

Effect of growth temperature on the ZnO nanowires prepared by thermal heating of Zn powders

Hyoun Woo Kim^{a,*}, Mesfin A. Kebede^a, Hyo Sung Kim^a, Buddhudu Srinivasa^a, Doo Young Kim^b, Jae Young Park^a, Sang Sub Kim^a

^a School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

^b Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA.

ARTICLE INFO

Article history:

Received 22 December 2008

Received in revised form 24 March 2009

Accepted 14 April 2009

Available online 3 May 2009

PACS:

81.07.-b

61.46.Km

68.37.Hk

68.37.Lp

78.55.-m

Keywords:

Nanostructures

Chemical synthesis

Transmission electron microscopy

ABSTRACT

ZnO nanowires have been synthesized by heating Zn powders under nitrogen (N₂) gas atmosphere. The influence of the growth temperature on the morphology, structure, and photoluminescence (PL) properties of ZnO nanowires has been investigated. At the higher-temperature growth process, thinner nanowires have been obtained. Interestingly, it is observed that the variation of growth temperature has significantly affected the photoluminescence spectra of the ZnO nanowires, showing an enhancement in the relative intensity of the green to UV emission bands with the increase of the growth temperature. In addition, the oxygen sensing properties of the as-synthesized ZnO nanowires were tested.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In recent times, zinc oxide (ZnO) as the II–VI semiconductor material has been drawing a special attention of the scientists and technologists across the globe because of its versatile and remarkable physical, optical and electronic properties. ZnO is an n-type wide direct bandgap oxide semiconductor material with bandgap energy of 3.37 eV and high exciton binding energy of 60 meV and hence it has transformed as a novel material of greater importance due to its intriguing and multi-optical functions [1–4]. Different kinds of ZnO nanostructures, such as one-dimensional (1D) nanowires, nanorods, nanorings, nanohelices, and two-dimensional (2D) nanosheets/nanoplates in many crystal morphologies are of great significance in the development of novel materials for their potential applications [5,6]. Among them, 1D nanowires have been considered as potential optical materials for their use in nanoscale electronics, optoelectronics and sensing and several other applications [7,8]. We have earlier reported on the temperature effects on the morphologies and luminescence analysis of the nanowires of Bi₂O₃ and MgO [9,10]. Although the growth temperature

affects the film properties more significantly than any other growth parameter during the thin film processes, the effect of temperature on the growth of low-dimensional nanostructures has not so far been sufficiently investigated. In view of this, in the present work we have undertaken the synthesis of the ZnO nanowires by heating Zn powders and carried out a systematic analysis of the effects of temperature on the structural and photoluminescence (PL) properties of the nanowires. Apart from these studies, we have also evaluated the oxygen sensing performance of the as-synthesized ZnO nanowires at the room temperature.

2. Experimental

We have synthesized ZnO nanowires by heating Zn powders in a vertical tubular furnace [11], in which Zn powders and Au-coated Si substrates, respectively, were placed on the lower and the upper holder in the center of the quartz tube. The heating time was set to 1 h. The gas flow rate of nitrogen (N₂) was 1.5–2 standard liters per min (slm). In order to investigate the temperature effects, we varied the growth temperature in the range of 900–1050 °C.

The as-synthesized nanowires were investigated using glancing angle (0.5°) X-ray diffraction (XRD, X'pert MPD-Philips with a CuKα₁ radiation of 1.5406 Å) with the contributions from the

* Corresponding author.

E-mail address: hwkim@inha.ac.kr (H.W. Kim).

substrates are minimized, scanning electron microscopy (SEM, Hitachi S-4200), and transmission electron microscopy (TEM, Philips CM-200) with energy-dispersive X-ray (EDX) spectroscopy installed. PL spectra were measured at the room temperature on a SPEC-1403 photoluminescence spectrometer with the 325 nm line from a He–Cd laser (Kimon, Japan). Oxygen sensing properties

were also measured in a system that has been conventionally used [12,13]. The oxygen pressure in the system was controlled in the range of 1.0×10^{-5} Torr to 1 Torr. The sensitivity of the fabricated sensor was determined as a function of oxygen pressure. Sensitivity is defined as the ratio of the resistivity in the presence of oxygen to the resistivity in the absence of oxygen [14].

