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Optical properties of Al-doped with zinc oxide (AZO) thin films with PLD technique

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Pulsed laser deposition (PLD) was used to deposit aluminum (Al)-doped zinc oxide (AZO) thin films with various Al ratios onto glass substrates. Ultraviolet (UV) -visible spectroscope was used to study the impact of Al doping on the physical properties of ZnO. Aluminum was doped into ZnO at 0, 6, and 12% concentrations successfully. The transmittance of the AZO films in the UV region is high, typically of 80% than that of ZnO films. AZO films' optical band gap (3.02-2.76 eV) was below that obtained in undoped ZnO films (3.37 eV). The ZnO thin films' reflectance (R) and refractive-index (n) were high in the UV region, but gradually diminished between 300 and 400 nm. The extinction coefficient decreased as the amount of Al increased in the ZnO thin films. The method used for the experiment and study findings is presented and fully discussed. The values were calculated and measured in comparison to previously published data.

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Keywords: Characterization, Doping, Zinc oxide, Aluminum zinc oxide, Pulsed laser deposition

1. Introduction

Zinc oxide has innumerable applications in many different areas. The ZnO has attracted more attention recently in the literature. The ZnO is the n-type semiconductor, the direct large band gap, with the high energy exciton binding at room temperature [1].

ZnO has wide applications because it is inexpensive, very stable, readily available, and safe [2]. These properties make it among the best materials used in optoelectronics [3,4]. To date, considerable research has been devoted to ZnO [5, 6].

N-type doping is easy with large band gap semiconductors such as ZnO, GaN, ZnS, and ZnSe, but it is difficult with p-type doping.

It is easy to use post-deposition treatments to tune ZnO's physical features such as incorporating gallium (Ga), tin (Sn), boron (B), copper (Cu), indium (In) and aluminum (Al) surface treatments and annealing [7-11]. Researchers have used gallium, aluminum and indium as dopants, which produced n-type ZnO films with high quality and conductivity [12-14].

Doping Al with ZnO films is considered as the one of the best elements for use in optoelectronics because of its excellent conductivity [1, 3, 15, 16-19]. AZO is safe, inexpensive, readily available, and its optical transmittance is very high [17-19]. AZO easily bonds and is very compatible with substrates. The association between the doping ratio of Al and AZO films' properties must be assessed. Several versions of methods are performed to prepare AZO thin films. Magnetron sputtering, atomic layer deposition "ALD", spray pyrolysis "SP", molecular beam-epitaxy "MBE", pulsed laser deposition "PLD" and sol-gel processing methods are used to deposit various AZO nanostructures on different substrates [20-25].

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PLD is the best conventional deposition method. It can produce vapor/species with different velocity and energy to grow films. It is utilized to fabricate films that are very smooth, uniform, and with precisely controlled thicknesses. The PLD method applied in this work was described in detail in a prior study [24-27]. In this study, PLD was used to deposit AZO thin films on soda-lime glass substrate. The doped Al's impact on ZnO's optical and other properties was assessed.

2. Materials and methods

2.1. Materials and sample preparation

Aluminum (Al), zinc oxide (ZnO), and soda-lime glass were purchased from Sigma-Aldrich. To prepare the Al sample, ZnO Al_2O_3 (99.99%) and ZnO (99.99%) were combined. The zinc oxide and Al_2O_3 samples were mixed in the correct ratio and dried to obtain AZO samples. The powders were thoroughly mixed and ground for several hours. The AZO sample was pressed into pellets approximately 1.2 cm in diameter and 0.2 cm thick. A 5-ton force was applied with a hydraulic press for 3-5 min at room temperature to produce the pellets. The glass substrates were ultrasonically cleaned with alcohol for 10 minutes. The glass substrate was then rinsed with deionized water and dried with nitrogen gas before it was deposited.

A focused Q-switched neodymium-doped yttrium aluminum garnet Nd: $Y_3Al_5O_{12}$ (Nd: YAG) in TEM00 mode laser was used, with primary and secondary harmonic outputs at 1064 nm and 532 nm, respectively. Prior to heating the source, the vacuum chamber pressure was evacuated to 10^{-3} Torr. The targets were ablated using the laser system, with a 6 Hz frequency, 600 pulse number, and 100 mJ/pulse energy [32]. The incident laser beam's target angle was 45°. The AZO sample was melted at a pulse duration of 10n s. The distance between the substrate and target was maintained at ~2.0 cm. The target and laser source distance was ~12 cm. The thicknesses of AZO thin films were 100 nm, as estimated utilizing an optical reflectometer (Model:Filmetrics F20). PLD was used to deposit the AZO pellets (Instruments, Iraq) on glass substrates [32].

3. Results and discussion

3.1. Optical properties

UV-VIS spectroscopy was used to characterize the visual properties of the ZnO. The spectra of undoped ZnO and Al-doped ZnO were measured from 200 nm to 1100 nm wavelengths. Fig. 1 shows the results.

The spectra of the undoped ZnO are shown in Fig. 1a, and the spectra of 6% Al: ZnO and 12% Al: ZnO are presented in Figs. 1b and 1c. Fig. 1 shows that as the Al ratios increased, the films' optical transmittance considerably improved. This was because the aluminum introduced improved the crystal structure, decreasing the surface roughness. As the Al ratios increased, the AZO samples' optical transmittance increased within a 200-110 nm wavelength region range. The pure ZnO films' optical transmittance spectra increased as the Al doping ratios increased. The films' optical transmittance spectra were higher than 80%. This indicated that the films can serve as transparent oxides in solar cells. The films' transmittance fell below 380 nm due to band edge absorption [33].

