

ZnO nanorods on ZnO thin films with different preferred orientation and their Ethanol gas sensing properties

Hyejin Park^a, Hosang Ahn^b, Sun-Hee Kim^{c,*} and Dong-Joo Kim^{a,*}

^aMaterials Research and Education Center, Auburn University, Auburn, AL 36849, USA

^bKorea Institute of Construction Technology, 283 Goyandaero, Ilsanseo-gu, Goyang, Gyeonggi 411-712, Korea

^cDepartment of i-Fashion Design, Yuhan University, Kyunginro 590 Bucheon-si, Gyeonggi 422-749, Korea

ZnO films with different preferred orientation or texturing were deposited via sol-gel method using different chelating agents. Thermolysis assisted chemical solution method was used to grow ZnO nanorods on ZnO films. The ZnO films with different preferred orientation and nanorods grown on those films were examined by characterization of gas sensing properties conducted at 300 °C using ethanol. Randomly grown ZnO films showed higher sensitivity comparing with oriented ZnO films due to larger specific surface area. When ZnO nanorods were grown on ZnO films with different orientation, no significant gas sensing response between two structures was observed. However, structural change from films to nanorods results in significant improvement in gas sensing properties. Therefore, the growth toward 3-dimensional nanostructure can play more important role in enhancing sensitivity than control of 2-dimensional film orientation.

Key words: ZnO, Nanostructure, Sol-gel, Crystallographic orientation, Gas sensing.

Introduction

Semiconducting metal oxides such as WO₃, SnO₂ and ZnO, have been attracting sustained interest for gas sensor applications because of their excellent responses to various gases [1, 2]. Especially, ZnO is one of the semiconductors that has been widely investigated for a variety of combustible and toxic gas detections [3, 4]. Most ZnO gas sensors use either thin film technologies or 3-D nanostructures to enhance their sensing ability. Understanding the structure of the sensing material is important to improve the properties of devices. Additionally, since the orientation of crystallographic structure is known to influence adsorption site and/or rate between materials and gases, orientation dependent gas sensing property is an important factor for applications.

To synthesize ZnO films with preferred orientation, various methods have been investigated from physical deposition methods such as pulsed laser deposition and sputter deposition [5, 6], to chemical based deposition such as precipitation method and sol-gel coating [7, 8]. Among these methods, sol-gel technique has been attracted as chemical solution deposition owing to its efficient way for easy fabrication of thin films. Although ZnO films by a sol-gel method often presented strong c-axis orientation, the change in preferred orientation by modifying chemical additives

of ZnO precursors was also reported [9, 10]. Such microstructural evolution of ZnO films driven by sol-gel parameters has been investigated, but few studies have been reported to link film orientation and crystallization of ZnO films to gas sensing properties.

In this study, ZnO films having different preferred orientations were prepared for ethanol gas sensing. In order to investigate relative roles on gas sensing properties between film orientation and nanostructures grown on films, ZnO nanorods were grown on films with different preferred orientation and their sensing properties were analyzed.

Experimental Setup

To synthesize ZnO films, zinc acetate dehydrate (Aldrich, (C₂H₃O₂)₂Zn·2H₂O) and 2-methoxyethanol (Aldrich, C₃H₈O₂) were used as Zn precursor and solvent, respectively. The molar concentrations of solutions were kept as 0.5 M constantly. Different chelating agents such as DEA (Aldrich, HN(CH₂CH₂OH)₂) and MEA (Aldrich, NH₂CH₂CH₂OH) were used to modify the preferred orientation of ZnO. The molar ratio between zinc acetate and the chelating agent was fixed to 1 : 1. The mixed precursor was stirred for 1 hr at 80 °C and then cooled down to room temperature. Transparent solution was prepared and used for coating on cleaned amorphous silicon nitride wafer. Spin coating of the precursor solution was performed at 3000 rpm for 30 sec. After spin coating, pyrolysis was performed: at 300 °C by MEA-chelated and 250 °C by DEA-chelated for 10 min. Films after five coatings cycle were annealed at

*Corresponding author:

Tel : +82-2-2610-0873, 1-334-844-4864

E-mail: shkim001@yuhan.ac.kr, dkim@auburn.edu

500 °C for 1 hr for crystallization. Then, 0.01 mol of zinc nitrate hexahydrate (Fisher chemical, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and the same mole of hexamethylenetetramine (Aldrich, HMT) were mixed to grow the ZnO nanorods in 400 mL deionized water. After stirring a mixed aqueous solution for 24 hrs to dissolve the raw materials, the mixed aqueous solution was dipped in a hot water bath (Fisher Scientific, IsoTemp 202 Water Bath) for 4 hrs at 85 °C. Substrates were taken out from the bath and washed with DI water for 1 min to remove by-products formed during 4 hr synthesis. Post-annealing was performed to remove rinsed water and residual chemicals at 300 °C for 1 hr.

