

Structural and Morphological Properties of Al doped ZnO Nanoparticles

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Abstract. Zinc oxide nanoparticles have a wide area of use because of their unique properties such as catalytic, electrical, and optical properties and low cost. Since the suitable additive materials can be changed the electrical and optical properties of zinc oxide, the demand of the industrial commercial area to the zinc oxide increased. In this study, Al doped ZnO nanoparticles produced by using the methods of reduction thought having materials of the $\text{Zn}(\text{NO}_3)_2$, AlCl_3 and NaOH . XRD, SEM and EDS used for making analyzing of structural and dimensional of particles. The analyses show that the large amount of the Al^{3+} ions did not substitute with Zn^{2+} successfully with the reduction method. XRD and EDS results confirm this situation.

1. Introduction

Zinc oxide (ZnO) is a material that widely studied for years on account of the fact that it exhibits semiconducting and piezoelectric dual properties. At the same time ZnO growth process is already working several decades [1, 2]. As well as a variety of unique properties such as including good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence it is the one of the promising materials for optoelectric applications such as transparent transistors and LEDs [3–6]. Otherwise, ZnO is a key technological material which is the control of the electrical conductivity, for example, p-type contribution is focused on the development of technologies for energy efficiency [7]. ZnO nanoparticles which different from those of their bulk materials because of the fact that quantum confinements make their properties unique so, ZnO is one of the most important semiconductor for nanostructure applications. ZnO can be doped different metal atoms for enhancement of their properties. There are some difficulties during the growth of the nanocrystals doped ZnO material. The reason is the limited amount of crystalline material growth techniques. The so-called hydrothermal method with high quality crystal doped ZnO bulk crystal is produced. However, this method is not suitable for producing single crystal doped. Because it is difficult to achieve simultaneous control of pH and impurity resolution [8].

Undoped ZnO shows n-type conductivity because of the existence of native defects [9–11]. ZnO has high electrical resistivity, but this disadvantage can be reduced by the doping with group III ions (B^{3+} , Al^{3+} , Ga^{3+} , and In^{3+}) [9–16]. These ions ensure extra electrons and improve ZnO optical, electrical, thermal, and magnetic properties. Al^{3+} is most preferred dopant element due to its small ionic radius and low material cost. The substitution of Zn^{2+} ions with Al^{3+} in ZnO lattice causes that the increase of electrical conductivity due to the increase of charge carriers [17, 18]. This situation is suitable for fabrication of transparent electrodes in solar cells, gas sensors and also for ultrasonic oscillators [19]. Doping, however, creates disorder locations in the crystal structure. It causes that the mobility of charge carriers is affected by scattering. Therefore doped ZnO particles have to be pure phase for good electrical conducting.[20].



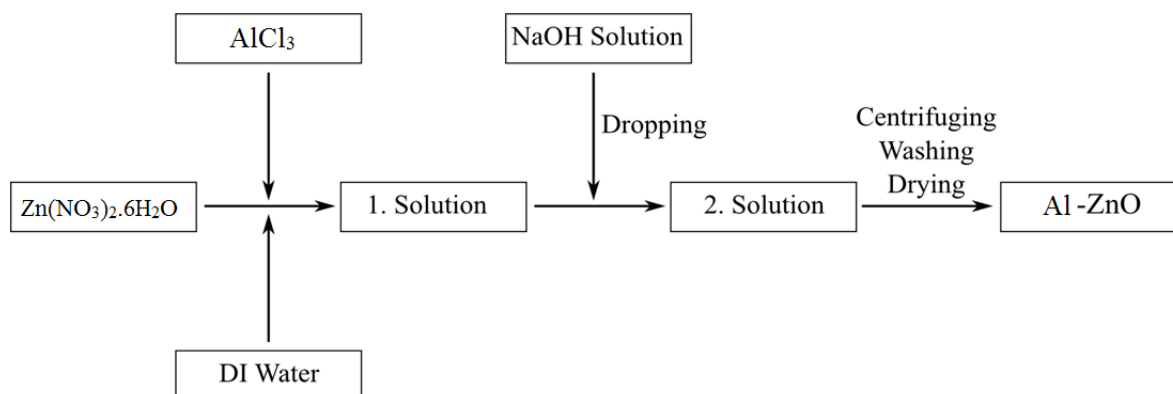
Al-doped ZnO (AZO) nanopowders use transparent electrode due to it is transparent in the visible region [21, 22]. Nowadays various methods have been reported for preparing AZO nanopowders such as sol-gel [23], spray pyrolysis [21], precipitation [24], and hydrothermal processes [25].

