X-ray Diffraction, XPS, and Raman Spectroscopy of Coated ZnO:Al (1–7 at%) Nanoparticles

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Group III elements doping for zinc oxide is currently attracting much attention for the study of absorber layer in nano-optoelectronic and photovoltaic devices as an alternative route to indium tin oxide (ITO) due to their optimized properties. In this report, Al-doped ZnO (AZO, Al: 1–7 at%) nanoparticles have been successfully deposited onto glass substrates using sol-gel process, and investigated by techniques such as X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The coated ZnO:Al nanoparticles at Al concentration up to 5 at% showed a nanosized polycrystalline structure with a c-plane preferred orientation. In AZO (7 at%), lower diffraction peaks were observed. The crystallite size calculated from XRD was ranged 38.7–43.5 nm. SEM showed spherical nanoparticles in shape with a smooth surface. The Raman results provided peaks located at 434, 435, 559, 851, and 1090 cm⁻¹. According to XPS, the as-grown nanoparticles present the most intense peak located at about 1021.8 eV, assigned to the Zn 2p₃/₂ corresponding to zinc oxide. It was concluded that the structural properties of AZO thin films were improved with Al (5 at%), and these samples may be considered as an alternative of costly ITO in thin-film photovoltaic applications.

Keywords: ZnO:Al (1–7 at%); X-ray; Raman; XPS; Structural properties

I. INTRODUCTION

Nowadays, doping semiconductor materials with two metal ions [Sn-doped In₂O₃ (ITO), SnO₂:Sb, ZnO:Ga, ZnO:Al, etc.] have been investigated due to their properties and applications in visible and UV-regime wavelengths [1–3]. These materials exhibit the highest microstructure in transparent electronics which is a relatively new science and technology, focused on producing invisible circuitry [3]. Doping is a process by which a small amount of impurities or elements are added to pure semiconducting materials in order to modify its properties for many applications [2, 3]. Among them, zinc oxide is an n-type semiconductor which presents new properties when doping with appropriate group III elements (Al, Ga, In, etc.) [4]. Based on the reported works of the doping effect of ZnO, Al element is considered as a suitable choice for dopant materials in terms of its availability, non-toxicity, more resistant to oxidation, Al ions which have a similar ionic radius compared to Zn, resulting in small zinc oxide lattice deformations, less reactive [4, 5], etc. Therefore, Al-doped ZnO (AZO) is one of the best n-type oxide materials reported to date to be an effective ITO alternative to enhance the microstructure, electrical and optical properties for various applications such as fabrication of photonics and optoelectronic devices [6–8], phthalocyanine-based organic photovoltaics [9].

Techniques addressed to study doped ZnO effects on the properties of AZO films including electrospray method [9],
pulsed laser deposition (PLD) [10], RF magnetron sputtering technique [11], atomic layer deposition [12], chemical bath deposition (CBD) [13], sol-gel process [14, 15], etc. have been used to deposit AZO nanoparticles. Furthermore, each of these methods results in particular properties of the resultant films. However, the sol-gel method is widely used, since it provides a low-cost equipment for a film with high surface uniformity and packing density. So far, it is interesting to note that the sol-gel process is the most favored chemical technique for samples to achieve best properties [14, 15].

Improved properties have been reported for Al doping in ZnO nanoparticles. Islama et al. [4] reported the structural, optical and photocatalysis properties of sol-gel deposited Al-doped ZnO. The results showed that thin films with better photocatalytic activity compared to the undoped ZnO films. Zhai et al. [16] have investigated the effects of Al doping on the properties of ZnO thin films deposited by atomic layer deposition and demonstrated the evolution from (002) to (100) diffraction peaks with increasing Al doping level, indicating the change in the growth mode of ZnO films. In addition, a blue shift of band gap and absorption edge can be observed with increasing carrier concentration after Al doping. Researchers [17–22] also studied the doped zinc oxide thin films and concluded for diverse properties.