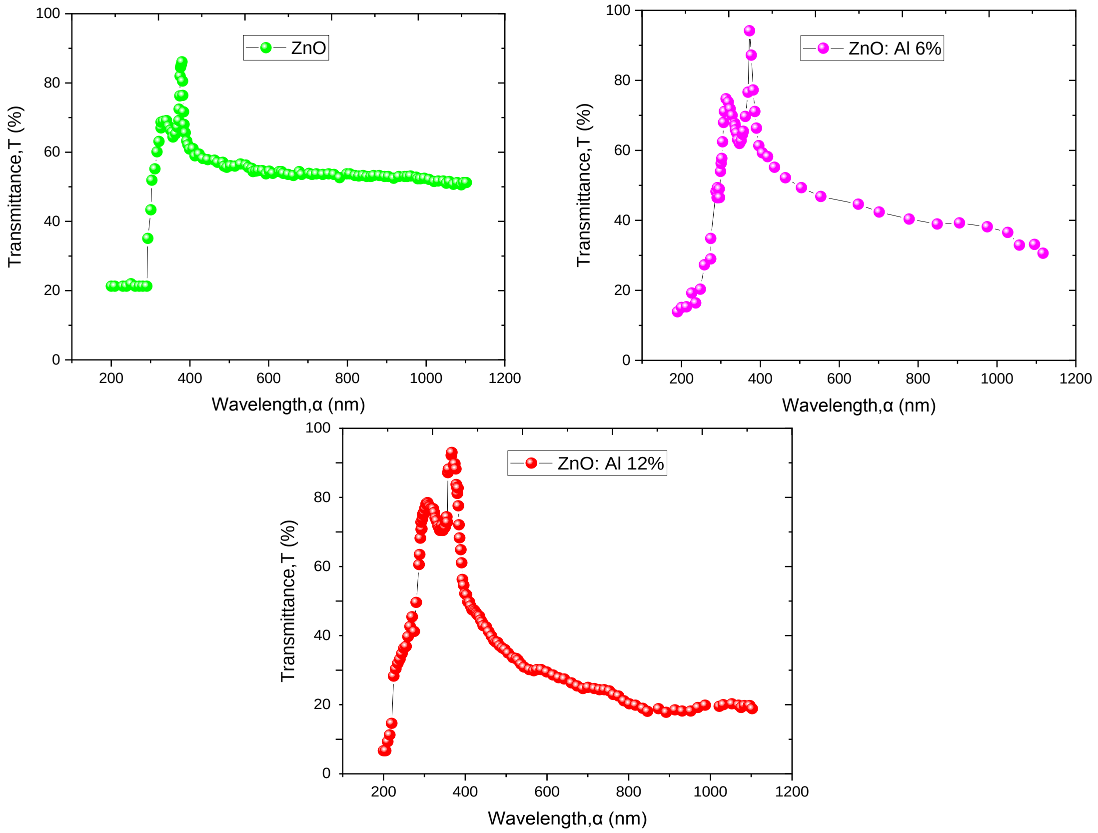

Fig. 1. Transmittance spectra of the undoped and Al-doped ZnO thin films deposited onto glass substrates: (a) pure ZnO, (b) Al-doped ZnO-6, and (c) Al-doped ZnO-12.