For measurement of gas sensing properties, interdigitated electrodes with 100 μm distance were coated by micro-fabrication process. Scanning electron microscope (SEM, JEOL JSM-7000F) was utilized to observe grown ZnO films and nanorods. X-ray diffractometer (XRD, Rigaku D/MAX B) characterization utilizing $\text{Cu K}\alpha$ radiation was performed to examine the preferred orientation of ZnO films and nanorods. For sensitivity measurement, ambient environment was controlled inside a chamber by flowing synthetic air. The electrical resistance was recorded by a Keithley 2400 sourcemeter (Keithley Instruments, Inc). The concentration of ethanol gas was calculated by

$$C_{\text{ethylene}}(\text{ppm}) = \frac{500 \times \text{MFC}_1}{\text{MFC}_1 + \text{MFC}_2 + \text{MFC}_3} \quad (1)$$

Here, MFC_1 , MFC_2 , and MFC_3 indicate 20 sccm of ethanol diluted gas, 20 sccm of oxygen, and 60 sccm of nitrogen respectively to obtain 10 ppm of ethanol atmosphere.

Results and Discussion

The preferred orientation of ZnO films and nanorods controlled by chelating agent was analyzed by XRD spectra. Fig. 1 shows the ZnO peaks of the films: black line represents the DEA-chelated films and red line presents the MEA-chelated films. The ZnO nanorods peaks are shown in Fig. 2 with same marks. The XRD spectra clearly present that different preferred orientation during ZnO growth was controlled by using different chelating agents. The intensity and the FWHM values of the peaks indicating (100), (002), and (101) of the DEA-chelated film indicated similar values. The MEA-chelated film, however, showed higher degree of (002) peak intensity, which indicates promoted c-axis preferred orientation. The change in preferred orientation occurs because the chelating agent influences chemical bonding in synthesized precursor structure. Different degrees of polymerization due to the molecules of the chelating agent will affect crystallization process when coated precursors or substances in an amorphous pyrolyzed state evolves into crystalline ZnO [8, 9, 11]. Significant difference was observed on ZnO nanorods since they were

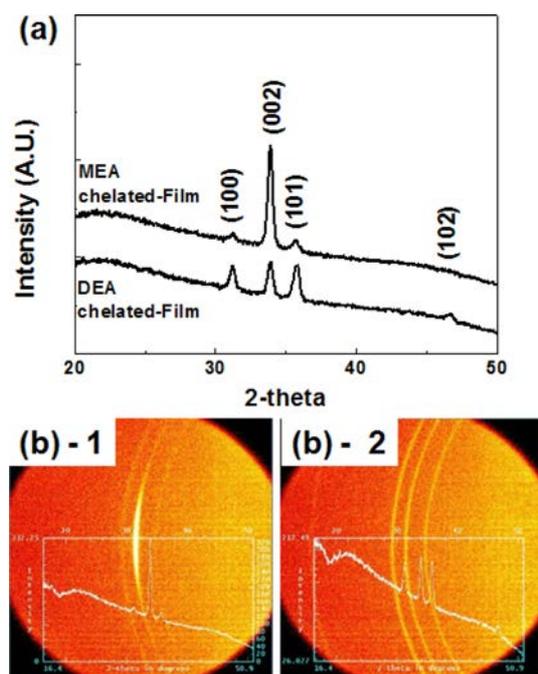


Fig. 1. XRD spectra of The ZnO thin films synthesized by different chelating agents. (a) point XRD spectra and (b) area XRD detection: (b)-1 is MEA-chelated ZnO films and (b)-2 is DEA-chelated ZnO NR.