When correlating the doping efficiency with the Al-dopant nanoparticles properties, it should be realized that several works have been done. Obviously, the doping level and the doping efficiency of Al-doped ZnO films prepared by different routes are important factors determining the performance of the films. Despite the considerable research works in growing ZnO:Al thin films, the improvement in performance of the films. Despite the considerable research works in growing ZnO:Al thin films, the improvement in the properties of Al doped ZnO materials still continues in order to develop a better understanding of its properties for new applications. Therefore, in this paper, we reported the synthesis of four AZO (Al: 1−7 at%) samples prepared by the sol-gel process, and the surface morphology, crystallinity, and chemical composition of these films were studied. The as-grown Al-doped ZnO nanoparticles were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy techniques.

II. EXPERIMENTAL

Zinc acetate dehydrate [Zn(CH3COO)2·2H2O] (99.5%, Merck) was first dissolved at room temperature into 2-methoxyethanol (2-Me) solution with the addition of sol stabilizer monoethanolamine (MEA). The molar ratio of MEA to zinc acetate 2-hydrate was kept at 1. The resulting solution was then stirred under reflux at 60°C during 1 h to yield a clear and homogeneous solution. The doping solution, composed of ethanolic solution of aluminum nitrate nonahydrate [Al(NO3)3·9H2O], was added drop by drop. The ratio of dopant (Al3+/Zn2+) varied from 1 at% to 7 at%. Then, it was left under reflux for 1 h at 60°C to obtain a clear and quite yellowish solution. This coating solution was removed and transferred into another flask and kept under stirring at room temperature to serve as AZO solution.

The above sol was then spin-coated uniformly on glass substrate at room temperature with a rate of 3000 rpm for 30 s. After each layer deposition, the spin-coated AZO/glass assembly was heat-treated at 300°C for 10 min to evaporate the solvent and remove organic residual. The processing step was repeated for five times to obtain a desired thickness. Finally, the AZO thin films were subsequently annealed at 550°C for 2 h.

The samples were characterized by XRD methods using a Philips diffractometer. The diffraction patterns were recorded at room temperature from 0° to 80° of 2θ using Cu Ka (λ = 1.54080 Å) radiation at 0.02° min−1 scanning speed and a counting time of 2 s per step. Surface morphology was observed using scanning electron microscopy (SEM, JSM-6490LV) operating at an accelerating voltage of 20 kV. The Raman spectra of the samples were recorded by using EZ Raman-N-785 spectrometer. The DC (I−V) characteristics of samples were analyzed between 25 V and 45 V using a Keithley 2636B source meter. XPS measurements were obtained with an X-ray photoemission spectrometer using Al Ka (hv = 1486.6 eV) radiation from an X-ray source operated at 10 kV with a current setting of 20 mA for detailed spectra and 5 mA for overview spectra. Photoelectrons were detected with a hemispherical analyzer. Binding energies (BE: ±0.1 eV) were calculated using advent C 1s = 284.6 eV as the reference.

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the Al-doped zinc oxide thin films grown on glass substrates, recorded in 2θ−2θ geometry in the range 0°−80°, are presented in Figures 1–4.