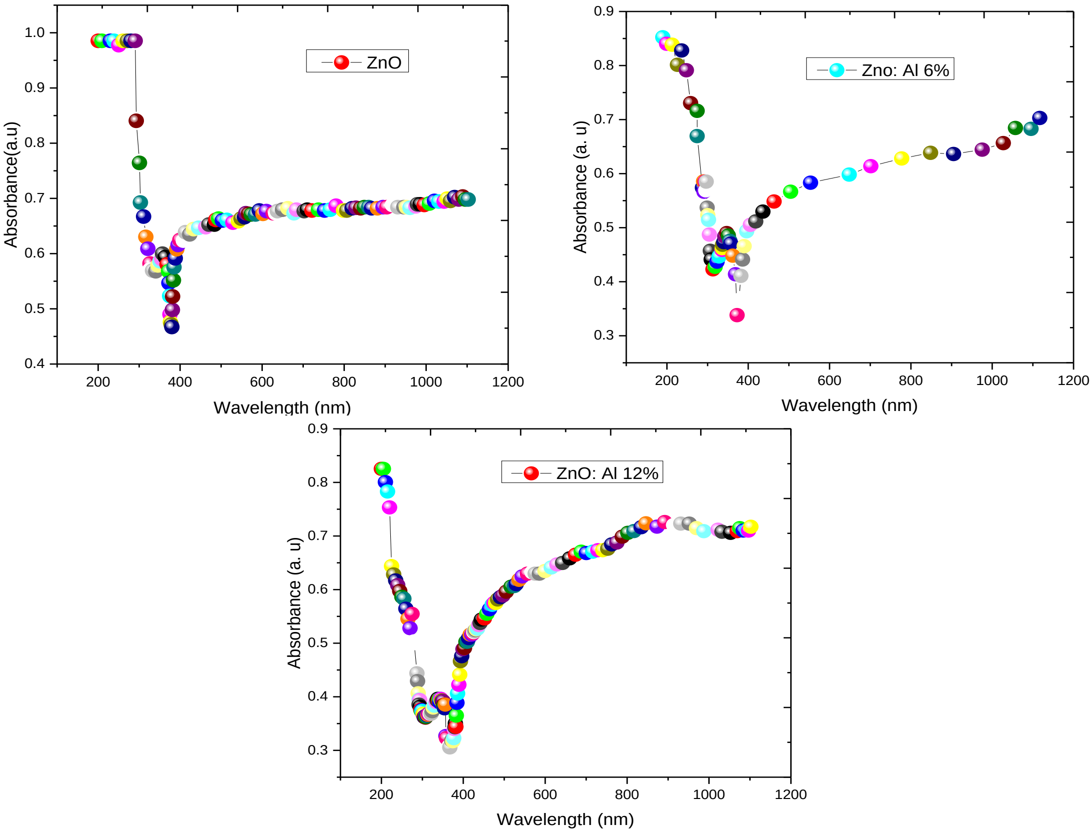

Fig. 2. Absorbance spectra of the undoped and Al-doped ZnO thin films deposited onto glass substrates: (a) pure ZnO, (b) Al-doped ZnO-6, and (c) Al-doped ZnO-12.

The optical absorbance was examined between a wavelength range of 200 nm and 1100 nm (Fig. 2). The spectra of the pure ZnO are shown in Fig. 2a, and the spectra of the 6% Al: ZnO and 12% Al: ZnO are presented in Figs. 2b and 2c. The undoped ZnO had a higher absorbance in the UV region compared to the doped sample. At a 200 nm wavelength, the film had a high spectral absorbance that fell sharply to 400 nm and decreased slowly as the wavelength increased, which differed with increased aluminum doping. These values were the same as those reported by Samuel I. Nworie and Emmanuel I. Ugwu [34].

The ZnO-Al films' transmittance data were used to calculate the spectral absorption coefficient. Lambert's formula was used to calculate the absorption coefficient α [35, 36]:

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \tag{1}$$

where d and T are the film's thickness and transmittance, respectively. Fig. 3 shows the visual absorption coefficient vs incident photon wavelength. The spectra of the undoped ZnO are shown in Fig. 3a, and the spectra of the 6% Al: ZnO and 12% Al: ZnO are presented in Figs. 3b and 3c. The absorption coefficients in the UV region were higher than those in the visible region and decreased with the Al doping. However, those in the UV region changed only slightly with the Al doping, possibly due to the decreasing optical band gap.

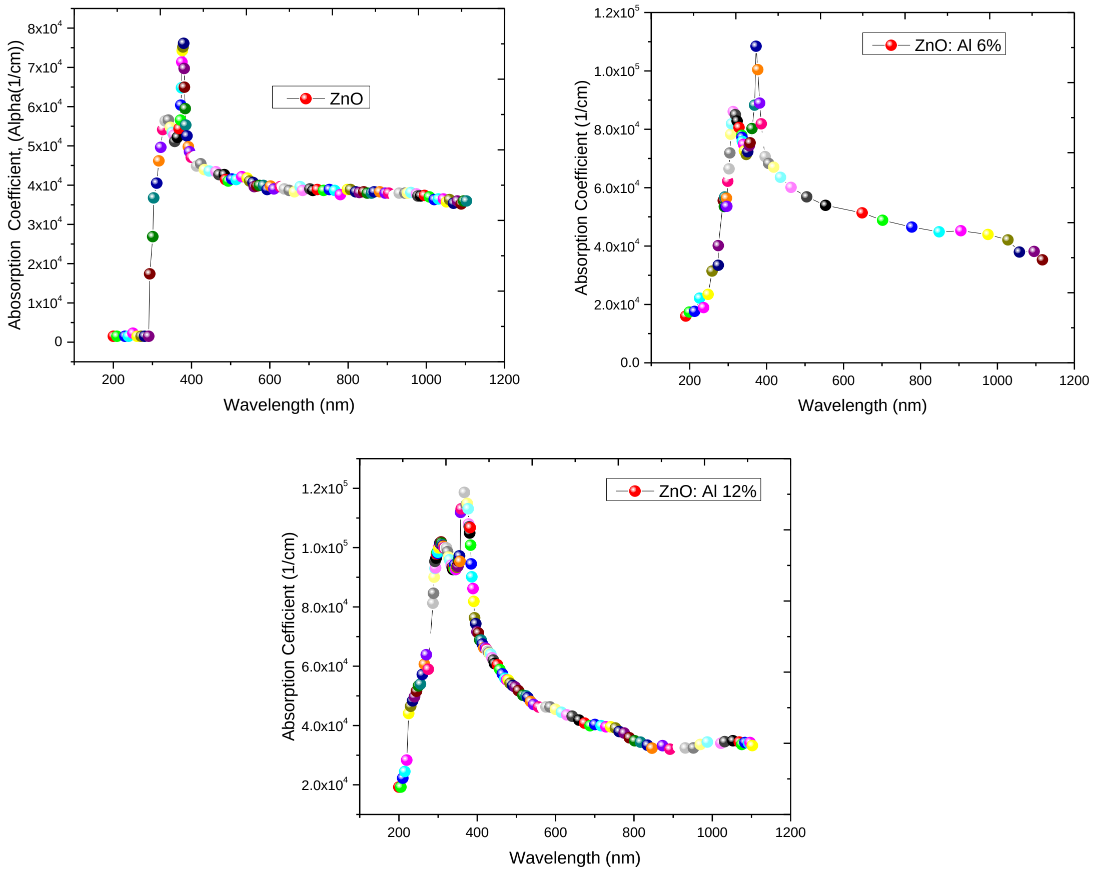

Fig. 3. Absorption coefficient spectra of the undoped and Al-doped ZnO thin films deposited onto glass substrates: (a) undoped ZnO, (b) Al-doped ZnO-6, and (c) Al-doped ZnO-12.

