

Effect of reaction time and applied voltage on the structural and optical properties of Al-doped ZnO nanostructures electrochemically deposited on indium-tin-oxide-coated glass substrates

Dohyun Oh^a, Se Chul Park^b, Ki Hyun Kim^a, Jin Young Kim^c, Je-Myung Jeong^a and Tae Whan Kim^{a,*}

^aDepartment of Electronics and Computer Engineering, Hanyang University, Seoul 133-791, Korea

^bDepartment of Electronic Engineering, Hanyang University, Seoul 133-791, Korea

^cDepartment of Electronic Material Engineering, Kwangjuon University, Seoul 139-701, Korea

Al-doped ZnO (AZO) nanostructures were electrochemically formed on indium-tin-oxide (ITO)-coated glass substrates. Scanning electron microscopy images showed that the density of the AZO nanostructures increased with increasing reaction time and applied voltage. X-ray diffraction patterns showed that the intensities corresponding to the (002) diffraction peak of the AZO nanostructures deposited at higher voltages of –1.3 and –1.4 V were relatively higher than those deposited at lower voltages of –1.1 and –1.2 V. Photoluminescence (PL) spectra for the AZO nanostructures formed on the ITO-coated glass substrates showed that the PL peak intensity related to the defects for the AZO nanostructures increased with increasing reaction time due to an increase in the thickness of the nanosheets.

PACS numbers: 61.10.Nz, 68.37.Hk, 78.55.-m, and 82.45.Aa

Key words: Al-doped ZnO nanostructures, Reaction time, Applied voltage, Structural property, Optical property.

Introduction

Semiconductor nanostructures, such as nanowires, nanorods, nanotubes, and nanobelts, have attracted a great deal of interest due to their excellent physical properties and potential applications in next-generation electronics and optoelectronics [1–3]. Among the various types of nanostructured materials, ZnO nanostructures have remarkable physical properties of direct wide band gaps, high chemical stabilizations, large bond strengths, large exciton binding energies, and good photoelectric and piezoelectric properties. These properties provide several advantages for promising applications in short-wavelength range devices [4–6]. The formation of the ZnO nanostructures have been extensively performed in vacuum by using metal organic chemical vapor deposition, molecular beam epitaxy, magnetron sputtering, and pulsed laser deposition method [7,8]. A solution process has been typically used to synthesize ZnO nanostructures, such as rods, columns, sheets, and complex column-to-rod bilayers [9,10]. An electrochemical deposition (ECD) method has been introduced to form nanostructures due to its advantages of high growth rate, large area, and low cost [11–14]. Even though some investigations concerning the formation and structural characteristics of the ZnO nanostructures electrochemically deposited on indium-tin-oxide (ITO)-coated glass substrates have been carried

out [15, 16], very few investigations concerning the effects of reaction time and applied voltage on the structural and optical properties of the Al-doped ZnO (AZO) nanostructures grown by using ECD have been conducted.

This paper reports the effect of reaction time and applied voltage on the structural and optical properties of AZO nanostructures deposited on ITO-coated glass substrates by using an ECD method. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements were performed to investigate the structural properties of the AZO nanostructures. Photoluminescence (PL) measurements were carried out in order to investigate the optical characteristics of the AZO nanostructures grown with different applied voltages and reaction times.

Experimental Details

ZnO nanostructures synthesized in this work were formed on ITO-coated glass substrates by using an ECD method in a conventional electrochemical cell with three electrodes. An ITO-coated glass substrate was used as a working electrode, a platinum plate electrode as a counter electrode, and a saturated calomel electrode as a reference electrode. ZnO nanostructures were formed from the reduction of the dissolved molecular oxygen in a zinc nitrate solution. The $\text{Zn}(\text{NO}_3)_2$ and the potassium chloride (0.1 M) were dissolved in 350 mL deionized water. The doping concentration of Al was fixed at 1 wt%. The KCl (Sigma-Aldrich, 99.0–100.5%) acted as a supporting precursor. The