From the diffractograms, we can observe indices (hkl) corresponding to (100), (002), (101), (102), (110), (103), (112), and (201) planes. No additional diffraction peaks related to Al2O3 or other impurities are observed, which show that Al3+ ions were substituted into Zn2+ ion sites or incorporated into the interstitial sites in the ZnO lattice [21, 22]. The presence of various diffraction peaks match well with the hexagonal wurtzite-type crystal structure of ZnO, having space group P63mc (JCPD 36-1451), and suggest that the coated films are polycrystalline in nature [23]. All the films present (002) peak in the XRD patterns indicating that the Al-doped zinc oxide films have a preferred orientation c-axis. Whereas, in Figure 4, the weaker orientations are observed. When the Al dopant concentration was increased to 5 at%, films exhibited an intense (002) preferential orientation with sharper defined diffraction peaks indicating an increase in the crystallinity. The dominance of the (002) peak, as well as the enhancement of the c-axis orientation with the Al concentration increasing was also observed in previous reports [15, 24]. By
comparing diffraction peaks of Al-doped samples in all of the four diffractograms, we find that the diffraction peaks decrease significantly with 7 at% Al concentration, which confirms a large amount of Al dopants produce lattice disorder in crystalline [14, 20]. The disordering of the crystalline for higher Al dopant concentration, due to impurity scattering, was concluded by Karmakar et al. [25]. The mean crystallite size ($D$) of the synthesized samples was estimated by the X-ray line broadening method using Scherrer’s formula [26]:

$$D = \frac{k\lambda}{\beta \cos \theta},$$  \hspace{1cm} (1)$$

where $k$ is the Scherrer’s constant usually taken to be 0.9, but its value depends greatly on the crystallite shape [27], $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg diffraction angle, and $\beta$ is the broadening of the diffraction line measured at half of its maximum intensity (rad).

The breadth of the peak is a combination of both instrument and sample dependent effects. To decouple these contributions, it is necessary to collect a diffraction pattern from the line broadening of a standard material to determine the instrumental broadening.

The instrument-corrected broadening $\beta$ corresponding to the diffraction peak of ZnO was estimated using the following equation [26]:

$$\beta^2 = \beta^2_{\text{measured}} - \beta^2_{\text{instrumental}},$$  \hspace{1cm} (2)$$

where $\beta_{\text{measured}}$ is the observed full-width half maximum from the XRD is pattern and $\beta_{\text{instrumental}}$ is the full-width half maximum of the standard material taken. Eq. (1) can be transformed as follows;

$$\cos \theta = \frac{k\lambda 1}{D \beta}.$$  \hspace{1cm} (3)$$

By plotting with $1/\beta$ on the $x$-axis and $\cos \theta$ along the $y$-axis for films prepared at different atomic concentrations.

Table 1: Crystallite sizes and dislocation density for as-deposited thin films.

| Sample (at%) | Crystallite size $D$ (nm) | $\delta$ ($10^{14}$ m$^{-2}$) |
|--------------|--------------------------|------------------|
| 1            | 38.4                     | 6.67             |
| 3            | 40.9                     | 5.97             |
| 5            | 43.5                     | 5.28             |
| 7            | 34.8                     | 8.25             |
of Al, and fitting the data, a straight line is obtained in which the slope indicates the mean crystallite size value ($D$). The typical Scherrer plot for Al (1 at%) is shown in Figure 5. The estimated values are presented in Table 1.

The dislocation density $\delta$ represents the magnitude of defects in a film and is determined as follows [28];

$$\delta = \frac{1}{D^2}.\quad (4)$$

For the as-grown Al doped-ZnO nanoparticles, the dislocation density is summarized in Table 1.

Figure 6 shows room temperature Raman spectra of 1, 3, 5, and 7 at% Al-doped ZnO measured in the range 0–1050 cm$^{-1}$. The Raman spectra of the samples show several peaks at 434, 435, 559, 851, and 1090 cm$^{-1}$. No other second phase like aluminum or Al2O3 is identified in all the as-grown films, which suggests that the Al ions are interstitially incorporated into ZnO lattice, confirming the X-ray diffraction results.

At the center of the Brillouin zone (the $\Gamma$ point), the phonons for wurtzite zinc oxide belong to the following irreducible representation [29]:

$$\Gamma_{\text{optical}} = A_1 + E_1 + 2B_1 + 2E_2,\quad (5)$$

where $A_1$, $E_1$, and $E_2$ are the first order Raman active modes. $B_1$ is forbidden, $E_1$ and $A_1$ are the polar Raman and infrared active modes, and they split into transverse optical (TO) and longitudinal optical (LO) phonons. According to the Raman selection rules, the $E_2$ and $A_1$ (LO) modes can be observed in unpolarized Raman spectra taken in backscattering geometry [30]. $E_2$ is nonpolar modes and splits into high and low frequency phonons.