ZnO is a direct band gap material [37]; to estimate its energy gap (E_g), there should be a direct transition between the valance and conduction bands. Tauc's model was used to calculate the thin films' optical band gaps [38]:

$$\alpha h\nu = A\,(h\nu - E_g)^{1/2} \tag{2}$$

where $h\nu$ is the photon energy, E_g is the optical band gap energy, and A is a constant and the material's refractive index.

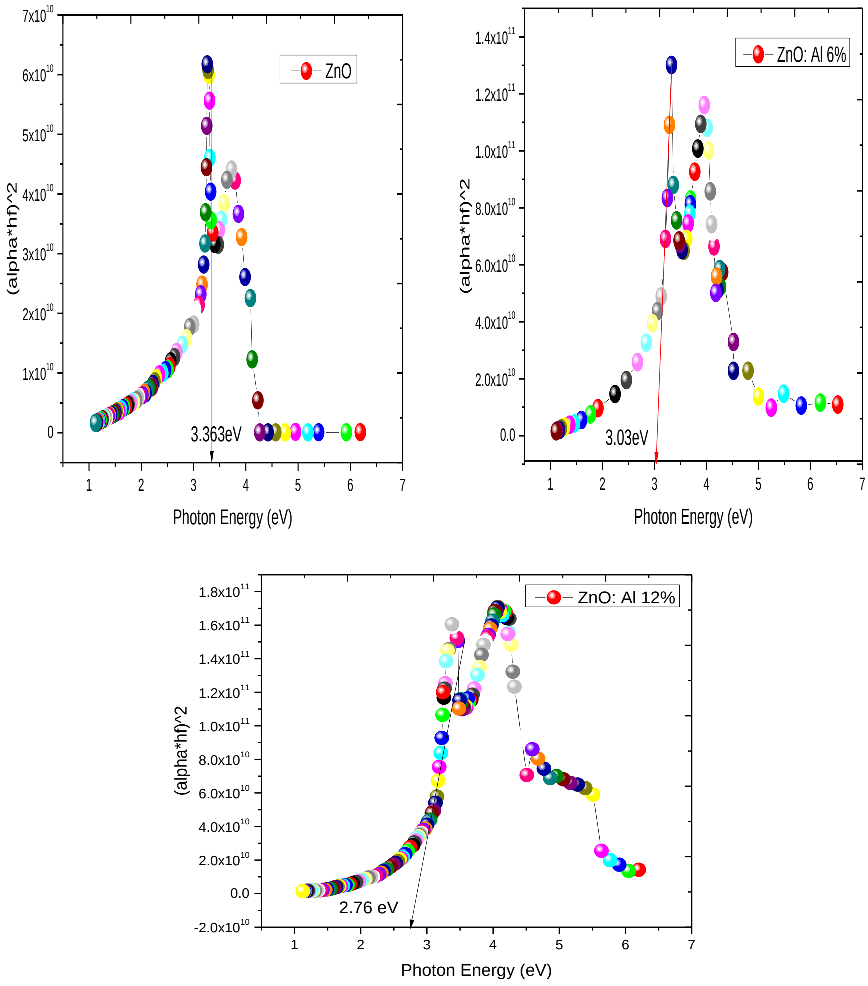

Fig. 4. Band gap energy spectra of the undoped and Al-doped ZnO thin films deposited onto glass substrates: (a) pure ZnO, (b) Al-doped ZnO-6, and (c) Al-doped ZnO-12.

A Tauc plot $(\alpha h\nu)^2$ vs $h\nu$ was used to calculate the optical band gap energy by setting the linear region in the graph to $(\alpha h\nu)^2 = 0$. Fig. 4 shows a plot of $(\alpha h\nu)^2$ vs hν of the pure and Al-doped ZnO films. The spectra of the undoped ZnO are shown in Fig. 4a, and the spectra of the 6% Al: ZnO and 12% Al: ZnO are presented in Figs. 4b and 4c. Incorporating Al decreased the Al: ZnO films' band gaps compared to the undoped ZnO films. In the 6% (3.03 eV) and 12% (2.76 eV) AZO films, the band gaps decreased compared to the undoped ZnO. This indicated that the absorption edge red shifted [39, 40]. The spectra of the Al-doped ZnO thin films' optical band gaps at various concentrations are shown in Fig. 5. The optical band gaps of the ZnO incorporated at 0% Al, 6% Al, and 12% Al were 3.37 eV, 3.03 eV, and 2.76 eV, respectively. As the Al concentration increased, the values of the band gap energies began to decrease.