The aim of the present work is to achieve that the Al^{3+} ions doped to ZnO nanoparticles using reduction method so to obtain AZO nanoparticles.

2. Experimental procedure

AZO nanoparticles were synthesized using the reduction method. The materials used in the study include: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH (Sigma Aldrich %99). Firstly, 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and concentration to be 2% by weight of deionized water using 100 ml AlCl_3 solution were prepared. The magnetic stirrer is thoroughly homogenizing the solution was stirred for half an hour. 150 ml 1 M NaOH solution per minute to mix 1.5 ml, continuously stirred on a magnetic stirrer at 60°C $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and AlCl_3 were added to the mixture dropwise. The resulting solution whether centrifuge at 4000 rpm for 5 times at 5 minute intervals, the residue obtained was washed with deionized water after each application. Finally synthesized Al:ZnO nanoparticles are dried for 4 hours at 80°C . The process is shown schematically in Scheme 1.

The crystal structure of the samples was analyzed using RIGAKU Part D/Max 2200 x-ray diffraction (XRD) system (Rigaku/Smartlab) with $\text{Cu K}\alpha$ irradiation ($\lambda=1.5418 \text{ \AA}$) operated at 40 kV and 30 mA at the room temperature. The surface morphology of Al doped ZnO nanoparticles was investigated with a scanning electron microscope (SEM) (FEI Inspect 550). Furthermore, the ratio of Al as weighting in the Al-ZnO nanoparticles was investigated by Energy Dispersive X-ray spectrometer (EDS) analyzer.



Scheme 1.

3. Results and Discussion

3.1 X-ray diffraction results

As mentioned in the experimental section AZO nanoparticles are investigated by XRD measurements as shown in Figure 1.

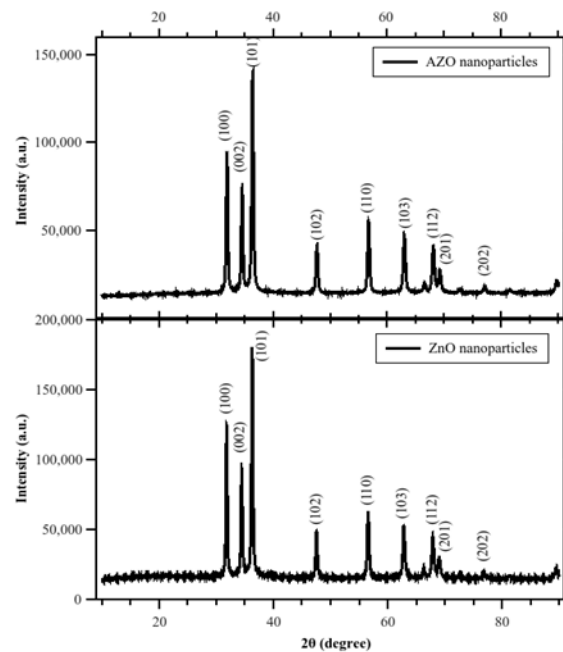


Figure 1. XRD analysis of Al-doped ZnO powder

XRD pattern of Al doped ZnO sample belongs to that crystal structure of pure and AZO nanoparticles are polycrystalline hexagonal wurtzite structure with (101) orientation at 36.35 degree. The *a*, *b*, and *c* parameter of the pure and AZO nanoparticles are refined by Cohen's Method of Least Squares using XRD data. The *a*, *b*, and *c* parameters of pure ZnO are found 3.253 Å, 3.253 Å, and 5.213 Å respectively. These values consistent with the literature [26]. Similarly *a*, *b*, and *c* parameters of AZO nanoparticles are found 3.245 Å, 3.245 Å, and 5.202 Å respectively. Changing of *a*, *b*, and *c* parameter of AZO shows that the doping process is successful. Otherwise, *c/a* parameters of pure and AZO nanoparticles are 1.602 and 1.603 respectively. The *c/a* parameters of samples very little changed. This result can interpret as a unchanged of wurtzite structure of nanoparticles. Preferred orientation of AZO is (101). The size of particles of crystal in the form of powder (*D*) and microstrain (*ε*) values over all peaks are determined by the Scherrer equations [24] as shown below.

