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The O_2-dependent growth of ZnO nanowires and their photoluminescence properties

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Abstract

ZnO nanowires were massively synthesized on a $Ni(NO_3)_2$-coated silicon substrate under oxygen-containing argon atmosphere by a simple chemical vapor deposition method. The average diameter of the ZnO nanowires was about 50 nm and the average length was about 20 μm. The morphologies of the ZnO nanowires strongly depended on oxygen content in the growth atmosphere. At low oxygen concentration (about 5–10 ppm), ZnO nanocones and nanoneedles were obtained, while at high oxygen concentration (about ~250 ppm), ZnO nanoparticles deposited on the substrate. The room temperature photoluminescence (PL) spectrum of the ZnO nanowires revealed that a strong UV band at 384 nm dominated the whole spectrum. These results indicate that the ZnO nanowires grown under oxygen-containing atmosphere possess better crystalline quality and UV luminescence properties than those grown in reducing hydrogen atmosphere. Based on the analysis of oxygen effect on the ZnO nanostructures, a vapor–liquid–solid mechanism assisted by the redox growth mode was proposed to understand the growth of the ZnO nanowires.
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1. Introduction

One-dimensional nanomaterials have stimulated great interest due to their importance in basic scientific research and potential applications. ZnO has a wide band gap of 3.37 eV and an excitation binding energy of about 60 meV, which makes it an ideal material for blue/ultraviolet (UV) photoelectronic devices [1]. Various vapor-phase methods, such as chemical vapor deposition (CVD) [2–8], metal organic chemical vapor deposition (MOCVD) [9–11], carbothermal reaction [12–14] and molecular beam epitaxy (MBE) [15] etc. were used to synthesize one-dimensional ZnO nanostructures, and various mechanisms such as vapor–liquid–solid (VLS) mechanism, vapor–solid (VS) mechanism and redox growth mechanism were proposed to understand their growth. The VLS mechanism is widely studied due to its effective control over the growth of nanowires. As a promising catalyst for the VLS process, metal oxides such as CuO, NiO, FeO have been used for the preparation of the nanowires [16–18]. Kim et al. [19] successfully synthesized ZnO nanowires with the assistance of nickel oxide in H_2 gas. However, the ZnO nanowires prepared in reducing hydrogen gas were reported to exhibit poor UV luminescence properties because of the increasing oxygen vacancies in the surface layers of the ZnO nanowires. To improve the UV luminescence properties, a method without any reducing gas will be expected to result in ZnO nanowires with high crystalline quality.

In this paper, we report the synthesis of the ZnO nanowires on $Ni(NO_3)_2$-coated Si substrate under oxygen-containing argon atmosphere. The weak oxygen effect and the growth mechanism of the ZnO nanowires are investigated in detail, and their photoluminescence properties are discussed.

2. Experimental

ZnO nanowires were fabricated on $Ni(NO_3)_2$-coated Si substrate under O_2-containing argon atmosphere in a self-designed horizontal CVD system. The $Ni(NO_3)_2$-coated Si substrate was prepared according to the following procedure: a scratched Si wafer was put in an ultrasonic bath of acetone and de-ionized water for 20 min to remove the impurities and native oxides on its surface. A 1.5 mol/L nickel nitrate water solution

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was prepared and dropped onto the Si wafer (80 mm × 6 mm in size). After being dried in the oven for 24 h, the $Ni(NO_3)_2$-coated Si substrate was placed at the center of a quartz tube, and a quartz boat filled with zinc powder (99.9%) was fixed near the gas input of the quartz tube. Then, the whole quartz tube was inserted into the horizontal tube furnace. O_2/Ar mixed gas (about 20 ppm O_2) was introduced into the reaction system at the flow rate of 100 standard cubic centimeters per minute (sccm). We controlled the additional oxygen amount by adjusting its relative flow rate to Ar gas (Purity >6N). Subsequently, the ZnO nanowires were grown at 550 °C for 60 min. After the furnace was cooled to room temperature, light gray products were obtained on the substrate. In addition, atmospheres with other oxygen concentrations of 5, 10 and 250 ppm were used for the growth of ZnO nanostructures to investigate the effect of additional O_2 on the growth of the ZnO nanowires.