*Corresponding author:
Tel : +82-2-2220-0354
Fax: +82-2-2292-4135
E-mail: twk@hanyang.ac.kr

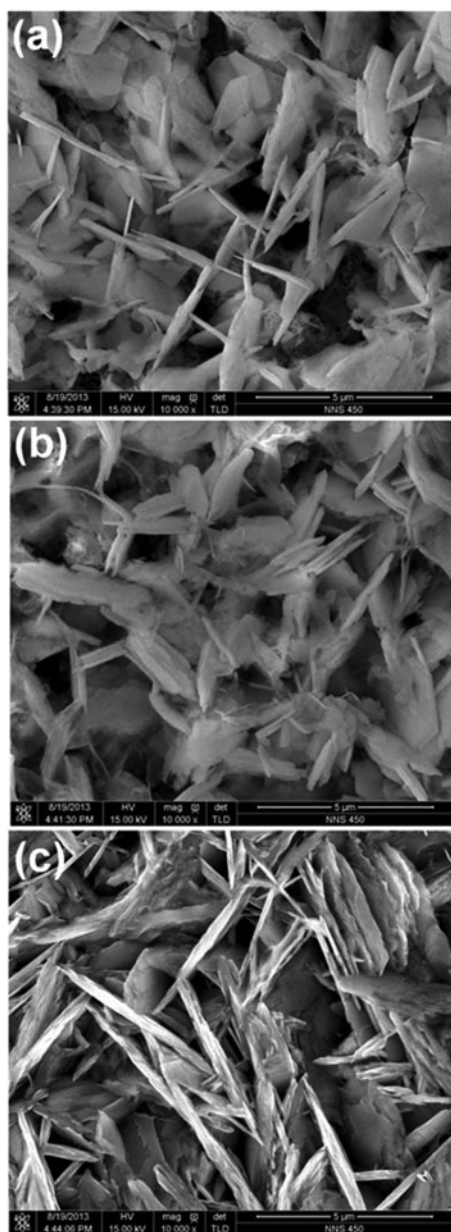


Fig. 1. Scanning electron microscopy images of the Al-doped ZnO nanostructures deposited on indium-tin-oxide-coated glass substrates with reaction times of (a) 5, (b) 10, and (c) 30 min.

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 98.0%) acted as a Zn^{2+} precursor. The concentration of $\text{Zn}(\text{NO}_3)_2$ was 0.1 M. The ZnO nanostructures were electrochemically deposited at a low temperature of 70 °C under an applied voltage from -1.1 to -1.4 V. The ZnO nanostructure samples were prepared without a post-annealing process.

XRD measurements were carried out using a Rigaku D/MAX-2500 diffraction meter with CuK_α radiation, which was operated at a scanning rate of 5 °/min for a 2θ range between 20 ° and 80 °. The X-ray tube voltage and current were set at 40 kV and 100 mA. SEM measurements were performed by using a field emission scanning electron microscope (NOVA Nano SEM 200, FEI Company). PL measurements were carried out using

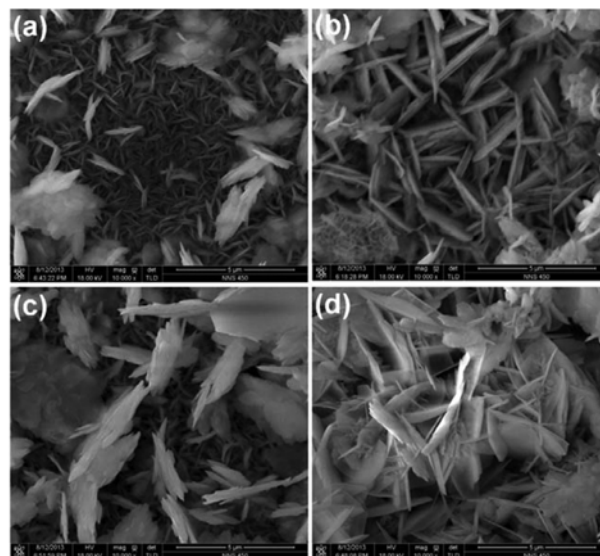


Fig. 2. Scanning electron microscopy images of the Al-doped ZnO nanostructures deposited on the indium-tin-oxide-coated glass substrates with applied voltages of (a) -1.1 , (b) -1.2 V, (c) -1.3 , and (d) -1.4 V.

a 75-cm monochromator equipped with a GaAs photomultiplier tube. The excitation source was the 325 nm line of a He-Cd laser. All measurements were performed at room temperature.

