JOURNALOF

Ceramic Processing Research

# Influence of Al doping on structural and optical properties of hydrothermally grown ZnO nanorods

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In this work, aluminum (Al) doped ZnO nanorods (NRs) were prepared by hydrothermal method by doping Al with 1, 2 and 3 in weight percentage (wt. %) in addition to undoped ZnO NR. The influence of Al doping on the structural and optical properties of ZnO NRs were studied in this paper systematically. The surface morphology and optical properties of all the doped and undoped ZnO NRs samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis spectroscopy and photoluminescence (PL) measurements. We found that the Al doping affected the structural and optical properties of the ZnO NRs, including their PL properties, absorption values and optical band gaps etc. It is observed from PL as well as UV-Vis spectroscopy that the bandgap value increases gradually with increase of the Al dopants concentration due to Burstein-Moss effect. The variation of bandgap according to Al dopants was extracted from PL also and compared with that of the UV-vis results.

Key words: Zinc Oxide, Hydrothermal, SEM, PL, Al doped ZnO, UV-Vis.

### Introduction

Zinc oxide (ZnO) is an II-VI compound semiconductor material with wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [1-3]. It has wide range of applications in the electronic devices like gas sensors, thin film transistors, solar energy conversion, nonlinear optics, pigments, photo-catalysis, organic light emitting diodes (LEDs), photoluminescent and cosmetic etc [3-5]. In order to improve the electrical and optical properties of ZnO nanostructures, various impurities such as Ga, Al, Mg, Mn, In and Ni are being used by different research-groups nowadays [6-9]. Among these, Al doped ZnO (AZO) nanostructures have attracted much attention because of its some merits like high refractive index, non-toxicity, thermal and chemical stability and low-cost synthesis [6, 10, 11]. It is also reported that the conductivity of AZO nanowires is very high and there is no any degradation in its crystallinity and optical transmission with increase in Al concentration [5]. Therefore, AZO is replacing the popularly used transparent conductive materials (like ITO etc.) in many applications [5, 6, 10, 11]. AZO nanostructures (nanowires, nanoparticles, nanotubes and nanobelts) can be grown by various methods, including sol-gel, electrochemical deposition (ECD), electrospinning, chemical bath deposition (CBD), RF

sputtering, hydrothermal, thermal evaporation and PLD etc [11-18]. However, these methods not only need costly apparatus but also are not appropriate for batchtype production. Among these above mentioned processes, the hydrothermal method is commonly used method for the growth of nanostructures because of its low-cost, simplicity and high efficiency. The Al-doped ZnO is studied by many groups, Wang *et al.* reported AZO NRs on graphene/Ni/Si substrate [5], Alkahlout *et al.* reported AZO NRs grown by three different aluminum precursors [4], García *et al.* reported AZO nanowires on plastic substrate [19]. However, study on the hydrothermally grown AZO NRs and the influences of the aluminum doping contents on the optical properties are very less.

In this work, we synthesized pure and Al-doped ZnO NRs on the Si and glass substrates using two step hydrothermal routes. The influence of the Al concentration on optical and structural properties of AZO NRs was investigated systematically by UV–vis spectroscopy, photoluminescence (PL), XRD and SEM [4-6].

#### Experiment

The undoped and Al doped ZnO NRs were grown on p-type silicon (Si) substrates and also on glass substrates, at room temperature. The substrates were cleaned ultrasonically by using acetone and methanol. Finally the wafers were rinsed with deionized water (DI) water. The DI water (resistivity  $\sim 18 \text{ M}\Omega\text{cm}$ ) was obtained from a DI water plant (Model Milli-Q, USA).

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At the last, the substrates were dried using dry nitrogen blow. The growth was done in two steps, seed layer of undoped ZnO is grown in the first step and then main growth was done for undoped and Al doped ZnO NRs layers.

60 mM precursor solution is made for the deposition of seed layer of ZnO on Si substrate. The solution contains, zinc acetate dehydrate powder [Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O, High Purity Chemicals, 98.0% purity] mixed with ethyl alcohol [High Purity Chemicals, 99.9% purity]. The solution is mixed with magnetic stirrer at the temperature of 80 °C for one hour.

ZnO NRs were then formed in a growth solution of 30 mM concentration. The solution was mixture of zinc nitrate hexahydrate (ZN) [Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Yakuri Pure Chemicals  $\geq$  98%purity], hexa-methylene-tetramine HMT (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, Kanto Chemicals Co. Inc. 99.0%) and DI water, stirred at 90 °C for one hour.