The as-prepared ZnO nanowires were characterized and analyzed by using scanning electron microscopy (SEM, Hitachi S-570), field emission scanning electron microscopy (FE-SEM, Jsm-6460), X-ray diffraction (XRD, Panalytiecal X'pert PRO), transmission electron microscopy (TEM, Hitachi H-800) and selective area electronic diffraction (SAED). The room

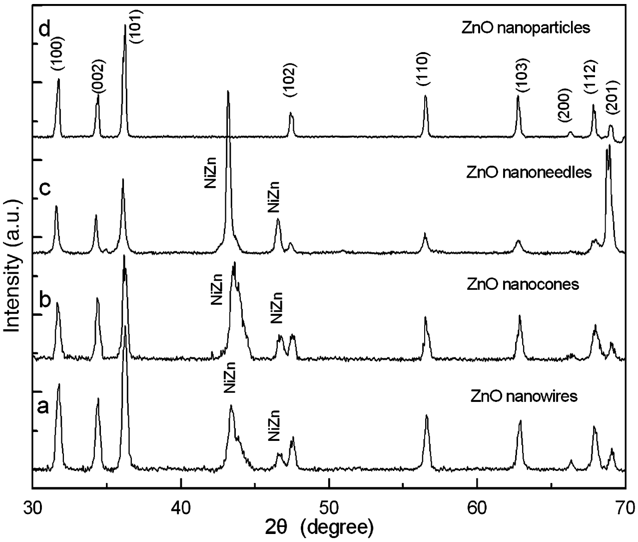

Fig. 1. XRD patterns of the as-grown ZnO nanostructures synthesized in the atmosphere with various oxygen contents. (a) ZnO nanowires grown in about 20 ppm O_2; (b) ZnO nanocones grown in about 5 ppm O_2; (c) ZnO nanoneedles grown in about 10 ppm O_2; (d) ZnO nanoparticles grown in about 250 ppm O_2.