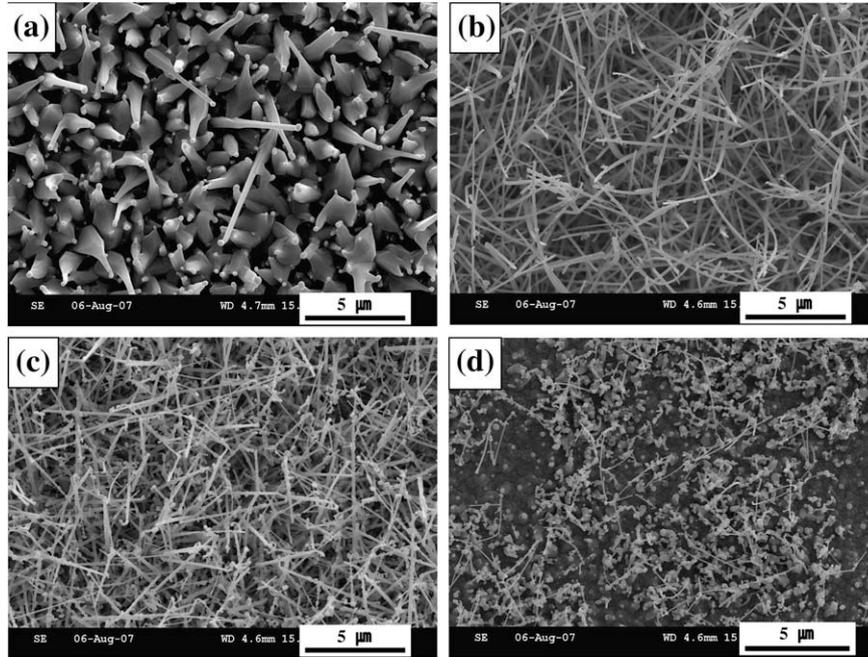


Fig. 1. SEM images of the product synthesized at (a) 900 °C, (b) 950 °C, (c) 1000 °C, and (d) 1050 °C.