Regarding previous works, the observed Raman modes for the as-grown Al-doped ZnO nanoparticles up to Al (5 at%) are assigned to standard modes of ZnO wurtzite structure lattice vibration with space group $C_{6h}^2$ ($P6_3mc$) [31]. Relative peaks $E_2^{\text{high}}$ located at 434 cm$^{-1}$ and 435 cm$^{-1}$ were observed in the 1 at% and 3 at% Al-doped ZnO samples compared to the usual position of a ZnO thin film at 437 cm$^{-1}$ [32]. This shift can be attributed to a decreased degree of order in the wurtzite phase. In the sample with 5 at% Al, three Raman modes were observed at 559, 851, and 1090 cm$^{-1}$. The peak located at 559 cm$^{-1}$ is assigned to the $A_1$ (LO) mode [33]. Another $A_1$ (TO) mode is observed at 1090 cm$^{-1}$, and this mode is related to defects like oxygen vacancy, zinc interstitial, or their complexes [34]. It can be seen absence of Raman peaks in the sample with 7 at% Al. All Raman peaks are found to be in agreement with previous reports [31, 35].

The XPS survey spectra acquired from all the coated thin films are depicted in Figures 7–10. The photoelectron peaks corresponding to the Zn, O, and C elements can be clearly observed. The detected C 1s peak (284.60 eV) originates from the carbon species adsorbed on the surface during the exposure of the samples to the ambient atmosphere and is used as a reference for charge shift correction since its position is very stable [36].

First, one may observe that all samples show similar characteristics as the pure ZnO spectra. In Figure 7, the presence of peaks arising due to Zn 3d, Zn 3p, Zn 3s, Zn 2p$_{3/2}$, and Zn 2p$_{1/2}$ core levels is recognized along with other characteristic peaks of the C 1s and O 1s levels. Two strong peaks appear at about 1021.8 eV and 1044.6 eV, which are in good agreement with the binding energies of the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ levels, respectively. The two peaks have narrow line widths, indicating that the Zn$^{2+}$ ions are dominant in the nanostructure. The Zn 3d peak appears at 9 eV, whereas the O 1s region is presented with a broad peak at 530 eV. However, in terms of Figures 8, 9, and 10, the only relevant peak of Zn 2p$_{3/2}$ can be observed located at 1021.9 eV with characteristic peaks of the C 1s and O 1s levels. All the films present the most intense peak located at about 1021.8 eV, which was assigned to the Zn 2p$_{3/2}$ level corresponding to the zinc oxide [37]. This peak is relatively narrow and symmetric, which indicates that Zn predominantly exists in an oxidized state [38]. The C 1s spectra recorded for all samples located at 530.37–531.12 eV correspond to O$^{2-}$ ions at the intrinsic sites on the wurtzite structure of hexagonal Zn$^{2+}$ with substituted Al$^{3+}$ [39].

Figure 5: Typical Scherrer plot for Al (1 at%).

Figure 6: Raman spectra of 1, 3, 5, and 7 at% Al-doped ZnO. Raman intensity in spectral range 50–700 cm$^{-1}$. 
To examine the morphology of the as-grown films, SEM has been used. Typical SEM images are shown in Figure 11(a−d). It is very clear that the obtained nanoparticles are spherical in shape with a smooth surface. A nonuniform strain was also observed, as revealed in Figure 11(a−d). In addition, the SEM images indicate that the shape and morphology of the nanoparticles change with the Al increasing concentration, as it can be detected in Figure 11(a) which is very dense comparing to the others.