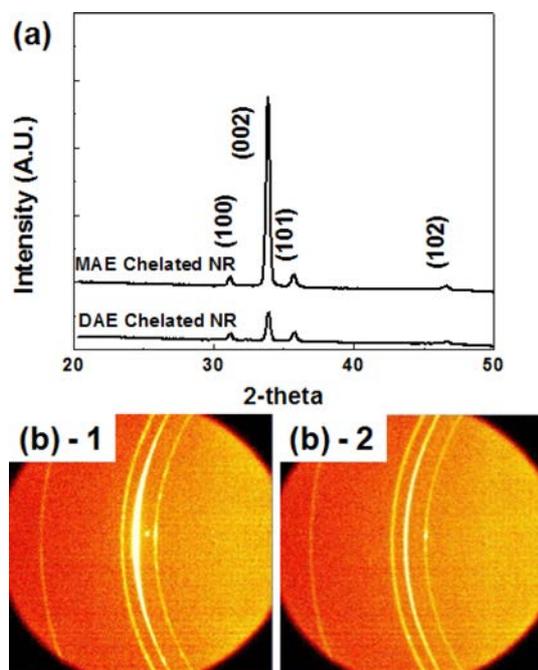


Fig. 2. XRD spectra of the ZnO nanorods grown on chelated ZnO films; (a) point XRD spectra and (b) area XRD detection: (b)-1 is MEA-chelated ZnO NR and (b)-2 is DEA-chelated ZnO NR.

more dominantly grown to (002) plane than ZnO film from MEA-chelated solutions. Relatively random growth was observed in ZnO nanorods when DEA-chelated solutions were used. Moreover, the preferred orientation of ZnO was more developed after growing ZnO nanorods as confirmed by XRD. ZnO nanorods grew to c-axis when a

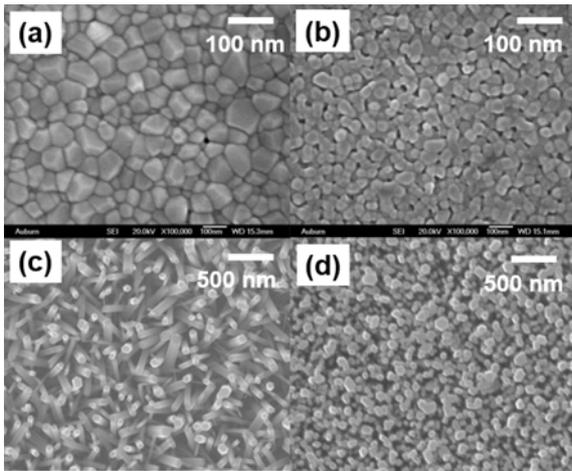
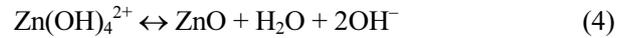
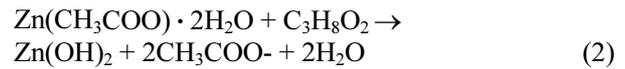


Fig. 3. SEM images of the surface morphologies of the ZnO thin films by (a) DEA and (b) MEA treatment and the ZnO nanorods over (c) the DEA treated film and (d) the MEA treated film.

thermally assisted chemical solution method was used. The intensity of (002) plane of ZnO nanorods on MEA-chelated ZnO films became stronger because MEA-chelated ZnO films were already oriented to c-axis. However, intensities among three major planes were not relatively distinguished in the case of ZnO nanorods on DEA-chelated ZnO thin films. XRD spectra confirmed that the orientation of the ZnO nanorods was influenced by the preferred orientation of ZnO thin films.

The relations between preferred orientation and morphology of ZnO films and nanorods were investigated. SEM images show the surface morphologies of ZnO films deposited via sol-gel using different chelating agents (Fig. 3(a-b)) and ZnO nanorods (Fig. 3(c-d)) grown on the films. Fig. 3(a) shows ZnO films with random orientation from DEA-chelated condition whereas the ZnO films shown in Fig. 3(b) has the c-axis oriented growth corresponding to Fig. 1. The average grain size of MEA-chelated ZnO films shows smaller grain size than randomly oriented films, i.e. DEA-chelated films. Additionally, the grains of DEA-chelated ZnO films had different morphology comparing with the grains of MEA-chelated ZnO films. Such observation could be resulted by different degree of polymerization by chelating agents. DEA-chelating agents promoted ZnO to grow faster even though nucleation rate was slower than MEA-chelating agents [8]. After growing ZnO nanorods on each film, it was obvious to observe the orientation effect driven by chelating agent as shown in the XRD results. ZnO nanorods on DEA-chelated films shows randomly oriented nanorods instead of perpendicularly grown ZnO nanorods on MEA-chelated films. To explore the effect of chelating agent on ZnO films, understanding the growth mechanism of ZnO from sol-gel precursors is important. The following processes can be considered as synthetic mechanism of ZnO using similar precursors [12]:



Breaking of the bonding in Zn precursor combined with OH precursor can be promoted by a chelating agent [9]. Meanwhile, the use of DEA influences higher nucleation barrier caused by the strong bonds formed between two OH groups in the DEA and Zn^{2+} ions whereas only one OH group was provided by MEA chelating agent to stabilize the Zn^{2+} ion [8, 11]. Therefore, ZnO assisted by MEA chelating agent only resulted in c-axis growth and by DEA provided various ZnO planes with higher nucleation energy. However, growth direction of the nanorods itself did not change in our solution system. The orientation of ZnO nanorods may be determined by film orientation by serving as a seed layer.