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$

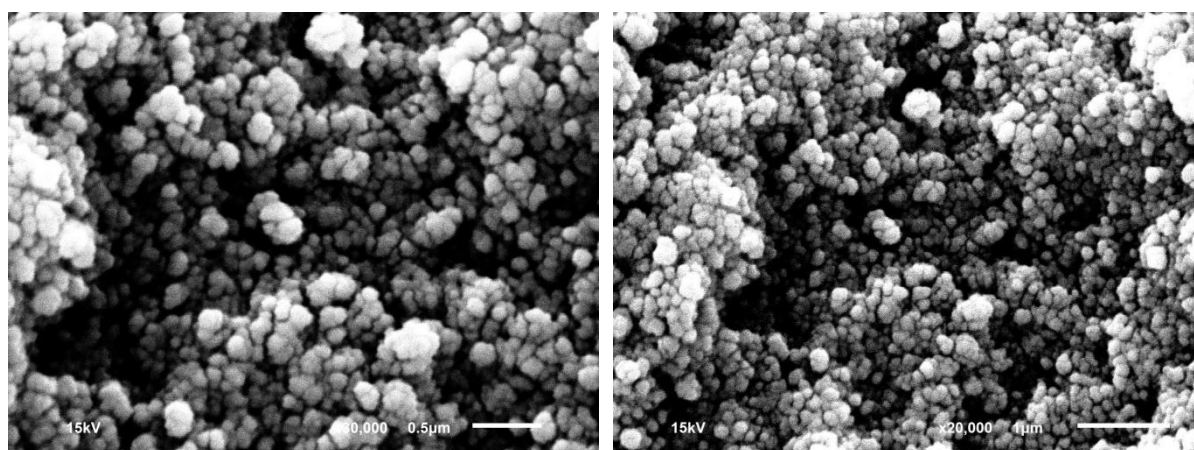
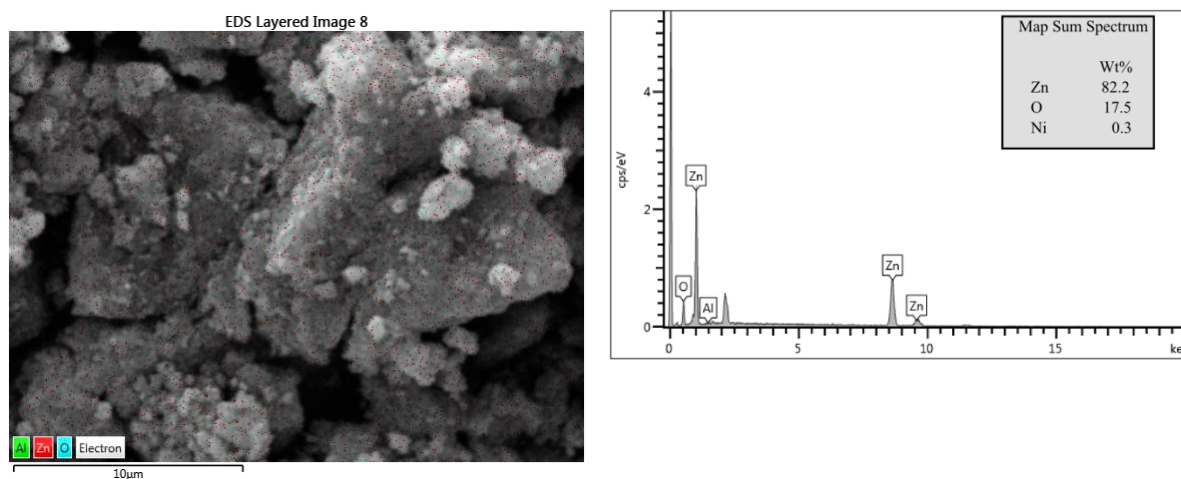
In these equations, β is full width at half of the peak maximum (FWHM) and calculated by Analysis of Variance (ANOVA), λ is the wavelength of the using X-ray and θ is the peak position which known as Bragg's angle. Calculated size of particles of nanocrystals and microstrain values of nanoparticles are given in Table 1.