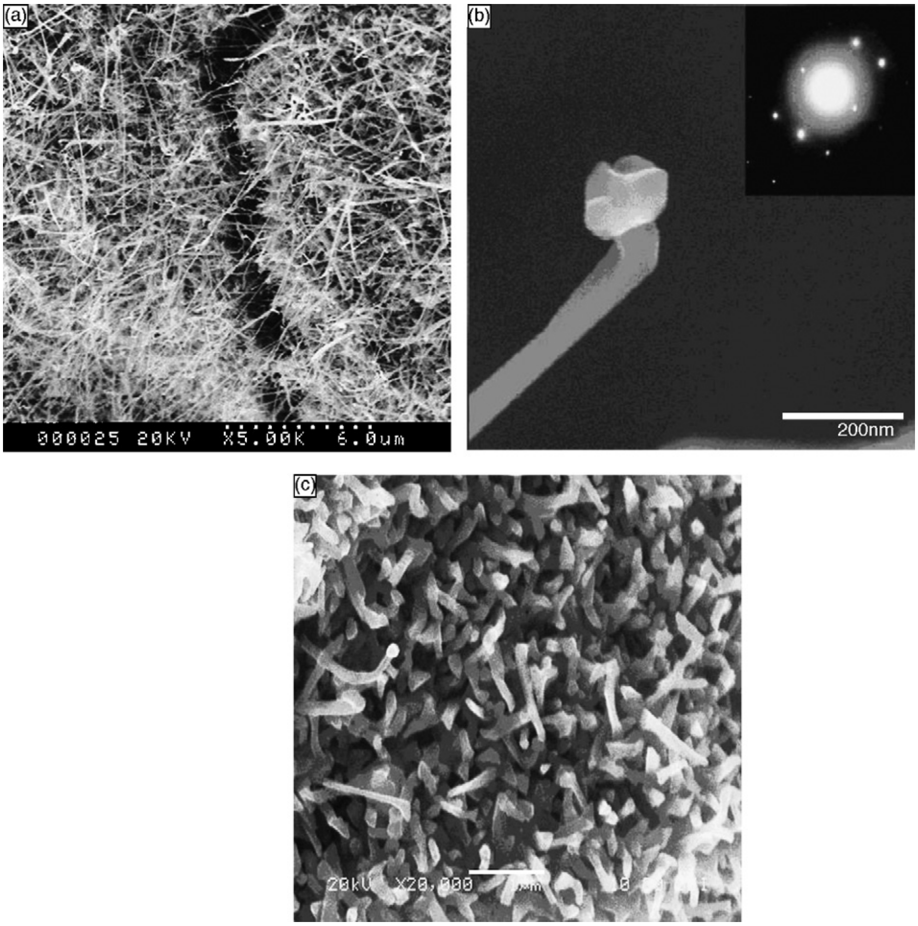

Fig. 2. SEM (FE-SEM) images of the ZnO nanowires synthesized under about 20 ppm-O_2-containing Ar atmosphere. (a) A typical morphology of the ZnO nanowires grown for 1 h; (b) the magnified image of a single ZnO nanowire with catalyst particle on its tip, the inset: the selected area electron diffraction pattern of the nanowire; (c) the FE-SEM image of the ZnO sample grown for 20 min.

temperature photoluminescence (PL) spectrum was measured on a Hitachi F-4500 spectrophotometer with a Xe lamp as the excitation source (the excitation wavelength: 325 nm).

3. Results and discussion

The XRD pattern of the ZnO nanowires synthesized in the atmosphere with the oxygen content of 20 ppm is shown in Fig. 1(a), which can be indexed to a hexagonal structure of ZnO. Two peaks at $2\theta = 43.4^\circ$ and 46.7° were related to the catalyst alloy of NiZn presenting in the grown products. Fig. 1(b–d) corresponds to the XRD patterns of the ZnO nanostructures grown at other oxygen contents of 5, 10 and 250 ppm, which will be discussed in the following text.

Fig. 2(a) depicts a typical SEM image of the ZnO nanowires. The ZnO nanowires had the average diameter of 50 nm and the average length of 20 μm. The magnified image of a single ZnO nanowire is shown in Fig. 2(b), the solidified catalyst droplet was observed clearly at tip of the ZnO nanowire, which implies that the VLS mechanism governs the growth of the ZnO nanowires [20]. The SAED pattern shown in the inset indicates that the ZnO nanowire is the single crystal in nature.

To investigate the formation process of the ZnO nanowires, another ZnO sample grown for shorter time (20 min) was prepared in the 20 ppm-O_2-containing atmosphere. The sample exhibits a morphology corresponding to the initial growth stage of the ZnO nanowires, as is shown in Fig. 2(c). The as-grown nanostructures, like bowlings, decreased gradually in the slopes along the growth direction. Their top and bottom widths were around 100 and 200 nm, respectively, and the lengths were more than 1 μm. Some catalyst particles could be found on the tops of the bowling-like ZnO nanostructures. These observations suggest that the ZnO nanowires may be large in diameters at the beginning of the growth process, but as the process continues, the diameters decrease slowly, and the whole structures have a tendency toward wires with constant diameters.

Fig. 3 shows the morphologies of the ZnO nanostructures synthesized at other oxygen contents of 5, 10 and 250 ppm. When the oxygen content was about 5 ppm, cone-like ZnO nanostructures shown in Fig. 3(a) were formed, being about 800 nm in bottom widths and 2 μm in lengths. The typical image of the ZnO nanocones is shown in the inset of Fig. 3(a). At the oxygen content of 10 ppm, thinner and longer ZnO nanoneedles with the lengths of 3–4 μm were obtained, as shown in Fig. 3(b). That no catalyst particles existed at tips of the ZnO cones and needles can be attributed to the fact that the catalyst droplets had slipped down from the tip due to the sharp slopes during the growth process. Above results imply that the additional O_2 strongly influences the morphologies of the ZnO

