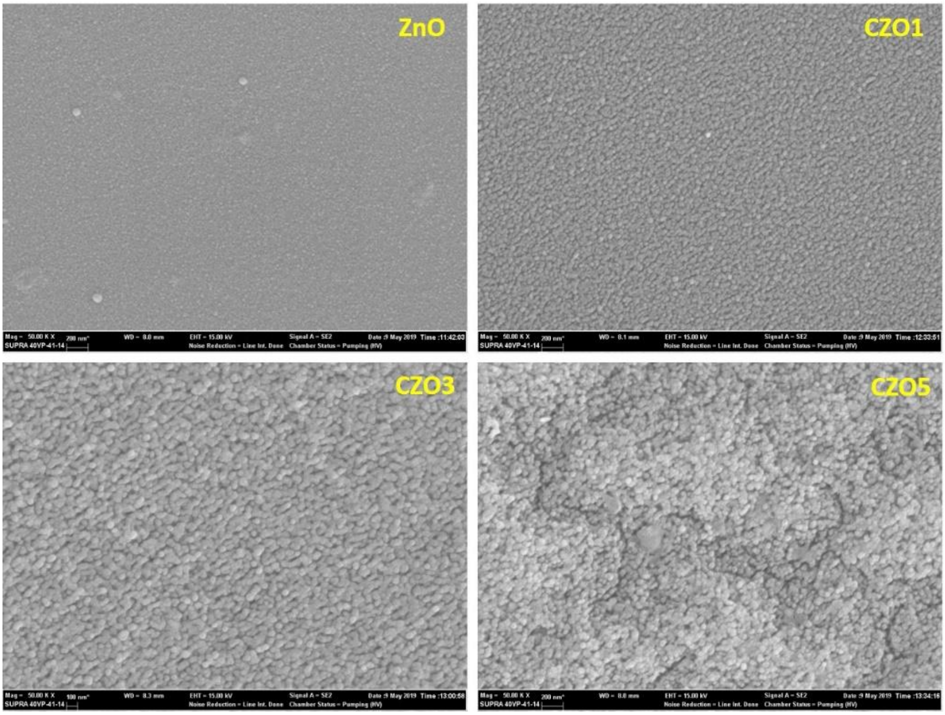

Figure 2. Comparative FESEM images of undoped ZnO and CZO

FESEM images revealed that the film was distributed almost homogeneously on its surface, that there were no gaps on the surface, and therefore consisted of particles of nanoscale that were better attached to each other. In addition, it was observed that Cd grains started to appear on the surface with the doping of Cd and these grains increased as the amount of doping increased.

Absorption spectra of thin films were examined by PERKIN ELMER LAMBDA 25 UV-Vis spectrophotometer in the wavelength range 300 - 1100 nm. By using these absorption spectrum data, the band gap values of the films were determined using the Tauc Method [18]. Band gap values of thin films are given in Table 3.

Table 3. Band gap values of thin films

Series	Energy Band Gap (eV)
ZnO	3,28
CZO1	3,17
CZO3	3,10
CZO5	3,03

As can be seen from the table, the band gap of undoped ZnO series was 3.28 eV, while this value decreased to 3.03 eV as the amount of Cd doping increased. This decrease in the band gap value is consistent with the results previously found in the literature for Cd-doped ZnO thin films.

4. CONCLUSION

With the novel magnetic spin coating technique, which was developed as an alternative to thin film production techniques requiring advanced technology and cost-effective device usage, Cd-doped ZnO thin films, composed of particles of nanoscale particles having better homogeneous surface distribution without gap, were produced. Cd doping was performed in 1%, 3% and 5% ratios, and hexagonal CdZn structure was observed in addition to ZnO structure. Additionally, the peak intensity of the ZnO structure from the comparative XRD spectrum was observed to decrease significantly as the doping ratio increased. From these results, it is understood that the level of crystallization decreases with increasing Cd ratio doping to ZnO structure. When the optical properties of Cd-doped ZnO thin films were examined, it was determined that the band gap values decreased with increasing amount of doping. These results are consistent with the characteristics of Cd doped ZnO thin films produced by different techniques in the literature. As can be understood from these examinations, with this technique, used for the first time in literature, Cd-doped ZnO thin films could be produced more easily and economically.