Results and Discussion

Figure 1 shows the SEM images of the AZO nanostructures deposited on the ITO-coated glass substrates with reaction times of (a) 5, (b) 10, and (c) 30 min. The SEM images show that the synthesized AZO structure consists of randomly distributed nanosheets, which have a relatively rough and cracked hexagonal structure. The layered nanosheets with thicknesses of 180 and 600 nm are displayed in Figs. 1(b) and 1(c), respectively. The thickness of the AZO nanosheets increases with increasing reaction time, indicating that a longer reaction time affects the lateral growth of the nanosheets.

Figure 2 shows the SEM images of the AZO nanostructures deposited on the ITO-coated glass substrates with applied voltages of (a) -1.1 , (b) -1.2 , (c) -1.3 , and (d) -1.4 V. A higher applied voltage results in the formation of thick nanosheets with planar dimensions due to the large growth ratio along the c-axis relative to the a-axis resulting from the fast nonequilibrium growth.

Figure 3 shows the XRD patterns of the AZO nanostructures deposited at different voltages from -1.1 to -1.4 V. XRD patterns indicate that the AZO nanostructures have wurtzite structures with cell parameters of $a = 0.3249$ nm and $c = 0.5026$ nm, which are in reasonable agreement with the literature values (JCPDS card). The intensities corresponding to the (002) diffraction peak of the AZO nanostructures deposited at higher voltages of -1.3 and -1.4 V are relatively higher in

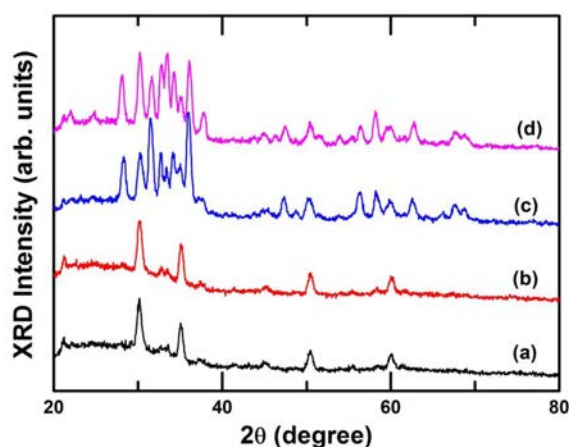


Fig. 3. X-ray diffraction curves of the Al-doped ZnO nanostructures deposited on the indium-tin-oxide-coated glass substrates with applied voltage of (a) -1.1 , (b) -1.2 , (c) -1.3 , and (d) -1.4 V.

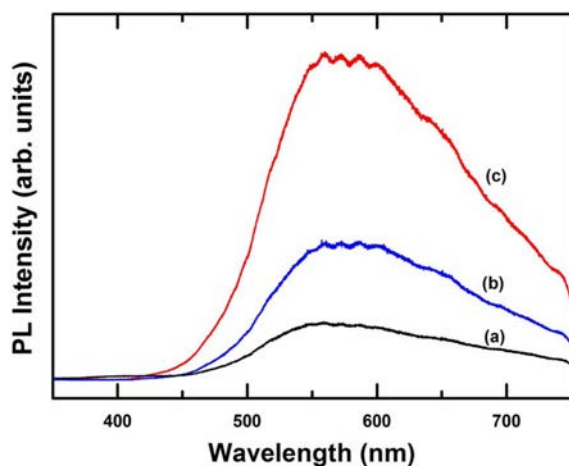


Fig. 4. Photoluminescence spectra for the Al-doped ZnO nanostructures with an applied voltage of -2.25 V and reaction times of (a) 5, (b) 10, and (c) 30 min.