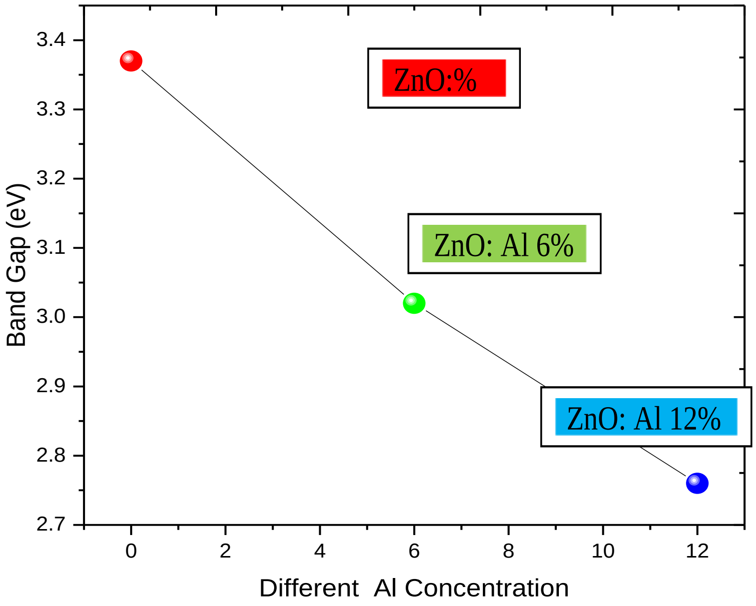

Fig. 5. Optical band gaps of the Al-doped ZnO thin films prepared at different concentrations.

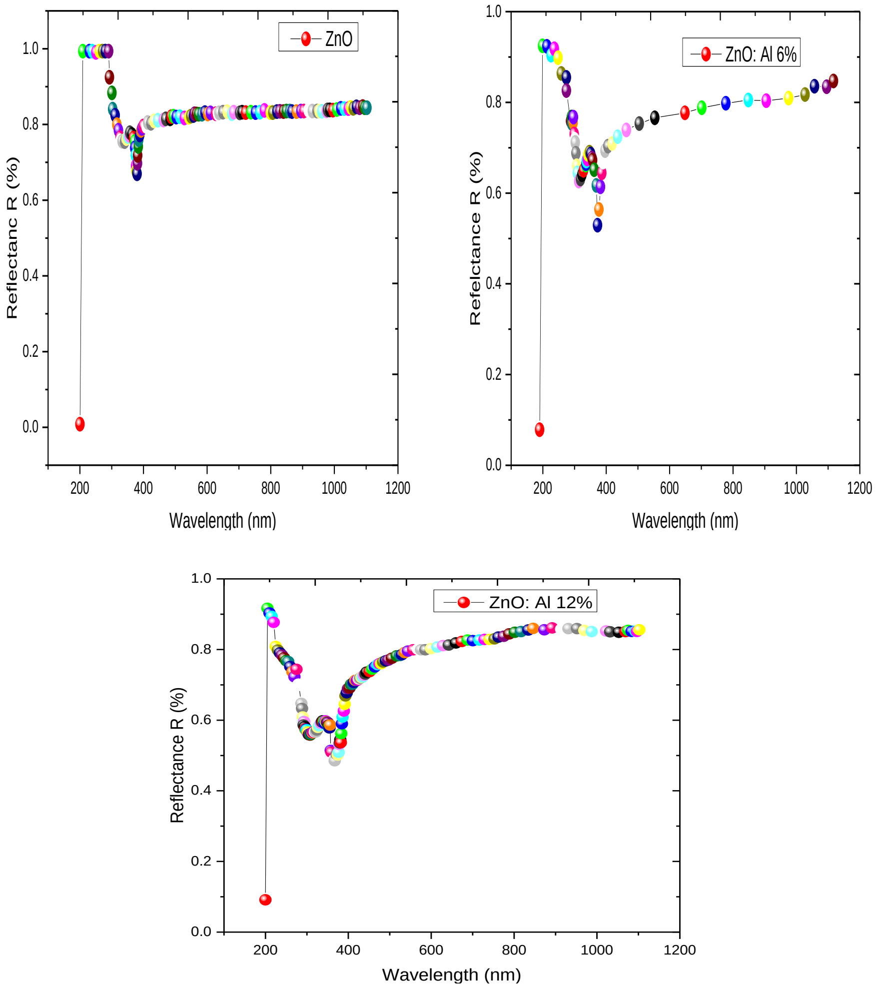

Fig. 6. Reflectance spectra of the undoped and Al-doped ZnO thin films deposited onto glass substrates: (a) pure ZnO, Al-doped ZnO-6, and (c) Al-doped ZnO-12.

Fig. 6 shows the optical reflectance in a wavelength range between 200 nm and 1100 nm. The spectra of the undoped ZnO are shown in Fig. 6a, and the spectra of the 6% Al: ZnO and 12% Al: ZnO are presented in Figs. 6b and 6c. The ZnO thin films' reflectance was high within the UV region and gradually decreased from 300 to 400 nm. The highest value was > 90% and the lowest was< 50%. The films' reflectance decreased as the doping ratio increased, suggesting that this material can be used in anti-reflection coating or for anti-reflectance applications.

The refractive index is a fundamental parameter of visual materials and uses. Fig. 7 shows the refractive indices calculated at wavelengths of 200 nm and 1100 nm. The refractive index n in the UV region obviously decreased as the wavelength and Al doping concentration increased. The spectra of the undoped ZnO are shown in Fig. 7a, and the spectra of the 6% Al: ZnO and 12% Al: ZnO are presented in Figs. 7b and 7c. The films' refractive index decreased slowly as the Al doping level increased. This indicated that the Al doping level could be used to modulate the refractive index. A decrease in the samples' refractive index indicated in increase in their visual transmission.