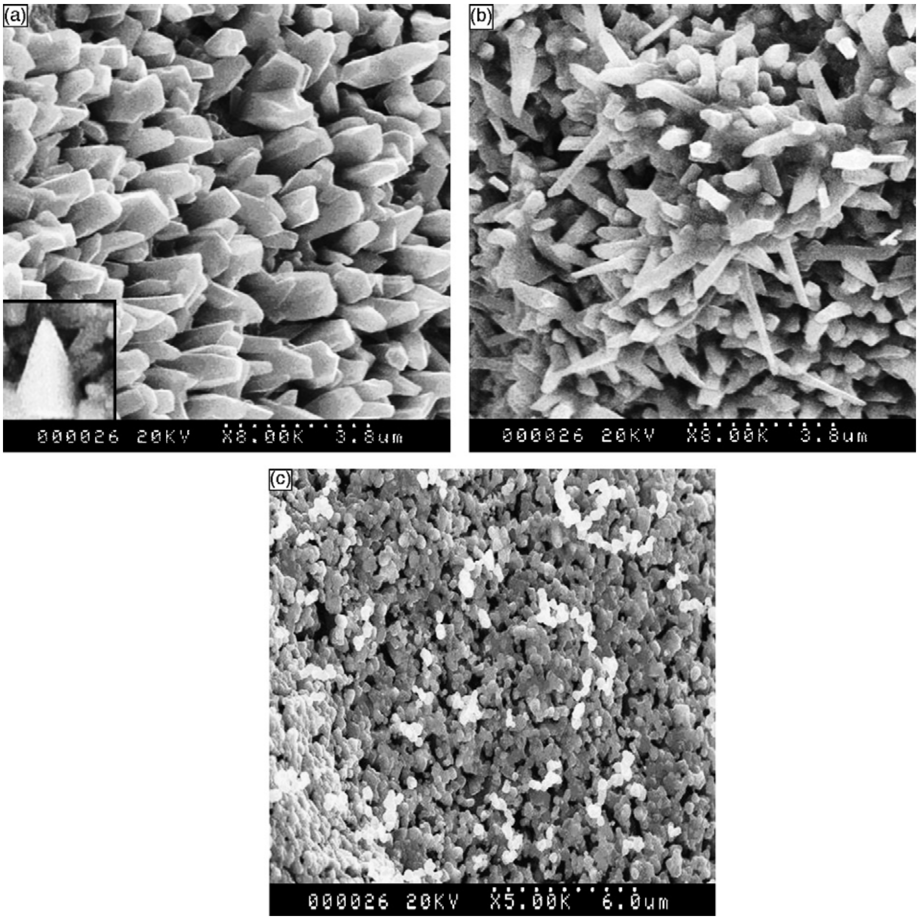

Fig. 3. SEM images of the ZnO nanostructures synthesized in the O_2/Ar atmosphere with other oxygen contents. (a) ZnO nanocones grown in about 5 ppm O_2. The inset shows the typical image of the ZnO nanocones. (b) ZnO nanoneedles grown in about 10 ppm O_2; (c) ZnO nanoparticles grown in about 250 ppm O_2.

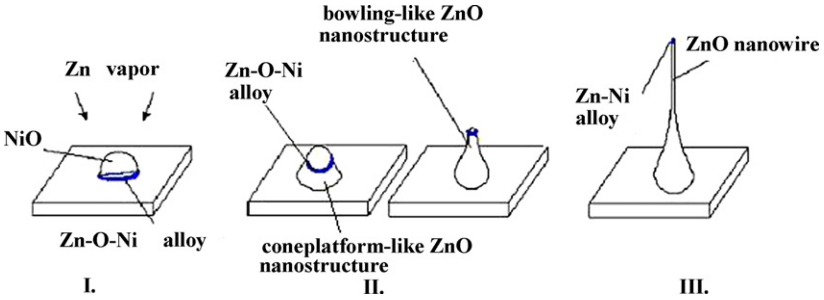

Fig. 4. The schematic diagram of the presented growth mechanism of the ZnO nanowires.

nanostructures: the ZnO nanostructure synthesized at the high oxygen content has lower slope than that synthesized at the low oxygen content. When the oxygen content was 250 ppm, a mass of ZnO nanoparticles were deposited on the Si substrate resulting from the quick oxidization of zinc vapor, as is shown in Fig. 3(c). The XRD measurements (Fig. 1(b–d)) indicate that the ZnO nanostructures, including nanocones, nanoneedles and nanoparticles, possess the hexagonal wurtzite structure.