comparison with the XRD patterns of AZO nanostructures deposited at lower voltages of -1.1 and -1.2 V. The shift of the (002) peak position in solution-processed AZO nanostructures is attributed to the variations of the lattice parameters resulting from the doping effect [17]. The substitution of zinc atoms by doping materials generates oxygen vacancies, which can change the lattice parameters of the AZO nanostructures. The XRD peaks at 30° , 50° , and 60° correspond to the ITO substrate.

Figure 4 shows the PL spectra at room temperature for the AZO nanostructures deposited with an applied voltage of -2.25 V and different reaction times of 5, 10, and 30 min. The PL spectra of the AZO nanostructures were obtained in wavelength ranges between 350 and 800 nm. Visible emissions of the PL spectra for the AZO nanostructures increased with increasing reaction time due to an increase in the thickness of the AZO nanosheets. A broad emission in the visible region obtained between 450 and 800 nm originates from the many defects, such as the zinc vacancy (V_{Zn}), zinc

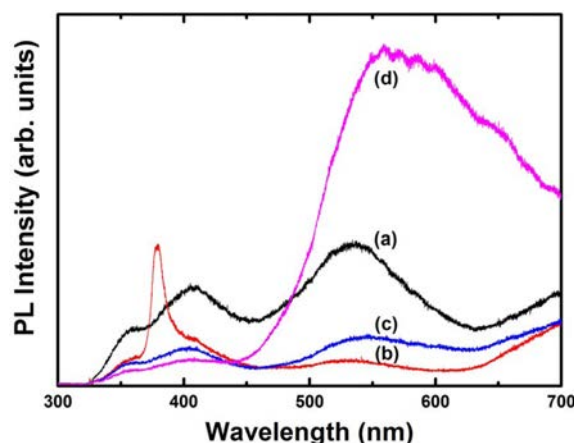


Fig. 5. Photoluminescence spectra for the Al-doped ZnO nanostructures with a reaction time of 5 min and applied voltages of (a) -1.1 , (b) -1.2 , (c) -1.3 , and (d) -1.4 V.

interstitial (Zn_i), oxygen vacancy (V_O), oxygen interstitial (O_i), and anti-site defects (Zn_O , O_{Zn}), which have been reported in the literatures [18, 19]. This result shows that the AZO nanostructures, acting as a luminescence center in a visible region, can be considered as a very promising material for optoelectronic devices, such as the white light-emitting diode.

Figure 5 shows the PL spectra of the AZO nanostructures deposited at room temperature with a reaction time of 5 min and different applied voltages from -1.1 to -1.4 V. The spectra exhibit mainly two emission peaks at ultra-violet (UV) emissions and visible ranges. The weak UV peak in the PL spectra is related to the near-band-edge (NBE) emissions of the AZO nanostructures, which involve a recombination of the free exciton, the bound exciton, and the free exciton longitudinal optical (LO) phonon replica. The PL intensity corresponding to the defects related to the emissions of the AZO nanostructures deposited at -1.4 V is much higher than those deposited at -1.1 , -1.2 , and -1.3 V. The defect-related emissions are attributed to several defects in the AZO nanostructures, such as V_{Zn} , Zn_i , V_O , and O_i .