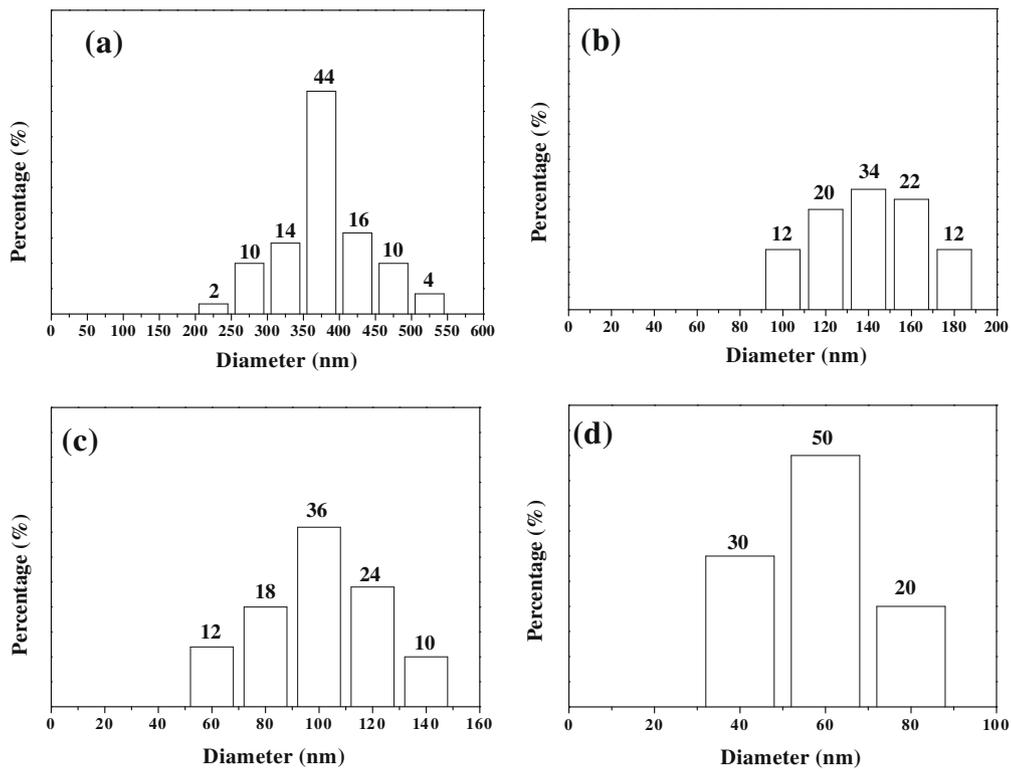


Fig. 2. Diameter distributions of the nanowires synthesized at (a) 900 °C, (b) 950 °C, (c) 1000 °C, and (d) 1050 °C.

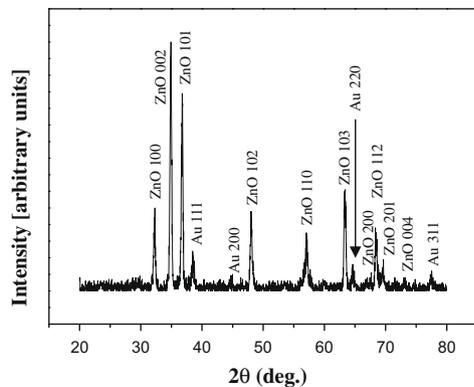


Fig. 3. Typical XRD spectrum of as-synthesized ZnO nanowires.

3. Results and discussion

Fig. 1a, b, c, and d show SEM images of the products that were synthesized at 900 °C, 950 °C, 1000 °C, and 1050 °C, respectively, revealing that the diameters of 1D structures are changing with the variation of the growth temperature. For a quantitative investigation on the nanowire diameters, we have plotted the diameter distributions of the nanowires in Fig. 2. Fig. 2a–d reveal that the average diameter of 1D structures grown at 900 °C, 950 °C, 1000 °C, and 1050 °C, respectively, are in the range of 200–550 nm, 90–190 nm, 50–150 nm, and 30–90 nm. Based on a simple calculation of the average diameters of 1D structures from the graph of the diameter distributions as shown in Fig. 2, the average

diameters of 900 °C-, 950 °C-, 1000 °C-, and 1050 °C-grown samples are approximately 379 nm, 140 nm, 100 nm, and 59 nm, respectively.

With the XRD spectra not being noticeably changed from varying the growth temperature, we have presented a typical spectrum (Fig. 3). Besides Au-associated peaks from substrates, recognizable peaks can be clearly determined as hexagonal ZnO structure (ICDD File No. 05-0664). No reflection peaks from the impurities, such as unreacted Zn or other zinc oxides, have been observed, indicating that the synthesized products are in high purity and good quality.