IV. CONCLUSIONS

The AZO (Al: 1−7 at%) thin films were successfully deposited onto glass substrates by the sol-gel process. It was found that the as-grown AZO thin films were polycrystalline, with a predominantly (002) preferred orientation. Increasing the Al amount dopant to 7 at%, resulted the weaker orientation of crystallites in films. A comparison of the four coated films shows that the crystallites in films deposited from a solution containing 5 at% Al, exhibited the best preferential growth along the [002] direction. The crystallite size calculated from XRD ranged from 38.7 nm to 43.5 nm.

Figure 7: XPS spectra of 1 at% Al-doped ZnO.

Figure 8: XPS spectra of 3 at% Al-doped ZnO.

Figure 9: XPS spectra of 5 at% Al-doped ZnO.

Figure 10: XPS spectra of 7 at% Al-doped ZnO.

Figure 11: SEM images of (a) 1 at%, (b) 3 at%, (c) 5 at%, and (d) 7 at% Al-doped ZnO.
The Raman results provided peaks at 434, 435, 559, 851, and 1090 cm\(^{-1}\). The as-grown nanoparticles present the most intense peak located at about 1021.8 eV, which was assigned to the Zn \(2p_{3/2}\) core level corresponding to zinc oxide according to XPS. SEM showed spherical nanoparticles in shape with a smooth surface.