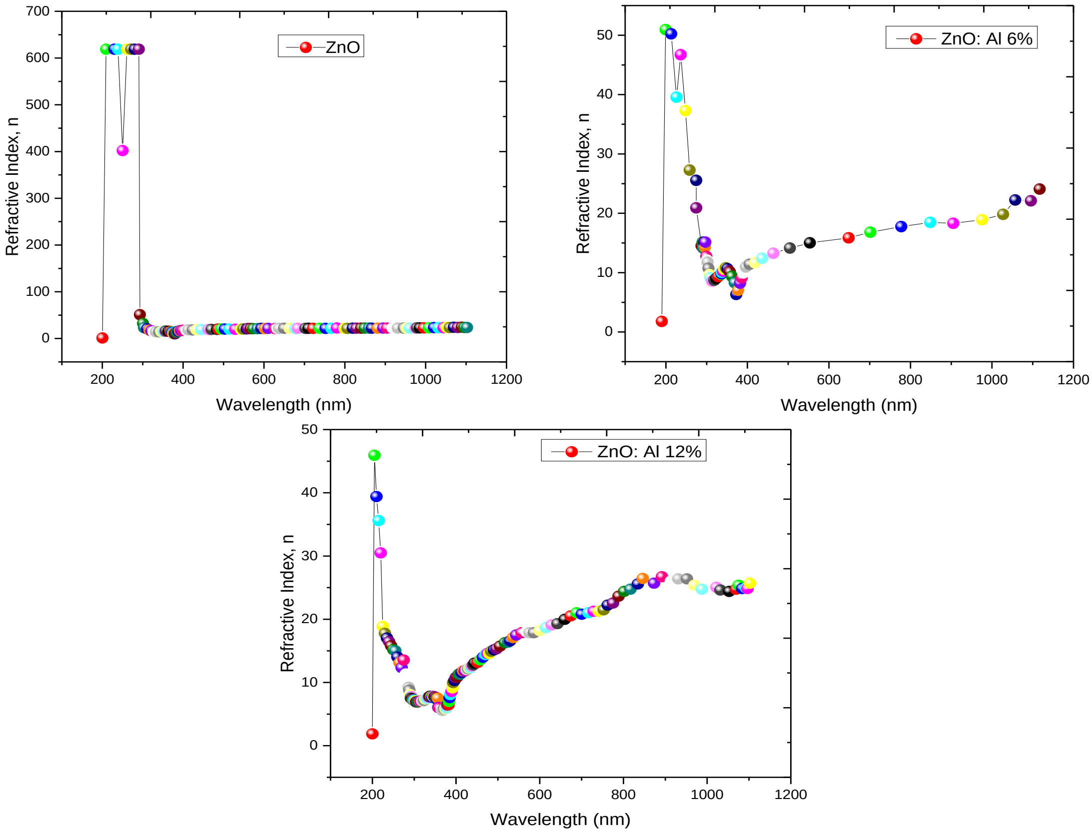

Fig. 7. Refractive index spectra of the undoped and Al-doped ZnO thin films deposited onto glass substrates: (a) Pure ZnO, (b) Al-doped ZnO-6, and (c) Al-doped ZnO-12.

The extinction coefficient (k) spectra of the undoped ZnO are shown in Fig. 8a, and the spectra of the 6% Al: ZnO and 12% Al: ZnO are presented in Figs. 8b and 8c. There extinction coefficient sharply decreased as the wavelength in the UV region increased. As demonstrated in Fig. 8, the extinction coefficient increased as the Al doping concentration increased. The optical constants of the undoped ZnO films obtained by ALD corroborated with our prior study [41].