In order to obtain detailed information on the structure and morphology of ZnO nanowires, we have carried out TEM analysis for the sample grown at 950 °C. Apart from the diameter of nanowires which depends on the growth temperature (as shown in Figs. 1 and 2), the crystalline structure and tip-morphology of the products as determined by TEM were not noticeably dependent on the temperature. TEM investigation has revealed that nanowires with a diverse morphology are produced. Fig. 4a shows a nanowire with a straight-line morphology. Although it is noteworthy that there exists no nanoparticle at the end of the nanowire, we are not sure that there was originally a tip nanoparticle prior to the TEM sample preparation. It is possible that the nanowires may have been broken away from the catalyst dots, due to the ultrasonic treatment during the TEM sample preparation [15]. Fig. 4b shows a nanowire with a wave-natured morphology with a periodically bumpy surface [16]. Fig. 4b indicates that no catalyst nanoparticle has been attached to the tip of the nanowire, denying the possibility that the nanowire has been grown via a vapor–solid–liquid (VLS) mechanism. Also, as shown in Fig. 4b, the diameter of ZnO nanowire gradually decreases near the tip part, suggesting that

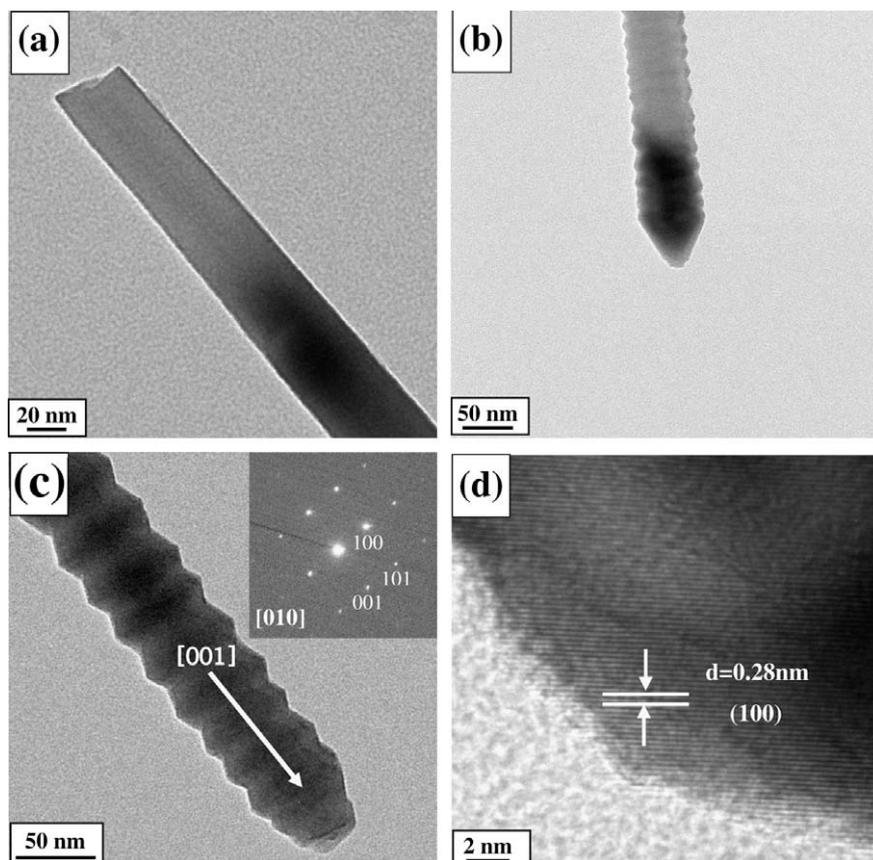


Fig. 4. (a) TEM image of a tip-particle-free nanowire with a straight-line morphology, which was grown at 950 °C. (b,c) TEM images of tip-particle-free nanowires with their diameter being modulated. Inset of (c) corresponds to an associated SAED pattern. (d) Lattice-resolved TEM image exhibiting an area near the surface of a ZnO nanowire as shown in (c).