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References

[1] J. Duan, Q. Xiong, D. Zhang, W. Li, H. Wang, and J. Hu, e-J. Surf. Sci. Nanotechnol. 14, 136 (2016).
[2] K. Tominaga, T. Tsuzuki, T. Maruyama, M. Mikawa, and T. Moriga, e-J. Surf. Sci. Nanotechnol. 7, 273 (2009).
[3] M. Wu, D. Sun, C. Tan, X. Tian, and Y. Huang, Materials 10, 359 (2017).
[4] M. R. Islam, M. Rahman, S. F. U. Farhad, and J. Poddar, Surf. Interfaces 16, 120 (2019).
[5] V. Avrutin, D. Silversmith, and H. Morkoc, Proc. IEEE 98, 1269 (2010).
[6] Q. Qiao, B. H. Li, C. X. Shan, J. S. Liu, J. Yu, X. H. Xie, Z. Z. Zhang, T. B. Ji, Y. Jia, and D. Z. Shen, Mater. Lett. 104 (2012).
[7] C. Klingshirn, J. Fallert, H. Zhou, J. Sartor, C. Thiele, F. Maier-Flaig, D. Schneider, and H. Kalt, Phys. Status Solidi B 247, 1424 (2010).
[8] Y. Jeong, C. Bae, D. Kim, K. Song, K. Woo, H. Shin, G. Cao, and J. Moon, ACS Appl. Mater. Interfaces 2, 611 (2010).
[9] G. Marinov, K. Lovchinov, V. Madjarova, V. Strijkova, M. Vasileva, N. Malinovska, and T. Babeva, Opt. Mater. 84, 390 (2019).
[10] J. Choi, S. K. Lee, J. H. Choi, E. H. Choi, R. Jung, and Y. Kim, Appl. Surf. Sci. Converg. Technol. 24, 273 (2015).
[11] D. K. Kim and H. B. Kim, Appl. Surf. Sci. Converg. Technol. 23, 279 (2014).
[12] Y. Wu, A. D. Giddings, M. A. Verheijen, B. Macco, T. J. Prosa, D. I. Larson, F. Roozeboom, and W. M. M. Kessels, Chem. Mater. 30, 1209 (2018).
[13] H. Kim and S. Choi, Appl. Surf. Sci. Converg. Technol. 27, 38 (2018).
[14] R. Ramadan, D. Romero, R. D. Carrascón, M. Cantero, J.-J. Aguileracorrea, J. P. G. Ruiz, J. Esteban, and M. M. Silván, ACS Omega 4, 11354 (2019).
[15] M. H. Nateq and R. Ceccato, Materials 12, 1744 (2019).
[16] 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, 407 (2016).
[17] Y. Caglar, A. Arslan, S. Ilican, E. Hür, S. Aksoy, and M. Caglar, J. Alloys Compd. 574, 104 (2013).
[18] M. W. Kadi, D. McKinney, R. M. Mohamed, I. A. Mkhulaid, and W. Sigmund, Ceram. Int. 42, 4672 (2016).
[19] L. Liu, L. Wang, X. Qin, L. Cui, and G. Shao, Thin Solid Films 605, 163 (2016).
[20] M. Caglar and F. Yakuphanoglu, Appl. Surf. Sci. 258, 3039 (2012).
[21] D. Fang, P. Yao, and H. Li, Ceram. Int. 40, 5873 (2014).
[22] D. Fang, K. Lin, T. Xue, C. Cui, X. Chen, P. Yao, and H. Li, J. Alloys Compd. 589, 346 (2014).
[23] T. V. Vimalakumar, N. Poornima, C. S. Kartha, and K. P. Vijayakumar, Mater. Sci. Eng. B 175, 29 (2010).
[24] V. Musat, B. Teixeira, E. Fortunato, R. C. C. Monteiro, and P. Vilarinho, Surf. Coat. Technol. 180, 659 (2004).
[25] R. Karmarkar, S. K. Neogi, A. Banerjee, and S. Bandyopadhyay, Appl. Surf. Sci. 263, 671 (2012).
[26] P. Scherrer, Nachr. Ges. Wiss. Göttingen 26, 98 (1918).
[27] F. K. Konan, J. S. N’cho, H. J. Tchognia Nkuissi, B. Hartiti, and A. Boko, Mater. Chem. Phys. 229, 330 (2019).
[28] H. P. Klug and L. E. Alexander, X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, 2nd ed. (Wiley, 1974).
[29] M. Tzolov, N. Tzenov, D. Dimova-Malinovska, M. Kalitzova, C. Pizzuto, G. Vitali, G. Zollo, and I. Ivanov, Thin Solid Films 379, 28 (2000).
[30] B. Cheng, Y. Xiao, G. Wu, and L. Zhang, Appl. Phys. Lett. 84, 416 (2004).
[31] R. Cuscó, E. Alarcón-Lladó, J. Ibáñez, L. Artús, J. Jiménez, B. Wang, and M. J. Callahan, Phys. Rev. B 75, 165202 (2007).
[32] V. Russo, M. Ghidelli, P. Gondoni, C. S. Casari, and A. Li Bassi, J. Appl. Phys. 115, 073508 (2014).
[33] J. Yang, M. Gao, L. Yang, Y. Zhang, J. Lang, D. Wang, Y. Wang, H. Liu, and H. Fan, Appl. Surf. Sci. 255, 2646 (2008).
[34] M. A. M. Ahmed, B. S. Mwankemwa, E. Carleschi, B. P. Doyle, W. E. Meyer, and J. M. Nel, Mater. Sci. Semicond. Process. 79, 53 (2018).
[35] S.-S. Lo, D. Huang, C. H. Tu, C.-H. Hou, and C.-C. Chen, J. Phys. D 42, 095420 (2009).
[36] M. Oku and K. Hirokawa, J. Electron Spectrosc. Relat. Phenomena 8, 475 (1976).
[37] R. Bhunia, D. Ghosh, B. Ghosh, S. Hussain, R. Bhar, and A. K. Pal, J. Compos. Mater. 49, 3089 (2015).
[38] X. C. Wang, W. B. Mi, S. Dong, X. M. Chen, and B. H. Yang, J. Alloy. Compd. 478, 507 (2009).
[39] E. De la Rosa, S. Sepúlveda-Guzman, B. Reeja-Jayan, A. Torres, P. Salas, N. Elizondo, and M. Jose Yacamán, J. Phys. Chem. C 111, 8489 (2007).

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