For growth of Al doped ZnO NRs, powder of Aluminum Nitrate Nonahydrate [AlN<sub>3</sub>O<sub>9</sub>.9H<sub>2</sub>O, Sigma-Aldrich  $\geq$  98% purity] was used with 30 mM solution of ZN and HMT. After that 1, 2 and 3 wt. % Al doped ZnO NRs samples were grown on Si and glass substrates.

#### Characterization

The structure and surface morphology of ZnO and AZO NRs were characterized by scanning electron microscope (SEM) HITACHI, S-4800 made in Japan and by PANalytical X'Pert Pro XRD system respectively. The optical properties of NRs were investigated by Photoluminescence (using a 325 nm continuous He-Cd laser: 24 mW) and UV-VIS spectroscopy. The thickness of ZnO and AZO NRs layer were measured by ellipsometer (Model: J.A Wollam, VB-400).

#### **Results and Discussion**

## Structural properties

Fig. 1(a-d) shows the XRD patterns of undoped and Al doped ZnO NRs samples respectively. All the XRD graphs show ZnO peaks (according to JCPDS data card no. 36-1451), without any indications of the phases related with alumina or Al [6, 20]. The XRD peaks corresponding to  $2\theta = 31.70$ , 34.51 and 36.30 are well matched with the (100), (002) and (101) orientations of ZnO crystal. It could be clearly seen that the XRD patterns of undoped and doped samples were dominated by a sharp (002) peak of wurtzite-type ZnO, implying that the preferred orientation of the ZnO nanorods was along the (002) direction [4, 6, 20-23].

The surface morphologies of the undoped and Al doped ZnO NRs were characterized by scanning electron microscopy (SEM) [5, 6, 24]. Fig. 2(a) to (d) show the SEM images of undoped and 1, 2 and 3 wt. % Al doped ZnO NRs respectively. The SEM image of the as grown ZnO NRs on Si substrate displays a high

density and randomly arranged NRs [5, 6, 24]. The effect of Al doping can be seen from the SEM image of Fig. 1(b-d). Fig. 2(b) shows that, the surface of 1% Al-doped ZnO NRs are not as dense as it is for undoped ZnO NRs. Again, the 2% Al doped ZnO surface has vertically grown NRs and 3% Al doped ZnO surface display denser vertically grown NRs. It is evident from these SEM images that the length and thickness of ZnO NRs decreases as we increase Al concentration [6]. This result is in quite good agreement with the results of various other research groups in the past [5, 6, 24].

The length and diameter of the undoped ZnO NRs were estimated from the cross-sectional SEM image (not shown here). The length of undoped ZnO NRs was approximately 750-780 nm and the diameter of



**Fig. 1.** (a) to (d) XRD spectra of undoped and Al doped ZnO NRs samples.



Fig. 2. (a) to (d) SEM image of undoped and Al doped ZnO NRs samples.

undoped ZnO NRs was in the range of 35 to 40 nm. The thickness of ZnO NRs decreases as we increasing Al doping concentration. The thickness of all the undoped and doped ZnO thin film samples was also measured by ellipsometer and it is found in the good agreement to the cross-sectional SEM results.

#### **Optical properties**

The effect of Al doping on the absorption characteristics of ZnO NRs was checked with UV-Vis spectroscopic measurements. Undoped and doped ZnO thin films were deposited on glass substrates for UVvis spectroscopy. The substrate absorbance was corrected by introducing a glass substrate (without ZnO thin film) of the same size as the reference. The



**Fig. 3.** (a) Optical absorption spectra of undoped ZnO NRs sample. (b) Optical absorption spectra of Al doped ZnO NRs samples.



**Fig. 4.** (a)  $(\alpha h v)^2$  vs. hí graph of undoped ZnO NRs sample. (b)  $(\alpha h v)^2$  vs. hí graph of Al doped ZnO NRs samples.

absorbance spectra of undoped and doped ZnO NRs are shown in Fig. 3(a) and (b) respectively. It can be seen from the graph that the strong absorption occurs in UV wavelength range of 350-375 nm. These optical characteristics of the ZnO NRs can be utilized for sensing UV light. It can be also seen from the Fig. 3 that the absorption is very weak in the visible wavelength range i.e. from 400 nm to 650 nm. The optical bandgap of undoped and doped ZnO NRs layer is extracted from the absorbance spectra, by applying the Tauc plot rules, as shown in the Fig. 4(a) and (b) [25]. The optical bandgap of ZnO samples was calculated by the standard relation reported by elsewhere [4, 10]. The bandgap estimated from this method were listed in the Table 1., which are in good agreement with

Table 1. Variation of bandgap with Al doping concentration (extracted from UV-vis and PL).