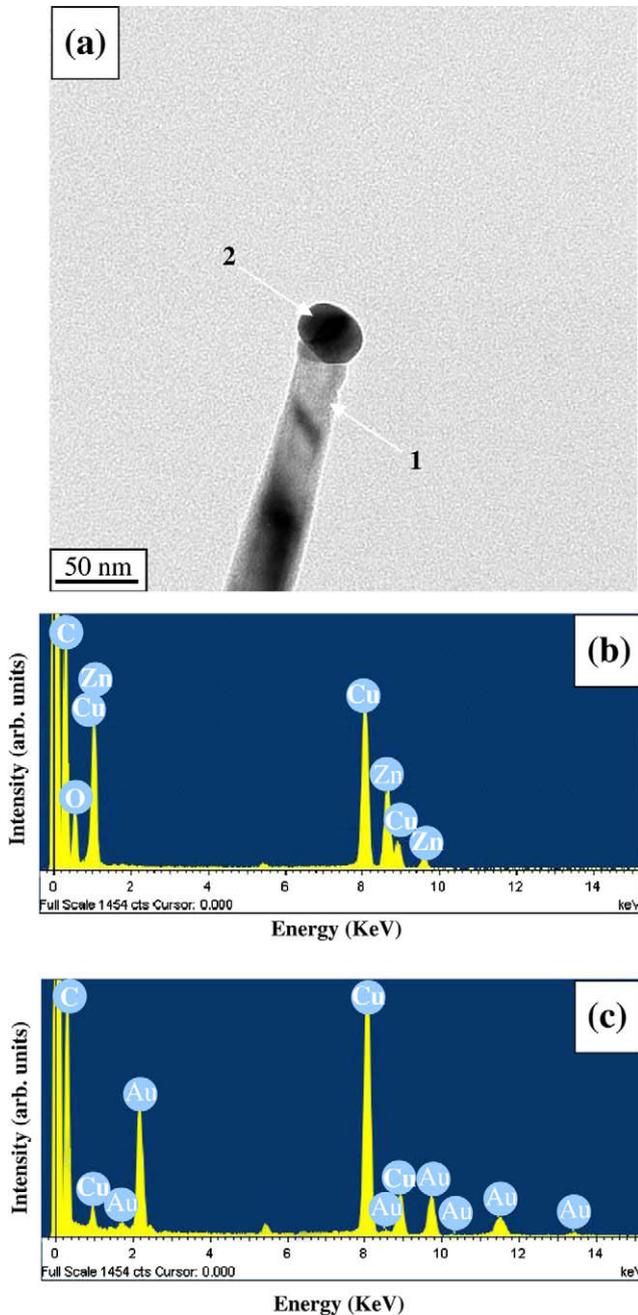


Fig. 5. (a) TEM image of a 950 °C-grown-nanowire with a tip nanoparticle. TEM-EDX spectra taken from (b) the area indicated by Arrow 1 in (a) and (c) the area indicated by Arrow 2 in (a).

the nanowire growth can be controlled by the vapor–solid (VS) mechanism [17–19].

Although previous studies suggested that the self-oscillating characteristics of the nanowire cross-section could be ascribed to the instability of the diameter of the liquid droplets during the VLS growth process [20–22], the mechanism of diameter modulation for a nanowire in Fig. 4b is not clear. We surmise that the diameter modulation in the present work can be related to the instability of a nanowire of small diameter under the influence of the effects of surface tension [23]. It is also possible that different crystalline plane has a different surface energy, with the low-energy plane being favored. Fig. 4c shows another ZnO nanowire with a modulating diameter. The inset of Fig. 4c corresponds to an associated selected area electron diffraction (SAED) pattern, exhibiting the