Summary and Conclusions

AZO nanostructures were electrochemically formed on ITO-coated glass substrates. SEM images showed that the density of the AZO nanostructures increased with increasing reaction time and applied voltage. XRD patterns showed that the AZO nanostructures had wurtzite structures and that the XRD intensities corresponding to the (002) diffraction peak of the AZO nanostructures deposited at higher voltages of -1.3 and -1.4 V were relatively higher than those deposited at lower voltages of -1.1 and -1.2 V. The PL spectra for the AZO nanostructures formed on the ITO-coated glass substrates showed that the PL intensity related to the defects for the AZO nanostructures increased with increasing reaction time due to an increase in the

thickness of the nanosheets. The PL intensity corresponding to the defects related to the emissions of the AZO nanostructures deposited at -1.4 V was much higher than those deposited at -1.1 , -1.2 , and -1.3 V. These results can help improve understanding of the effect of reaction time and applied voltage on the structural and optical properties of the AZO nanorods.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2013-016467). J. Y. Kim was supported by a Research Grant from Kwangwoon University in 2014.

References

1. K. Gong, F. Du, Z. Xia, M. Durstock, and L. Dai, *Science* 323 (2009) 760-764.
2. E. Garnett and P. Yang, *Nano Lett.* 10 (2010) 1082-1087.
3. Z. Xiong and X.S. Zhao, *J. Am. Chem. Soc.* 134 (2012) 5754-5757.
4. M. Chen, M. Lu, Y. Wu, J. Song, C. Lee, Z.L. Wang, and L. Chen, *Nano Lett.* 10 (2010) 4387-4393.
5. J. Chung, J. Myoung, J. Oh, and S. Lim, *J. Phys. Chem. C* 114 (2010) 21360-21365.
6. J. L. Hou, S.J. Chang, C.H. Wu, and T.J. Hsueh, *IEEE Electron Device Lett.* 34 (2013) 1023-1025.
7. A. Marzouki, F. Falyouni, N. Haneche, A. Lusson, P. Galtier, L. Rigutti, G. Jacopin, M. Tchernycheva, M. Oueslati, and V. Sallet, *Mater. Lett.* 64 (2010) 2112-2114.
8. D. Wang, A. Pierre, K. Cui, X. Han, K.H. Bevan, H. Guo, S. Paradis, A. Hakima, and Z. Mi, *Nano Lett.* 11 (2011) 2353-2357.
9. S.H. Ko, I. Park, H. Pan, N. Misra, M.S. Rogers, C.P. Grigoropoulos, and A.P. Pisano, *Appl. Phys. Lett.* 92 (2008) 154102-1-154102-3.
10. A. Umar, M.S. Chauhan, S. Chauhan, R. Kumar, G. Kumar, S. A. Al-Sayari, S.W. Hwang, and A. Al-Hajry, *J. Colloid Interface Sci.* 363 (2011) 521-528.
11. J. Elias, M. Bechelany, J. Michler, G. Wang, and L. Philippe, *Adv. Mater.* 22 (2010) 1607-1612.
12. H. Wei, H. Gong, Y. Wang, X. Hu, L. Chen, H. Xu, P. Liu, and B. Gao, *Crystengcomm.* 13 (2011) 6065-6070.
13. C. Xu, B. Kim, J. Lee, M. Kim, S.W. Hwang, B.L. Choi, E.K. Lee, J.M. Kim, and D. Whang, *Mater. Lett.* 72 (2012) 25-28.
14. S. Sanchez, C. Levy-Clement, and V. Ivanova, *J. Electrochem. Soc.* 159 (2012) D705-D712.
15. Q.F. Han, Y.I. Jeong, J.H. Heo, C.M. Shin, H. Ryu, M.S. Park, W.J. Lee, J.H. Yoon, J.E. Yang, and H. Choi, *J. Nanosci. Nanotechnol.* 12 (2012) 3677-3681.
16. T.G. Kim, J. Jang, H. Ryu, and W. Lee, *J. Alloy. Compd.* 579 (2013) 558-563.
17. M. Ohyama, H. Kozuka, and T. Yoko, *Thin Solid Films* 306 (1997) 78-85.
18. M.A. Reshchikov, B. Nemeth, J. Nause, and A. Osinsky, *Physica B* 401 (2007) 358-361.
19. C.H. Ahn, Y.Y. Kim, D.C. Kim, S.K. Mohanta, and H.K. Cho, *J. Appl. Phys.* 105 (2009) 013502-1-013502-5.