Table 1. Structural parameters which calculated XRD patterns of pure and AZO nanoparticles.

| Pure ZnO nanoparticle | | | | | AZO nanoparticles | | | | |
|-----------------------|-------|-------|--------|---------------------------------|-------------------|-------|-------|--------|---------------------------------|
| a,b (Å) | c (Å) | c/a | D (nm) | ϵ ($\times 10^{-3}$) | a,b (Å) | c (Å) | c/a | D (nm) | ϵ ($\times 10^{-3}$) |
| 3.253 | 5.213 | 1.602 | 30.21 | 1.95 | 3.245 | 5.202 | 1.603 | 25.48 | 2.31 |

Although XRD patterns of ZnO and AZO nanoparticles are same, their lattice parameters varied a little. At the same time nanoparticle size was decreased. Because atomic radius of Al atoms is slightly smaller than the atomic radius of Zn atoms and the covalent bond length of Al–O is estimated to be shorter than Zn–O, the length of the c-axis is shorten in the AZO nanoparticles. These factors result in a decrease in the unit cell dimensions of AZO. In addition, the position of the (002) zincite peak did not shift Al-doping concentration at in comparison with an undoped zincite powder. As a result small change in the crystal size of doped nanostructures shows that the substitution is not desired amount.

3.1 SEM and EDS results

**Figure 2.** SEM images of AZO nanoparticles.**Figure 3.** SEM images and EDS results on the nanoparticles with 2 wt.% AZO

The scanning electron microscopy (SEM) images of AZO nanoparticles given in Figure 2. The composition of the Al doped ZnO nanoparticles was determined by energy dispersive X-ray spectroscopy (EDS). EDS spectra of Al doped ZnO nanoparticles and the composition of elements in ZnO structure which viewing area are given in Figure 3.

SEM images show that the AZO nanoparticles have spherical shape. EDS spectra clearly confirm the existence of Zn, Al and O elements in the Al doped ZnO nanoparticles. But Al concentration is very low according to the other elements. This is evidence of that the large amount of the Al atoms did not enter the ZnO nanostructure. This situation compatible with XRD results.

4. Conclusion

In this study, AZO nanoparticles were synthesized using the reduction method and the success of doping is determined by XRD and SEM/EDS analyses. XRD measurements showed that Doping ZnO with aluminum reduced the particle size. The powder structure, shape and composition of weight of atoms were investigated by SEM/EDS. It was found that AZO nanocrystals have spherical shape. EDS analysis shows that the large amount of the Al^{3+} ions did not substitute with Zn^{2+} successfully.

References

- [1] R.A. Laudise, A.A. Ballman "Hydrothermal synthesis of zinc oxide and zinc sulfide" J. Phys. Chem. 64 (1960) 688.
- [2] L.N. Demianets, D.V. Kostomarov "Mechanism of zinc oxide single crystal growth under hydrothermal conditions" ANN CHIM-SC. 26(1) (2001) 193.
- [3] P.F. Carcia, R.S. McLean, M.H. Reilly, G. Nunes "Transparent ZnO thin-film transistor fabricated by rf magnetron sputtering" Appl. Phys. Lett. 82 (2003) 1117.
- [4] A. Ohtomo, S. Takagi, K. Tamura, T. Makino, Y. Segawa, H. Koinuma, M. Kawasaki "Photo-Irresponsible Thin-Film Transistor with $Mg_xZn_{1-x}O$ Channel" Jpn. J. Appl. Phys. 45 (2006) Part 2, N.24-28, L694.
- [5] J.-C. Sun, H.-W. Liang, J.-Z. Zhao, J.-M. Bian, Q.-J. Feng, L.-Z. Hu, H.-Q. Zhang, X.-P. Liang, Y.-M. Luo, G.-T. Du "Ultraviolet electroluminescence from n-ZnO:Ga/p-ZnO:N homojunction device on sapphire substrate with p-type ZnO:N layer formed by annealing in N_2O plasma ambient" Chem. Phys. Lett. 460 (2008) 548.
- [6] S.-J. Jiao, Z.-Z. Zhang, Y.-M. Lu, D.-Z. Shen, B. Yao, J.-Z. Zhang, B.-H. Li, D.-X. Zhao, X.-W. Fan, Z.-K. Tang "ZnO p-n junction light-emitting diodes fabricated on sapphire substrates" Appl. Phys. Lett. 88 (2006) 031911.
- [7] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, M. Kawasaki "Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO" Nat. Mater. 4 (2005) 42.
- [8] W. Lin, D. Chen, J. Zhang, Z. Lin, J. Huang, W. Li, Y. Wang, F. Huang "Hydrothermal Growth of ZnO Single Crystals with High Carrier Mobility" Cryst. Growth Des., 9 (10) (2009) pp 4378.
- [9] B. Claflin, D. C. Look, S. J. Park, and G. Cantwell, "Persistent n-type photoconductivity in p-type ZnO," Journal of Crystal Growth, vol. 287, no. 1 (2006) pp. 16–22.
- [10] A. Janotti and C. G. van de Walle, "Native point defects in ZnO," Physical Review B, vol. 76, no. 16 (2007) pp. 1–22.
- [11] A. Janotti and C. G. van de Walle, "New insights into the role of native point defects in ZnO," Journal of Crystal Growth, vol. 287, no. 1 (2006) pp. 58–65.
- [12] P. Jood, R. J. Mehta, Y. Zhang et al., "Al-doped zinc oxide nanocomposites with enhanced thermoelectric properties," Nano Letters, vol. 11, no. 10 (2011) pp. 4337–4342
- [13] A. Favier, D. Muñoz, S. Martín de Nicolás, and P.-J. Ribeyron, "Boron-doped zinc oxide layers grown by metal-organic CVD for silicon heterojunction solar cells applications," Solar Energy Materials and Solar Cells, vol. 95, no. 4 (2011) pp. 1057–1061.