According to the preliminary analysis of the ZnO nanowires formation and the weak oxygen influence on the morphologies of the ZnO nanostructures, a possible growth mechanism of the ZnO nanowires is proposed below. The growth process of the ZnO nanowires is schematically presented in Fig. 4.

Firstly, $Ni(NO_3)_2$ starts to decompose into NiO and NO_2 via reaction (1) at 260 °C.

$$Ni(NO_3)_2(s) \rightarrow NiO(s) + NO_2(g) \qquad (1)$$

At the growth temperature, the NiO nanoclusters are uniformly produced on the Si substrate by calcination and serve as nucleation sites of the ZnO nanowires (Fig. 4I). Zinc vapor, generated constantly from the zinc powder source, is absorbed onto the NiO particles, and a miscible Zn–O–Ni alloy droplet is formed on the surfaces. Then, zinc reacts with NiO to produce ZnO and Ni inside the droplet via reaction (2) which is thermodynamically feasible because of its low free energy of $-99.53\ \mathrm{kJ\ mol^{-1}}$ at 550 °C.

$$NiO(l) + Zn(l) \rightarrow ZnO(l) + Ni(l) \qquad (2)$$

The produced ZnO accumulates near the droplet/substrate interface by diffusion. When supersaturation occurs, nano-scale ZnO is precipitated at the interface to form a ZnO nanostructure. As the reaction proceeds, the catalyst droplet reduces due to the consumption of the NiO particle, which results in the rapid decrease of the ZnO nanostructure in diameter [5]. After grown for some time, the coneplatform-shaped ZnO nanostructure with the droplet on the top is formed due to the redox effect, as shown in Fig. 4II. In this process, ZnO is produced through reaction (2) inside the droplet, so the oxygen component originates mainly from NiO instead of O_2 with high bonding energy (5.16 eV) in the atmosphere.

But when the growth proceeds to certain extent, resulting from the further reduction of the NiO particle, NiO concentration in the alloy droplet probably starts to decrease while zinc concentration increases. When zinc becomes surplus in the droplet, the unreacted zinc will accumulate at the droplet/ZnO-coneplatform interface to be supersaturated and react with O_2 in the atmosphere to form ZnO by the VLS mechanism (reaction (3)).

$$Zn(l) + 0.5O_2(g) \rightarrow ZnO(s) \qquad (3)$$

Thus, the ZnO nanostructure are grown according to both the redox mechanism and the VLS mechanism, and the NiO particle and O_2 act as the oxygen source together. In fact, the ZnO produced by the VLS process does not consume the NiO particle, which means that the catalyst droplet should be constant in size by continuously absorbing zinc vapor, and the nanostructure with constant diameters should be obtained. Considering this fact, the formed ZnO coneplatform decreases slowly in diameter and tends to exhibit lower slope than before. With the growth process, the interaction between the redox mechanism and the VLS mechanism results in the formation of the bowling-like ZnO nanostructure (Fig. 4II), which is confirmed by Fig. 2(c).