The effects of crystallographic orientation on ZnO properties were examined by measuring gas sensing performance under flowing ethanol and air gases. To activate ZnO adsorption sites, the temperature of a sensing stage was elevated to 300 °C. Gas response was measured by introducing 100 ppm ethanol gas into

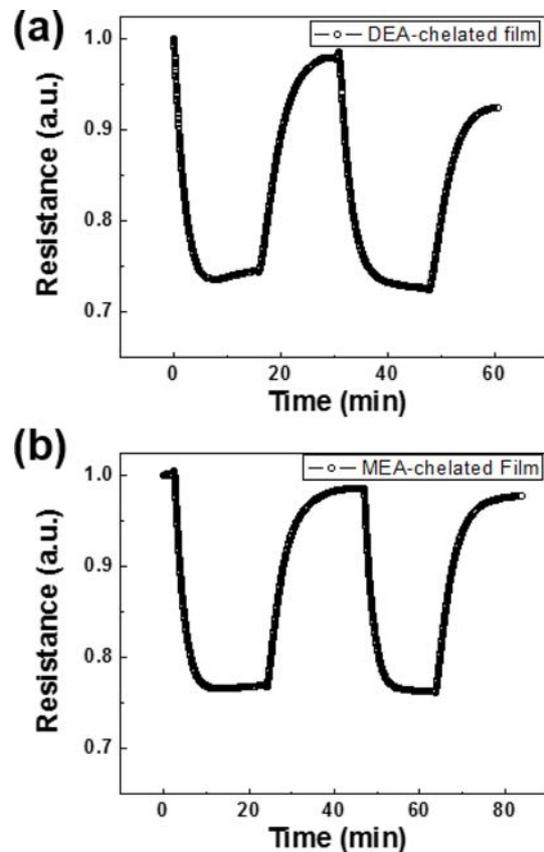


Fig. 4. 100 ppm ethanol gas sensing behaviors of the ZnO thin films by (a) DEA and (b) MEA treatment.

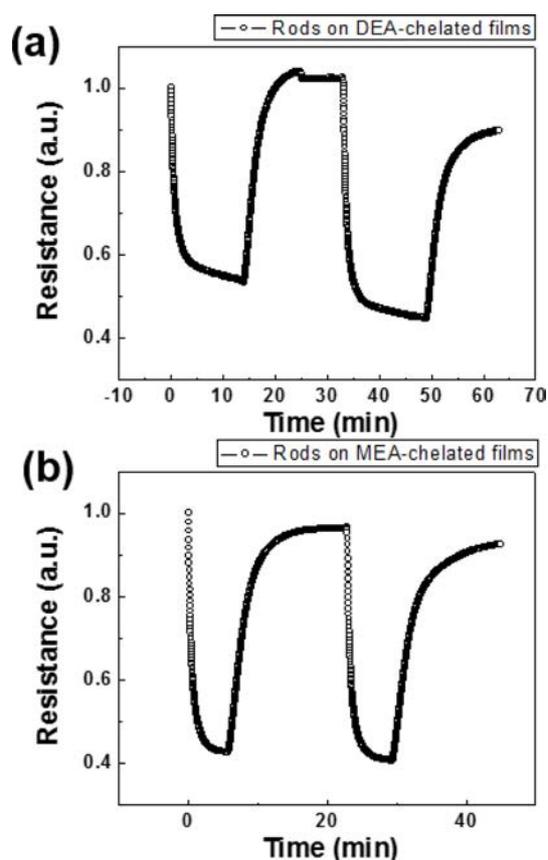


Fig. 5. 100 ppm ethanol gas sensing behaviors of the ZnO nanorods by (a) the DEA-chelated ZnO NRs and (b) the MEA-chelated ZnO NRs.

Table 1. Summary of ZnO gas sensing behaviors.