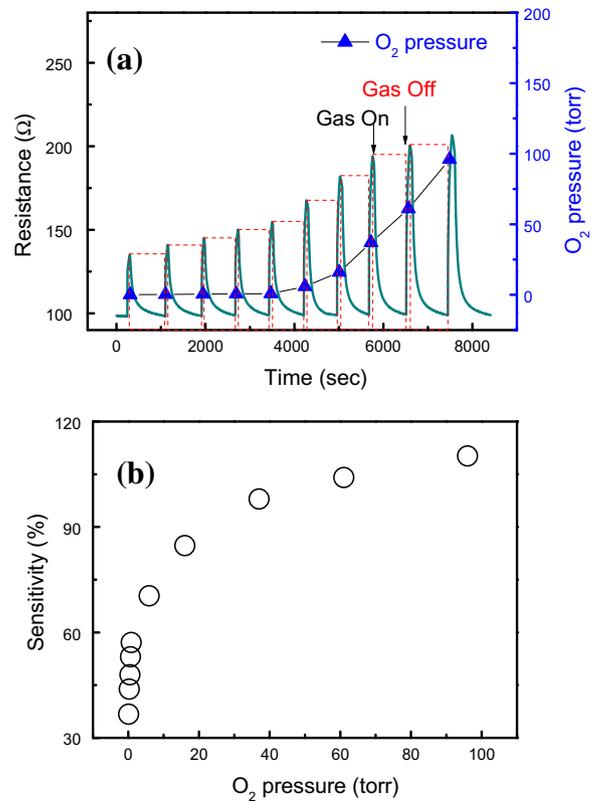


Fig. 6. (a) Variation of resistance as a function of oxygen pressure measured at room temperature for a sensor fabricated from the as-synthesized ZnO nanowires. (b) Variation of sensitivity depending on different O₂ pressures.

[0 1 0] zone axis of hexagonal ZnO. Fig. 4d is a lattice-resolved TEM image near the surface of the nanowire shown in Fig. 4c. The interplanar spacing was about 0.28 nm, corresponding to (1 0 0) planes of the hexagonal ZnO.

Fig. 5a shows a TEM image of a nanowire with a tip nanoparticle being attached. EDX spectra for the nanowire stem (Arrow 1 in Fig. 5a) and the dark nanoparticle (Arrow 2 in Fig. 5a) indicate that the nanowire stem is composed of Zn and O (Fig. 5b), whereas the nanoparticle comprises Au (Fig. 5c). Cu and C signals originate from the microgrid mesh supporting the nanowires. Accordingly, some nanostructures are indeed nanowires having Au-associated nanoparticles at the tip, whose growth is dominated by a VLS process. Based on Figs. 4 and 5, we conclude that the growth process of ZnO nanowires in the present study can be attributed to a combination of VLS and VS mechanisms.

In addition, the SEM results reveals that the average diameter of the ZnO nanowires has been decreased with increasing growth temperature (Figs. 1 and 2). This result is in discord with previous results that the nanowires became thicker with increasing growth temperature [24,25]. It is possible that the growth of ZnO nanowires in the present study occurs in a diffusion-controlled regime. In this case, the diffusion of adatoms on nanowire surface becomes smooth and faster with increasing the temperature. Accordingly, at a higher-temperature, more adatoms will be diffused to the tips, which are energetically favorable sites, instead of being remained on the side surface of nanowire. On the contrary, the reduction of temperature slows down the diffusion of the adsorbed species, resulting in the formation of thicker nanowires. Another possibility is that higher-temperature enables a faster desorption of the adsorbed species. Since the tip part is more energetically stable region than the stem part, the adatoms on the nanowire side surface will be more likely to be detached than those on the tip. This tendency

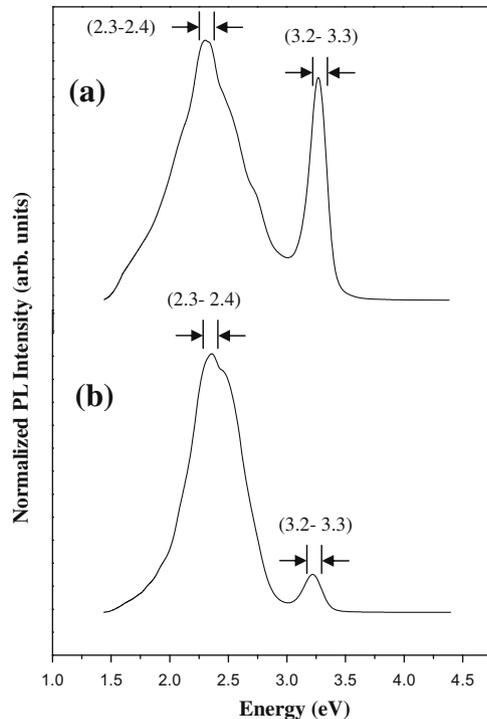


Fig. 7. PL spectra of ZnO nanowires synthesized at (a) 900 °C and (b) 1000 °C.