When reaction (2) is finished, the pure Zn–Ni liquid alloy remains at the tip of the ZnO structure. The process is dominated subsequently by the VLS mechanism with O_2 as the unique oxygen source. Finally, ZnO nanowires with constant diameters are achieved. During the whole process, especially at the late stage, it is easily found that the presence of O_2 in the

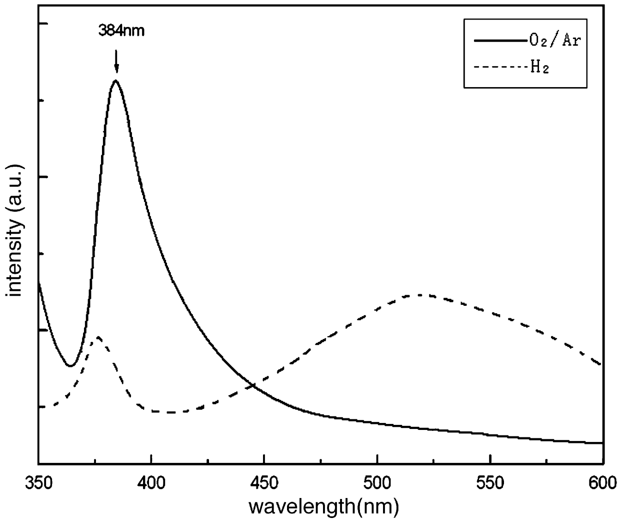

Fig. 5. PL spectra of the ZnO nanowires synthesized in about 20 ppm-O_2-containing Ar atmosphere and H_2 atmosphere [19], respectively.

atmosphere plays the key role on the formation of the ZnO nanowires.

The room temperature PL spectrum of the ZnO nanowires is shown in Fig. 5. Compared with those grown in H_2 atmosphere, the ZnO nanowires synthesized in 20 ppm O_2 exhibited an excellent UV emission corresponding to the band-edge emission of ZnO [17]. No green emission peak is observed, which indicates that less oxygen vacancies exist in the surface layer of the ZnO nanowires [21]. Moreover, it has been reported that the improvement of crystal quality (structure defects such as oxygen vacancies, etc.) can cause high UV emission [22,23]. Therefore, in our experiment, the strong UV emission and dramatically-weakened green emission imply that the ZnO nanowires are of the high crystalline quality.

4. Conclusions

We have successfully synthesized ZnO nanowires on $Ni(NO_3)_2$-coated Si substrate under 20 ppm-O_2-containing argon atmosphere by a simple CVD method. The crystal quality and UV luminescence properties of the as-grown ZnO nanowires were noticeably improved when compared with those synthesized in reducing hydrogen gas. The low O_2 content in the atmosphere plays a crucial role in the formation of the ZnO nanowires with constant diameters. A redox-assisted VLS mechanism is proposed to understand the growth of the ZnO nanowires.

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References

[1] R.F. Service, Will UV laser beat the blues, Science 276 (1997) 895.

[2] H.Y. Lu, S.Y. Chu, S.H. Cheng, The vibration and photoluminescence properties of one-dimensional ZnO nanowires, J. Cryst. Growth 274 (2005) 506–511.

[3] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H.J. Choi, Controlled growth of ZnO nanowires and their optical properties, Adv. Funct. Mater. 12 (2002) 323–331.

[4] Y.C. Kong, D.P. Yu, B. Zhang, W. Fang, S.Q. Feng, Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach, Appl. Phys. Lett. 78 (2001) 407–409.

[5] T.Y. Kim, J.Y. Kim, S.H. Lee, H.W. Shim, S.H. Lee, E.K. Suh, K.S. Nahm, Characterization of ZnO needle-shaped nanostructures grown on NiO catalyst-coated Si substrates, Synth. Met. 144 (2004) 61–68.

[6] J.S. Lee, M.I. Kang, S. Kim, M.S. Lee, Y.K. Lee, Growth of zinc oxide nanowires by thermal evaporation on vicinal Si(1 0 0) substrate, J. Cryst. Growth 249 (2003) 201–207.

[7] C.L. Xu, D.H. Qin, H. Li, Y. Guo, T. Xu, H.L. Li, Low-temperature growth and optical properties of radial ZnO nanowires, Mater. Lett. 58 (2004) 3976–3979.

[8] H. Ham, G.Z. Shen, J.H. Cho, T.J. Lee, S.H. Seo, C.J. Lee, Vertically aligned ZnO nanowires produced by a catalyst-free thermal evaporation method and their field emission properties, Chem. Phys. Lett. 404 (2005) 69–73.