REFERENCES

[1] L. T. Jule *et al.*, "Wide visible emission and narrowing band gap in Cd-doped ZnO nanopowders synthesized via sol-gel route," *J. Alloys Compd.*, vol. 687, pp. 920–926, Dec. 2016.

[2] J. Y. Kim, J. Kim, J. Roh, H. Kim, and C. Lee, "Efficiency Improvement of Organic Photovoltaics Adopting Li- and Cd-Doped ZnO Electron Extraction Layers," *IEEE J. Photovoltaics*, vol. 6, no. 4, pp. 930–933, Jul. 2016.

[3] S. M. N, M. V N Prasad, V. Gaddam, K. Rajanna, and M. Nayak, "Development of a Novel Acoustic Sensor using Sputtered ZnO Thin Film," 2019.

[4] P. Dumrongrojthanath, A. Phuruangrat, S. Thongtem, and T. Thongtem, "Photocatalysis of Cd-doped ZnO synthesized with precipitation method," *Rare Met.*, Jul. 2019.

[5] L. Xu, G. Zheng, F. Xian, and J. Su, "The morphological evolution of ZnO thin films by Sn ions doping and its influence on the surface energy and photocatalytic activity," *Mater. Chem. Phys.*, 2019.

[6] K. P. Ghoderao, S. N. Jamble, and R. B. Kale, "Hydrothermally synthesized Cd-doped ZnO nanostructures with efficient sunlight-driven photocatalytic and antibacterial activity," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 12, pp. 11208–11219, Jun. 2019.

[7] K. J. Chen, F. Y. Hung, S. J. Chang, and S. J. Young, "Optoelectronic characteristics of UV photodetector based on ZnO nanowire thin films," *J. Alloys Compd.*, vol. 479, no. 1–2, pp. 674–677, Jun. 2009.

[8] M. Debbichi, M. Souissi, A. Fouzri, G. Schmerber, M. Said, and M. Alouani, "Room temperature ferromagnetism in Cd-doped ZnO thin films through defect engineering," *J. Alloys Compd.*, 2014.

[9] B. A. H. Ameen, A. Yildiz, W. A. Farooq, and F. Yakuphanoglu, "Solar Light Photodetectors Based on Nanocrystalline Zinc Oxide Cadmium Doped/p-Si Heterojunctions," *Silicon*, 2019.

[10] A. G. S. Kumar *et al.*, "Structural, Electrical and Optical Properties of Cd Doped ZnO Thin Films by Reactive dc Magnetron Sputtering," *JOM*, 2015.

[11] J. Charlesbabu, K. Gopalakrishnan, M. Elango, and K. Vasudevan, "Preparation and characterization of Cd-doped ZnO thin films by spin coating method," *Inorg. Nano-Metal Chem.*, 2017.
[12] L. N. Bai, B. J. Zheng, J. S. Lian, and Q. Jiang, "First-principles calculations of Cd-doped ZnO thin films deposited by pulse laser deposition," *Solid State Sci.*, 2012.
[13] E. Vinoth, S. Gowrishankar, and N. Gopalakrishnan, "RF magnetron sputtered Cd doped ZnO thin films for gas-sensing applications," *Mater. Manuf. Process.*, 2017.
[14] B. Rahal *et al.*, "Sol-gel synthesis and nanostructured semiconductor analysis of undoped and Cd-doped ZnO thin films," *Optik (Stuttg).*, 2018.
[15] A. Buyukbas-Ulusan, İ. Taşçıoğlu, A. Tataroğlu, F. Yakuphanoğlu, and S. Altındal, "A comparative study on the electrical and dielectric properties of Al/Cd-doped ZnO/p-Si structures," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 13, pp. 12122–12129, Jul. 2019.
[16] N. Kumar and A. Srivastava, "Faster photoresponse, enhanced photosensitivity and photoluminescence in nanocrystalline ZnO films suitably doped by Cd," *J. Alloys Compd.*, vol. 706, pp. 438–446, Jun. 2017.
[17] B. D. Cullity and S. R. Stock, *Elements of x-ray diffraction*. Prentice Hall, 2001.
[18] J. Tauc, "Amorphous and liquid semiconductors", Plenum, New York, 1976.