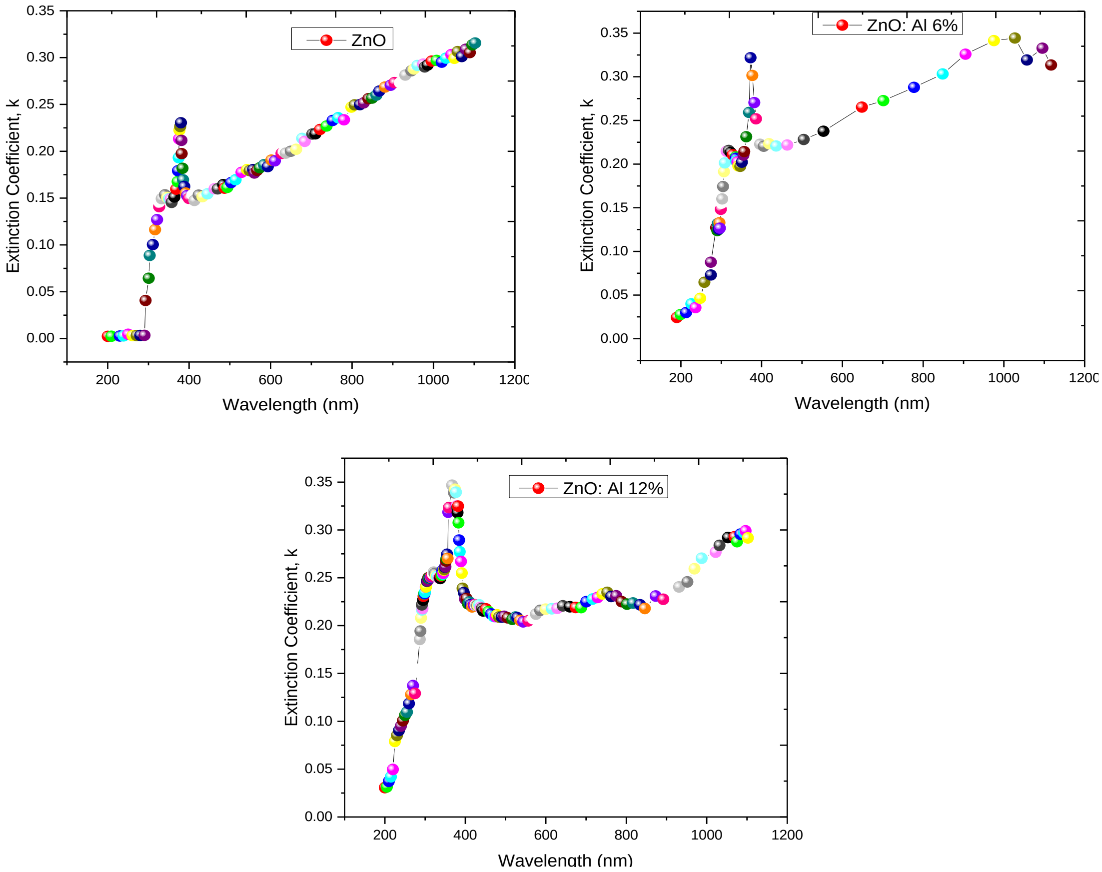

Fig. 8. Extinction coefficient spectra of the pure and Al-doped ZnO thin films deposited onto glass substrates: (a) pure ZnO, Al-doped ZnO-6, and (c) Al-doped ZnO-12.

4. Conclusion

PLD was successfully used to deposit undoped and Al-doped ZnO films onto glass substrates. This study analyzed the thin films' optical properties. The undoped ZnO films' optical transmittance values were higher than 80% in the UV region and decreased as the Al doping concentration increased. The absorption coefficient spectra showed that the films were clearly seen in the UV region and had high absorption properties in the UV region. The optical band gap energy decreased as the doping ratio increased. The refractive index values decreased as the Al doping ratio increased, increasing the doped samples' transmittance. The ZnO thin films' extinction coefficient decreased as the Al concentration increased.

Acknowledgments

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References

[1] B. K. Sharma, N. Khare and D. Haranath Solid State Commun., 150 (2010) 2341; https://doi.org/10.1016/j.ssc.2010.10.002

[2] M. G. Faraj and M. H. Eisa, Dig. J. Nanomater. Biostructures. , 14 (2019) 471.

[3] H. W. Lee, S. P. Lau, Y. G. Wang, K. Y. Tse, H.H. Hng and B. K. Tay, J. Cryst. Growth, 268 (2004) 596; https://doi.org/10.1016/j.jcrysgro.2004.04.098

[4] S. B. Ghaffari, M. H. Sarrafzadeh, Z. Fakhroueian, S. Shahriari and M. R. Khorramizadeh, Mater. Sci. Eng. C ,79(2017) 465; https://doi.org/10.1016/j.msec.2017.05.065

[5] S. Sruthi, J. Ashtami and P. V. Mohanan, Mater. Today Chem. , 10 (2018) 175; https://doi.org/10.1016/j.mtchem.2018.09.008

[6] K. McNamara and S. A. M. Tofail, Adv. Phys. : X, 2 (2017) 54; https://doi.org/10.1080/23746149.2016.1254570

[7] S.M. Park, T. Ikegami and K. Ebihara, Thin Solid Films, 513 (2006) 90; https://doi.org/10.1016/j.tsf.2006.01.051

[8] T. Tynell, H. Yamauchi, M. Karppinen, R. Okazaki and I. Terasaki, J. Vac. Sci. Technol. A,31 (2013) 01 A109; https://doi.org/10.1116/1.4757764

[9] H. Gong, J. Q. Hu, J. H. Wang, C. H. Ong and F. R. Zhu, Sensors Actuators B: Chem., 115 (2006) 247; https://doi.org/10.1016/j.snb.2005.09.008

[10] S. Singh, R. Nunna, C. Periasamy and P. Chakrabarti, Int. J. Contemp. Res. Eng. Tech., 1(2011) 14.

[11] C. Periasamy and P. Chakrabarti, J. Electron. Mater.,40 (2011) 259; https://doi.org/10.1007/s11664-010-1428-5

[12] S. Y. Myong, S. J. Baik, C. H. Lee, W. Y. Cho, and K. S. Lim, Jpn. J. Appl. Phys., 36(1997) L1078; https://doi.org/10.1143/JJAP.36.L1078

[13] V. Assuncao, E. Fortunato, A. Marques, H. Aguas, I. Ferreira, M. E. V. Costa, and R. Martins, Thin Solid Films 427(2003) 401; https://doi.org/10.1016/S0040-6090(02)01184-7

[14] M.G.Faraj and P. Taboada, J. Mater. Sci. Mater. Electron ., 28 (2017) 16504; https://doi.org/10.1007/s10854-017-7562-6

[15] E. B. Pollock and R. J. Lad J. Vac. Sci. Technol. A, 32 (2014), 041516; https://doi.org/10.1116/1.4885063