[9] J.B. Baxter, E.S. Aydil, Epitaxial growth of ZnO nanowires on *a*- and *c*-plane sapphire, J. Cryst. Growth 274 (2005) 407–411.

[10] M.C. Jeong, B.Y. Oh, W. Lee, J.M. Myoung, Comparative study on the growth characteristics of ZnO nanowires and thin films by metalorganic chemical vapor deposition, J. Cryst. Growth 268 (2004) 149–154.

[11] S.W. Kim, S. Fujita, ZnO nanowires with high aspect ratios grown by metalorganic chemical vapor deposition using gold nanoparticles, Appl. Phys. Lett. 86 (2005) 153119–153122.

[12] M. Lorenz, J. Lenzner, E.M. Kaidashev, H. Hochmuth, M. Grundmann, Cathodoluminescence of selected single ZnO nanowires on sapphire, Ann. Phys. (Leipzig) 13 (2004) 39–42.

[13] C.H. Liu, W.C. Yiu, F.C.K. Au, J.X. Ding, C.S. Lee, S.T. Lee, Electrical properties of zinc oxide nanowires and intramolecular *p–n* junctions, Appl. Phys. Lett. 83 (2003) 3168–3170.

[14] S.Y. Li, C.Y. Lee, T.Y. Tseng, Copper-catalyzed ZnO nanowires on silicon (1 0 0) grown by vapor–liquid–solid process, J. Cryst. Growth 247 (2003) 357–362.

[15] Y.W. Heo, D.P. Norton, L.C. Tien, Y. Kwon, B.S. Kang, F. Ren, S.J. Pearton, J.R. LaRoche, ZnO nanowire growth and devices, Mater. Sci. Eng. R 47 (2004) 1–47.

[16] K. Yu, Y.S. Zhang, R. Xu, D.S. Jiang, L.Q. Luo, Q. Li, Z.Q. Zhu, W. Lu, Field emission behavior of cuboid zinc oxide nanorods on zinc-filled porous silicon, Solid State Commun. 133 (2005) 43–47.

[17] S.C. Lyu, Y. Zhang, H. Ruh, H.J. Lee, H.W. Shim, E.K. Suh, C.J. Lee, Low temperature growth and photoluminescence of well-aligned zinc oxide nanowires, Chem. Phys. Lett. 363 (2002) 134–138.

[18] C.C. Tang, S.S. Fan, Marc Lamy De La Chapelle, P. Li, Silica-assisted catalytic growth of oxide and nitride nanowires, Chem. Phys. Lett. 333 (2001) 12–15.

[19] T.Y. Kim, J.Y. Kim, M. Senthil Kumar, E.-K. Suh, K.S. Nahm, Influence of ambient gases on the morphology and photoluminescence of ZnO nanostructures synthesized with nickel oxide catalyst, J. Cryst. Growth 270 (2004) 491–497.

[20] R.S. Wagner, W.C. Ellis, Vapor–liquid–solid mechanism of single crystal growth, Appl. Phys. Lett. 4 (1964) 89–90.

[21] K. Vanheusden, W.L. Warren, C.H. Seager, D.K. Tallant, J.A. Voigt, B.E. Gnade, Mechanism behind green photoluminescence in ZnO phosphor powders, J. Appl. Phys. 79 (1996) 7983–7990.

[22] (a) D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, Optically pumped lasing of ZnO at room temperature, Appl. Phys. Lett. 70 (1997) 2230–2232;
(b) D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, High temperature excitonic stimulated emission from ZnO epitaxial layers, Appl. Phys. Lett. 73 (1998) 1038–1040.

[23] D.M. Bagnall, Y.F. Chen, M.Y. Shen, Z. Zhu, T. Goto, T. Yao, Room temperature excitonic stimulated emission from zinc oxide epilayers grown by plasma-assisted MBE, J. Cryst. Growth 185 (1998) 605–609.