	Bandgap estimated by UV-vis	Reported by others	ZnO peak (λ) obtained from PL	Bandgap estimated by PL	ZnO peak (λ) obtained from PL(Reported by others)	Bandgap estimated by PL (Reported by others)
Undoped ZnO	3.22 eV	3.67 eV [10]; 3.15 eV [4]; 3.206 eV[25]; 3.20 eV [26];	380 nm	3.26 eV	380 nm [20]; 399 nm [11]; 376.2 nm [27]; 378 nm [24]; 377.7 nm [22];	3.261 eV [6]; 3.3 eV [27];
1% AZO	3.28 eV	3.1 eV [10]; 3.25 eV [26];	376 nm	3.29 eV	$(\lambda \text{ decreasing with increase of Al content)}[22];$	(Bandgap increasing with increase of Al content) [22];
2% AZO	3.30 eV		372.4 nm	3.32 eV	For 1.67 at % Al doping; 375.5 nm [24]	3.279 eV [6]
 3% AZO	3.29 eV		374 nm	3.31 eV		

(d -0-3% AZO Intensity PL (a. u.) % AZO % AZO (a Undoped ZnO

Fig. 5. (a) to (d) PL spectra of of undoped and Al doped ZnO NRs samples.

Wavelength  $\lambda$  (nm)

405

540 675 810 945 1080



Fig. 6. Estimation of bandgap from UV-vis and PL with increase of Al doping concentration.

the result reported by others [26, 27].

Fig. 5(a-d) shows the room temperature PL spectra of undoped and doped ZnO NRs layers. The shapes of all the PL spectra are similar to those reported by others [6, 11]. The PL spectra of all the layers are dominated by strong near band edge UV emission peak. This sharp peak is arisen at wavelength 380 nm for the PL spectra of undoped ZnO NRs layer. Basically this UV emission peak comes from free exciton emission as shown by other researchers [20, 22, 24, 28], and as it is shown in the Table I, that this peak corresponds to the bandgap of ZnO equal to 3.26 eV. Again from the Fig. 5(a-d) we can see one broad peak in the wavelength range of 400-700 nm for all the PL spectra. Basically this peak arises from ZnO NRs; hence it is confirming the formation of vertical NRs above seed layer after main growth. The broad band at the wavelength range of 400-700 nm in the Fig. 5(a-d), is corresponds to the collection of radiative recombination through point defects in a ZnO crystal, such as a zinc vacancy, an oxygen interstitial, an oxygen vacancy, anti-site defects and zinc interstitial [20, 22, 24, 28].

The estimation of bandgap done with PL and UV-vis, for undoped and doped ZnO NRs layers were

summarized in the Table I. It is clear from the Table 1, that as soon as we increase the Al dopant concentration in the undoped ZnO sample, the bandgap increases. The variation of bandgap with increase of Al content is plotted in the Fig. 6. We can see the similar trend for bandgap obtained from UV-vis and PL measurements i.e. increase of bandgap with addition of Al contents [11, 20, 22, 24, 28]. Table I also shows the results reported by other research-group for AZO NRs samples during last ten years.

## Conclusions

In summary, ZnO NRs with 1, 2 and 3 wt. % doping contents of Al were successfully grown with hydrothermal method. XRD, SEM, UV-vis spectroscopy and photoluminescence were well correlated with the structural and optical characteristics of the undoped and Al-doped ZnO NRs samples. The effect of Al doping on the morphology and optical characteristics of the ZnO NRs thin film samples has been studied. UV-vis spectroscopy and PL is used to extract the optical band gap and to study the influence of Al doping on the optical properties of AZO NRs thin films. The optical bandgaps of the ZnO and AZO NRs thin film samples estimated from UV-vis measurement, the values were 3.22 for 0 wt.%, 3.28 for 1.0 wt.%, 3.30 for 2.0 wt.%, and 3.29 for 3.0 wt.%. These bandgap values obtained from PL measurement were in good agreement to the results from UV-vis. This visible blind property of AZO thin films could be utilized for fabrication and characterization of optoelectronic applications.