[16] D. J. Lee, H. M. Kim, J. Y. Kwon, H. Choi, S. H. Kim, K. B. Kim, Adv. Funct. Mater., 21 (2011) 448; https://doi.org/10.1002/adfm.201001342

[17] L. Gong, J. Lu and Z. Ye, Solar Energy Materials Solar Cells 94 (2010) 937; https://doi.org/10.1016/j.solmat.2010.02.026

[18] F. Maldonado and A. Stashans, J. Phys. Chem. Solids, 71 (2010) 784; https://doi.org/10.1016/j.jpcs.2010.02.001

[19] P. Raghu, N. Srinatha, C. S. Naveen, M. H. Mahesh and B. Angadi, J. Alloys Compd. 694 (2017) 68; https://doi.org/10.1016/j.jallcom.2016.09.290

[20] C. Agashe, O. Kluth, J. Hüpkes, U. Zastrow and B. Rech, Int. J. Appl. Phys., 95 (2004) 1911; https://doi.org/10.1063/1.1641524

[21] H. M. Zhou, D. Q. Yi, Z. M. Yu, L.R. Xiao and J. Li, Thin Solid Films, 515 (2007) 6909; https://doi.org/10.1016/j.tsf.2007.01.041

[22] X. Wang and Y. Zhang, Mater. Lett. , 188 (2017) 257; https://doi.org/10.1016/j.matlet.2016.10.119

[23]C-H. Zhai, R-J. Zhang, X.Chen , Y-X. Zheng, S-Y. Wang, J. Liu, N. Dai and L.Y. Chen , Nanoscale Res. Lett. 11 (2016) 407; https://doi.org/10.1186/s11671-016-1625-0

[24] G. Kaurn, A. Mitra and K.L. Yadav, Prog. Nat. Sci., 25 (2015) 12; https://doi.org/10.1016/j.pnsc.2015.01.012

[25] R. Ayouchi, D. Leinen, F. Martín, M. Gabas, E. Dalchiele and J. R. Ramos-Barrado, Thin Solid Films 426(2003) 68; https://doi.org/10.1016/S0040-6090(02)01331-7

[26] L. Zhao, J. Lian, Y. Liu and Q. Jiang, Appl. Surf. Sci., 252 (2006) 8451; https://doi.org/10.1016/j.apsusc.2005.11.054

[27] H. Sankur and J. T. Cheung, J. Vac. Sci. Technol, A 1(1983) 1806; https://doi.org/10.1116/1.572219

[28] T. Nakayama, Surf. Sci. , 133 (1983) 101; https://doi.org/10.1016/0039-6028(83)90486-7

[29] K. Wasa, M. Kitabatake and H. Adachi, 'Deposition of Compound Thin Films', in "Thin Film Materials Technology - Sputtering of Compound Materials", Ch. 5, William Andrew Inc, Norwich, New York, USA, (2004) 191-403; https://doi.org/10.1016/B978-081551483-1.50006-X

[30] W.Y. Zhang, D.K. He, Z.Z. Liu, L.J. Sun and Z.X. Fu, , J. Optoelectron. Adv. Mater - Rapid Commun. 4 (2010) 1651.

[31] H. J. Choi, W. Jang, B. C. Mohanty, Y. S. Jung, A. Soon and Y. S. Cho, J. Phys. Chem. Lett., 9 (2018) 5934; https://doi.org/10.1021/acs.jpclett.8b02474

[32] M. H. Eisa, Mater. Sci. Semicond. Process. , 110 (2020) 104966; https://doi.org/10.1016/j.mssp.2020.104966

[33] J. I. Pankove, "Optical Process in Semiconductors", Dover Publishing, Inc., New York. (1971).

[34] S. I. Nworie and E. I. Ugwu , Pac. j. sci. technol. , 21 (2020) 40.

[35] R. K. Shukla, A. Srivastava, A. Srivastava and K.C. Dubey, J. Cryst. Growth, 294 (2006) 427; https://doi.org/10.1016/j.jcrysgro.2006.06.035

[36] Y.J. Choi, S.C. Gonga, D.C. Johnson, S. Golledge, G.Y. Yeom and H.H. Park, Appl. Surf. Sci., 269 (2013) 92; https://doi.org/10.1016/j.apsusc.2012.09.159

[37] N. Choudhury and B. K. Sarma, Bull. Mater. Sci. , 32 (2009) 43; https://doi.org/10.1007/s12034-009-0007-y

[38] X. Li, H. Zhu, J. Wei, K. Wang, E. Xu, Z. Li and D. Wu, Appl. Phys. A, 97 (2009) 341; https://doi.org/10.1007/s00339-009-5330-z

[39] M. Ahmad, E. Ahmed, Y. Zhang, N. R. Khalid, J. Xu, M. Ullah and Z. Hong, Curr. Appl. Phys., 13 (2013) 697; https://doi.org/10.1016/j.cap.2012.11.008

[40] C. Wu, L. Shen, H. Yu, Q. Huang and Y.C. Zhang, Mater. Res. Bull. , 46 (2011) 1107; https://doi.org/10.1016/j.materresbull.2011.02.043

[41] Z-H. Dai, R-J. Zhang, J. Shao , Y-M Chen, Y-X Zheng, J-D W and L-Y. Chen, J Korean Phys Soc.,55 (2009) 1227; https://doi.org/10.3938/jkps.55.1227