will contribute to the formation of thinner nanowires. Further systematic study in this direction is considered necessary.

For the purpose of proving the potential of the as-synthesized ZnO nanowires in chemical sensors, we have tested their oxygen sensing properties. Fig. 6a is a response curve to the oxygen gas measured at room temperature for a sensor made from ZnO nanowire networks. The sensor responds quickly to the change of oxygen environment. Its resistance increases upon exposure to oxygen, whereas the resistance decreases upon the absence of oxygen. It is notable that the sensor responses were very stable and reproducible for repeated testing cycles, which promises its practical use in chemical sensors. Fig. 6b shows the change of sensitivity as a function of O₂ pressure. It shows an increasing sensitivity initially and saturation at higher O₂ pressures.

The normalized PL spectra of ZnO nanowires synthesized at 900 °C and 1000 °C are presented in Fig. 7a and b, respectively, for a comparison. Both spectra exhibit a relatively sharp ultraviolet (UV) emission band in addition to a broad green emission band, being analogous to typical PL spectra of ZnO nanowires reported previously [26–28]. The UV emission band peaking at an energy of 3.2–3.3 eV corresponds to the near band edge (NBE) emission, being associated with the excitons in ZnO [29,30]. The broad green emission band centered at 2.3–2.4 eV can be ascribed to the emission from deep trapping site corresponding to defects such as oxygen vacancies in ZnO [26,27,29,30]. By comparing Fig. 7b with Fig. 7a, we noticed that the relative intensity of the green to UV emission is increased with the increasing of the growth temperature. Accordingly, we surmise that a larger amount of structural defects in ZnO nanowires are generated during the nanowires synthesis process at high temperature. Further detailed investigation will be carried out soon.

4. Conclusions

In summary, we conclude that we have succeeded in the fabrication of high quality ZnO nanowires by heating Zn powders. We have investigated the effects of the growth temperatures on the morphology, structure, and PL properties of ZnO nanowires. SEM images have revealed that the average diameter of ZnO nanowires has been decreasing with an increase in the growth temperature. TEM investigations suggest that the growth of ZnO nanowires has mainly been controlled by both VS and VLS mechanisms. The growth temperature has significantly affected the PL spectra, in which the relative intensity of the green to UV emissions has been increasing with increasing of the temperature, presumably due to the generation of additional defects at higher growth temperature. In addition, we have fabricated a sensor using as-synthesized ZnO nanowires. Its oxygen sensing properties were measured at room temperature.

Acknowledgments

This work is the outcome of a Manpower Development Program for Energy and Resources supported by the Ministry of Knowledge and Economy (MKE).