#### References

- S. K. Hong, J. H. Lee, B. H. Cho, and W. B. Ko, J. Ceram. Process. Res. 12 (2011) 212-217.
- C. C. Chen, N. Ye, C. F. Yu, and T. Fan, J. Ceram. Process. Res. 15 (2014) 102-106.
- A. B. Djurisic, X. Chen, Y. H. Leung and A. M. C. Ng, J. Mater. Chem. 22 (2012) 6526-6535.
- 4. A. Alkahlout, N. Al Dahoudi, I. Grobelsek, M. Jilavi, and P. W. de Oliveira, J. Mater. 2014 (2014) 1-8.
- L. L. Wanga, B. Z. Lin, M. P. Hung, L. Zhou, G. N. Panin, T. W. Kang, and D. J. Fu, Solid-State Electron. 82 (2013) 99-102.
- 6. S. Kim, G. Nam, H. Park, H. Yoon, S. Lee, J. S. Kim, J. S.

Kim, D. Y. Kim, S. O. Kim, and J. Y. Leem, Bull. Korean Chem. Soc. 34 (2013) 1205-1211.

- Y. H. Liu, S. J. Young, L. W. Ji, T. H. Meen, C. H. Hsiao, C. S. Huang, and S. J. Chang, IEEE T. Electron. Dev. 61 (2014) 1541-1546.
- F. C. Romeiro, J. Z. Marinho, A. C. A. Silva, N. F. Cano, N. O. Dantas, and R. C. Lima, J. Phys. Chem. C 117 (2013) 26222-26227.
- L. Yanmei, W. Tao, S. Xia, F. Qingqing, L. Qingrong, S. Xueping, and S. Zaoqi, Appl. Surf. Sci. 257 (2011) 6540-6545.
- E. Burunkaya, N. Kiraz, O. Kesmez, H. E. Camurlu, M. Asilturk, and E. Arpac, J. Sol-Gel Sci. Technol. 55 (2010) 171-176.
- X. Chong, L. Li, X. Yan, D. Hu, H. Li, and Y. Wang, Physica E 44 (2012) 1399-1405.
- F. H. Wang, C. T. Chou, T. K. Kang, C. C. Huang, H. W. Liu, and C. Y. Kung, J. Ceram. Process Res. 14 (2013) 149-152.
- D. Oh, S. C. Park, K. H. Kim, J. Y. Kim, J. M. Jeong, and T. W. Kim, J. Ceram. Process Res. 15 (2014) 366-369.
- D. Lin, H. Wu, and W. Pan, Adv. Mater. 19 (2007) 3968-3972.
- 15. C. H. Hsu, and D. H. Chen, Nanotechnology 21 (2010) 285603 (8pp).
- A. B. Rosli, M. M. Marbie, S. H. Herman, and M. H. Ani, J. Nano Mat. 2014 (2014) 1-7.
- S. Suhaimi, S. Sakrani, T. Dorji, and A. K. Ismail, Nanoscale Res. Lett. 9:256 (2014) 1-10.
- H. Kumarakuru, D. Cherns, and G. M. Fuge, Surf. Coat. Tech. 205 (2011) 5083-5087.
- C. M. García., E. D. Valdés, A. M. P. Mercado, A. F. M. Sánchez, J. A. A. Adame, V. Subramaniam, and J. R. Ibarra, Adv. Mater. Phys. Chem. 2 (2012) 56-59.
- 20. G. H. Nama, S. H. Baek, and I. K. Park, J. Alloy. Compd. 613 (2014) 37-41.
- D. Somvanshi, A. Pandey, and S. Jit, J. Nanoelectron. Optoe. 8 (2013) 349-354.
- 22. J. Liu, L. Xu, B. Wei, W. Lv, H. G, and X. Zhang, Cryst. Eng. Comm. 13 (2011) 1283-1286.
- 23. R. R. Piticescu, R. M. Piticescu, and C. J. Monty, J. Eur. Ceram. Soc. 26 (2006) 2979-2983.
- 24. Y. M. Lu, and J. F. Tang, Int. J Sci. Eng. 3 (2013) 11-15.
- 25. S. Singh, and P. Chakrabarti, Adv. Sci. Eng. Med. 5 (2013) 1-6.
- 26. S. Kim, M. S. Kim, G. Nam, H. Park, H. Yoon, and J. Y. Leem, J. Nanosci. Nanotechnol. (2013) 6183-8.
- M. C. Jun, and J. H. Koh, J. Electr. Eng. Technol. 8 (2013) 163-167.
- 28. I. J. No, S. Lee, S. H. Kim, J. W. Cho, and P. K. Shin, Jpn. J. Appl. Phys. 52 (2013) 025003 (1-5).