	Films		Nanorods	
	DEA	MEA	DEA	MEA
$\Delta R/R_i$	1.36	1.30	2.30	2.31

an isolated chamber. As reported, ZnO showed n-type semiconducting behavior, i.e. decreased resistance with ethanol gas as ionized oxygen on oxide surface gave off the electrons to an oxide material [13]. Then, the resistance recovered up to 90% of initial resistance without ethanol gas as oxygen was adsorbed to ZnO surface. Fig. 4 show gas sensing behaviors of ZnO films with different preferred orientations and Fig. 5 show gas sensing behaviors of ZnO nanorods on chelated ZnO films. The initial resistance of the films was lower comparing with those of the nanorods. The oxygen concentration on oxide surface contributes to initial resistance of a sensing material, and initial resistance value of nanorods was much higher than that of thin films [14]. As the structure changes from thin film to nanorod, gas response increased up to 1.7 times higher, which indicate that more reactive sites may exist on nanorod surfaces than on film surface. The gas response was also influenced by preferred orientation of ZnO. However, the difference became almost negligible

especially on nanorods. Each crystallographic planes has different amount of active site for gas absorption, but increased total number of the active sites driven by construction of nanostructures on film can reduce the effect of crystallographic planes. Therefore, the control of crystallographic orientation for gas sensing performance may be ineffective comparing with designing three-dimensional hierarchical structure of sensing materials including nanorods.

Conclusions

The effect of ZnO films and nanorods with preferred orientation on gas sensing properties has been investigated. The preferred orientation of ZnO thin films was successfully controlled via sol-gel process using different chelating agents (MEA/DEA). The chelating agents influenced the nucleation and growth rate of ZnO film. After the growth of ZnO nanorods on chelated ZnO films, the topography of the sensing layers was changed dramatically. In ethanol atmosphere, the ZnO films and the ZnO nanorods showed stable n-type gas sensing behaviors. The effect of structure change from 2-D film to 3-D nanorod was more significant on gas sensing properties than the effect of preferred orientation in polycrystalline. Therefore, design of three-dimensional hierarchical structure would be more important for gas sensor or e-nose applications.

Acknowledgments

This research was partially supported by the Korea Institute of Energy Technology Evaluation and Planning (20158520000210) grant funded by the Korea Government Ministry of Trade, Industry and Energy, a grant from a Strategic Research Project (2016-0156) funded by the Korea Institute of Construction Technology, and Auburn University IGP.

References

1. Y.H. Ko, M.S. Kim, W. Park, and J.S. Yu, *Nanoscale Res. Lett.* 8[1] (2013) 1-8.
2. Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho and H. Morkoc, *J. appl. Phys.* 98[4] (2005) 041301.
3. T. Seesaard, in *Proceeding s of the 2012 IEEE International Conference* (2012).
4. Z. Lim, Z. Chia, M. Kevin, A. Wong and G. Ho, *Sensor Actuat. B-Chem.* 151[1] (2010) 121-126.
5. J.-M. Myoung, W.-H. Yoon, D.-H. Lee, I. Yun, S.-H. Bae and S.-Y. Lee, *Jpn. J. Appl. Phys.* 41[1R] (2002)28.
6. K.H. Kim, K.C. Park and D.Y. Ma, *J. Appl. Phys.* 84[1] (1998) 660-660.
7. B. Wessler, F. Lange and W. Mater, *J. Mater. Res.* 17[07] (2002) 1644-1650.
8. S.H. Yoon, D. Liu, D. Shen, M. Park and D.-J. Kim, *J. Mater. Sci.* 43[18] (2008) 6177-6181.
9. L. Znaidi. *Mater. Sci. Eng-B.* 174[1] (2010) 18-30.

10. S.B. Yahia, L. Znaidi, A. Kanaev and J. Petit, *Spectrochim Acta A: Mol. Biomol. Spectrosc.* 71[4] (2008) 1234-1238.
11. I. Winer, G.E. Shter, M. Mann-Lahav and G.S. Grader, *J. Mater. Res.* 26[10] (2011) 1309-1315.
12. S. Rani, P. Suri, P. Shishodia and R. Mehra, *Sol. Energ. Mat. Sol. C.* 92[12] (2008) 1639-1645.
13. H. Ahn, J.-H. Park, S.-B. Kim, S. H. Jee, Y. S. Yoon and D.-J. Kim, *Electrochem. Solid-State Lett.* 13[11] (2010) J125-J128.
14. S.R. Morrison, *Sens. Actuat.* 12[4] (1987) 425-440.