- [14] V. Bhosle, J. T. Prater, F. Yang, D. Burk, S. R. Forrest, and J. Narayan, "Gallium-doped zinc oxide films as transparent electrodes for organic solar cell applications," *Journal of Applied Physics*, vol. 102, no. 2 (2007) pp. 1–5.
- [15] P. S. Venkatesh, V. Ramakrishnan, and K. Jeganathan, "Vertically aligned indium doped zinc oxide nanorods for the application of nanostructured anodes by radio frequency magnetron sputtering," *CrystEngComm*, vol. 14, no. 11 (2012) pp. 3907–3914.
- [16] J. M. Lin, Y. Z. Zhang, Z. Z. Ye et al., "Nb-doped ZnO transparent conducting films fabricated by pulsed laser deposition," *Applied Surface Science*, vol. 255, no. 13-14 (2009) pp. 6460–6463.
- [17] Ü. Özgür, Y. I. Alivov, C. Liu et al., "A comprehensive review of ZnO materials and devices," *Journal of Applied Physics*, vol. 98, no. 4 (2005) pp. 1–103.
- [18] T. Minami, "Transparent conducting oxide semiconductors for transparent electrodes," *Semiconductor Science and Technology*, vol. 20, no. 4 (2005) pp. S35–S44.
- [19] Hong-ming Zhou, Dan-qing Yi, Zhi-ming Yu, Lai-rong Xiao, Jian Li "Preparation of aluminum doped zinc oxide films and the study of their microstructure, electrical and optical properties" *Thin Solid Films*, 515 (2007) pp. 6909–6914.
- [20] Ç. Kiliç and A. Zunger, "Origins of coexistence of conductivity and transparency in SnO₂," *Physical Review Letters*, vol. 88, no. 9 (2002) pp. 1–4.
- [21] A. Verma, F. Khan, D. Kar, B. C. Chakravarty, S. N. Singh and M. Husain "Sol–gel derived aluminum doped zinc oxide for application as anti-reflection coating in terrestrial silicon solar cells" *Thin Solid Films* 518 (2010) pp.2649.
- [22] E. Hamarberg, A. P. Schwab and C. Feldmann "Microwave-assisted polyol synthesis of aluminium- and indium-doped ZnO nanocrystals" *J. Colloid. Interface Sci.* 334 (2009) pp.29.
- [23] H. Serier, M. Gaudon and M. Menetrier "Al-doped ZnO powdered materials, Al Solubility limit and IR absorption properties" *Solid State Sci.* 11 (2009) pp.1192-1197.
- [24] S. F. Du, Y. J. Tian, H. D. Liu, J. Liu and Y. F. Chen "Calcination effects on the properties of gallium-doped zinc oxide powders" *J. Am. Ceram. Soc.* 89 (2006) 2440-2443.
- [25] W. H. Zhang, W. D. Zhang and J. F. Zhou "Solvent thermal synthesis and gas-sensing properties of Fe-doped ZnO" *J. Mater. Sci.* 45(2009) pp.209-241.
- [26] H. Schulz, K.H., Thiemann "Structure parameters and polarity of the wurtzite type compounds SiC—2H and ZnO" *Solid State Commun.*, 32 (1979) pp.783-785.