References

- [1] J. Hupkes, B. Rech, S. Calnan, O. Kluth, U. Zastrow, H. Siekmann, M. Wuttig, *Thin Solid Films* 502 (2006) 286.
- [2] C.Y. Lee, S.Y. Li, P. Lin, T.Y. Tseng, *IEEE Trans. Nanotechnol.* 5 (2006) 216.
- [3] S.Y. Li, P. Lin, C.Y. Lee, T.Y. Tseng, *J. Appl. Phys.* 95 (2004) 3711.
- [4] S.N. Bai, T.Y. Tseng, *Thin Solid Films* 515 (2006) 872.
- [5] R.Q. Guo, J. Jishimura, M. Matsumoto, M. Higashihata, D. Nakamura, J. Suehri, T. Okada, *Appl. Phys. B* 90 (2008) 539.
- [6] F. Jones, F. Leonard, A.A. Talin, N.S. Bell, *J. Appl. Phys.* 102 (2007) 014305.
- [7] P.C. Chang, C.J. Chien, D. Stichtenoth, C.R. Jia, G. Lu, *Appl. Phys. Lett.* 90 (2007) 113101.
- [8] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P.D. Yang, *Nat. Mater.* 4 (2005) 455.
- [9] H.W. Kim, J.W. Lee, C. Lee, *J. Korean Phys. Soc.* 50 (2007) 1308.
- [10] H.W. Kim, S.H. Shim, C. Lee, *J. Korean Phys. Soc.* 49 (2007) 628.
- [11] H.W. Kim, N.H. Kim, *Appl. Phys. A* 80 (2005) 537.
- [12] R.K. Sharma, M.C. Bhatnagar, G.L. Sharma, *Sens. Actuators, B* 46 (1998) 194.
- [13] H.W. Kim, S.H. Shim, J.W. Lee, J.Y. Park, S.S. Kim, *Chem. Phys. Lett.* (2008), doi:10.1016/j.cplett.2008.03.024.
- [14] R.K. Sharma, M.C. Bhatnagar, *Sens. Actuators, B* 56 (1999) 215.
- [15] C.-Y. Wang, L.-H. Chan, D.-Q. Xiao, T.-C. Lin, H.C. Shih, *J. Vac. Sci. Technol., B* 24 (2006) 613.
- [16] C.W. Na, S.Y. Bae, J. Park, *J. Phys. Chem. B* 109 (2005) 12785.
- [17] H.W. Kim, S.H. Shim, *Chem. Phys. Lett.* 422 (2006) 165.
- [18] L.F. Dong, J. Jiao, M. Coulter, L. Love, *Chem. Phys. Lett.* 376 (2003) 653.
- [19] H.-X. Zhang, J.P. Ge, Y.-D. Li, *Chem. Vap. Deposition* 11 (2005) 147.
- [20] R. Gupta, Q. Xiong, G.D. Mahan, P.C. Eklund, *Nano Lett.* 3 (2003) 1745.
- [21] E.I. Givargizov, *J. Cryst. Growth* 20 (1973) 217.
- [22] J. Jie, G. Wang, X. Han, J. Fang, Q. Yu, Y. Liao, B. Xu, Q. Wang, J.G. Hu, *J. Phys. Chem. B* 108 (2004) 8249.
- [23] H.Y. Peng, Z.W. Pan, L. Xu, X.H. Fan, N. Wang, C.-S. Lee, S.-T. Lee, *Adv. Mater.* 13 (2001) 317.
- [24] P. Paiano, P. Prete, N. Lovergine, A.M. Mancini, *J. Appl. Phys.* 100 (2006) 094305.
- [25] R.S. Wagner, C.J. Doherty, *J. Electroceram. Soc.* 113 (1996) 1300.
- [26] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H.-J. Choi, *Adv. Funct. Mater.* 12 (2002) 323.
- [27] Q. Wan, Z.T. Song, W.L. Liu, C.L. Lin, T.H. Wang, *Nanotechnology* 15 (2004) 559.
- [28] H.W. Kim, S.H. Shim, J.W. Lee, C. Lee, S.C. Jeoung, *Opt. Mater.* 30 (2008) 1221.
- [29] D.C. Reynolds, D.C. Look, B. Jogai, C.W. Litton, T.C. Collins, W. Harsch, G. Cantwell, *Phys. Rev. B* 57 (1998) 12151.
- [30] S.W. Jung, W.I. Park, H.D. Cheong, G.-C. Yi, H.M. Jang, S. Hong, S.T. Joo, *Appl. Phys. Lett.* 80 (2002) 1924.