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# Catalytic growth of semiconducting zinc oxide nanowires and their photoluminescence properties

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## Abstract

Semiconducting ZnO nanowires have been produced in bulk quantity by heating Zn powders (99.99%) containing Au nanoparticles at 900°C. Scanning electron microscopy and transmission electron microscopy observations show that the ZnO nanowires have diameters ranging from 30 to 60 nm and lengths up to several tens of micrometers. The growth of ZnO nanowires is controlled by the conventional vapor–liquid–solid (VLS) mechanism. A green light emission was observed at room temperature, which could be attributed to the singly ionized oxygen vacancy formed in the ZnO nanowires. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Quasi one-dimensional nanostructured materials such as nanotubes or nanowires have been successfully synthesized and have received much attention due to their peculiar physical properties and potential application in nanodevices [1]. Considerable effort has been placed on the bulk synthesis of nanotubes or nanowires using laser ablation [2–4], template [5], solution [6], and other methods [7]. Most of these works, which focused on semiconductor systems such as Si [1], GaN [8], GaAs [9], have been investigated in detail. Over

the past few years, several oxide nanowires, including MgO [7,10], SiO<sub>2</sub> [11], GeO<sub>2</sub> [12] and Ga<sub>2</sub>O<sub>3</sub> [13], have been reported.

As a wide band-gap (3.2 eV) semiconductor, ZnO is of interest in low-voltage and short wavelength (green or green/blue) electro-optical devices such as light emitting diodes and diode lasers [14]. Most of the ZnO nanomaterials studied are in the form of nanoparticles, although needle crystals and large whiskers have been reported [15]. Polycrystalline ZnO nanowires have also been fabricated within a porous alumina template [16]. Most recently, large-scale synthesis of ZnO nanowires have been achieved on Au-coated silicon substrates by physical evaporation of the mixture of ZnO and graphite powders [17]. Here, we report another simple method to synthesize large-scale

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ZnO nanowires by heating Zn powders containing Au nanoparticles as catalyst to direct the growth of the ZnO nanowires at 900°C. Photoluminescence (PL) characterization of the ZnO nanowires shows that these nanowires exhibit strong UV emissions.

## 2. Experimental procedure

We used Zn (99.99%) powders containing Au nanoparticles as starting material to synthesize ZnO nanowires. The Au nanoparticles were prepared by the reaction of gold salt and sodium citrate. Sodium citrate (60 mg) in 100 ml water was boiled and 1 ml of aqueous solution containing 9.5 mg HAuCl<sub>4</sub> was added. Boiling was then continued for 15 min [18], and then some Zn powders were immersed in the solution containing Au nanoparticles for several days and dried at room temperature. After that, the immersed Zn powders were placed in an alumina boat. Substantially, the alumina boat, which being covered with a quartz plate in order to maintain a higher zinc vapor pressure, has been placed at the center of the quartz tube that was inserted in a horizontal tube furnace. Under a constant flow of Ar (90%)/O<sub>2</sub> (10%) gas (100 sccm), the furnace was rapidly heated to 900°C (about 4 min) and held at this temperature for 10 min, and then cooled to room temperature. It was observed that white sponge-like products had appeared on the surface of source materials.

The synthesized products were characterized using scanning electron microscopy [(SEM) JEOL JSM-6300], X-ray diffraction [(XRD) MXP18AHF] by means of an automatized diffractometer with Cu K<sub>α</sub> radiation, and transmission electron microscopy [(TEM) JEM-200CX]. The specimens for TEM were prepared by putting the as-grown products in ethanol and immersing them in an ultrasonic bath for 15 min, then dropping a few drops of the resulting suspension containing the synthesized materials onto a TEM grid. The PL measurements were carried out on a HITACHI 850-type visible-ultraviolet spectrophotometer with a Xe lamp as the excitation light source at room temperature.

## 3. Results and discussion

The morphology of the as-synthesized products was examined using SEM. A typical SEM image for ZnO nanowires is shown in Fig. 1(a). The image shows that large-scale ZnO nanowires were formed in high yield. The diameters of the nanowires range from 30 to 60 nm and their lengths are up to several tens of micrometers. Bulk quantity of the products was analyzed by XRD. As shown in Fig. 1(b), the XRD pattern of the ZnO nanowires can be indexed to a hexagonal structure of bulk ZnO with cell constants of  $a_0 = 3.24 \text{ \AA}$  and  $c_0 = 5.19 \text{ \AA}$ . No diffraction peaks from Zn or other impurities have been found in our samples. Representative TEM images (Fig. 2) reveal the general morphology of the nanowires. It can be seen that the diameter of this ZnO nanowire is about 50 nm. It should be noted that a few nanoparticles do exist at the tip of the ZnO nanowires (Fig. 2(b)), as is indicated with arrowheads, and the diameters of these nanoparticles are about 2.0 times of that of the connected nanowires. Energy-dispersed X-ray spectrometry (EDX) analysis shows that the nanoparticles only contain Zn and Au. The same highly dispersed selected area electron diffraction (SAED) patterns [inset, Fig. 2(b)] taken from different places along the axis of a single ZnO nanowire without tilting the specimen, show complete diffraction pattern, indicating that the ZnO nanowires are of single crystalline phase.

There are two possible models for the growth of conventional crystal whiskers or nanowires, the screw dislocation and vapor–liquid–solid (VLS). It is well known that the presence of a liquid drop is essential for the effective operation of the VLS mechanism. The solidified spherical droplets at the tips of the nanowires are commonly considered to be the evidence for the operation of the VLS mechanism, which is in agreement with our experimental conditions and the observed results (Fig. 2(b), indicated with arrowheads). The EDX analysis shows that these nanoparticles only contain Zn and Au. Why there is no atomic oxygen in the alloy drops at the tips of the nanowires? It is well known that the bonding energy of O<sub>2</sub> is as high as 5.16 eV, which makes it

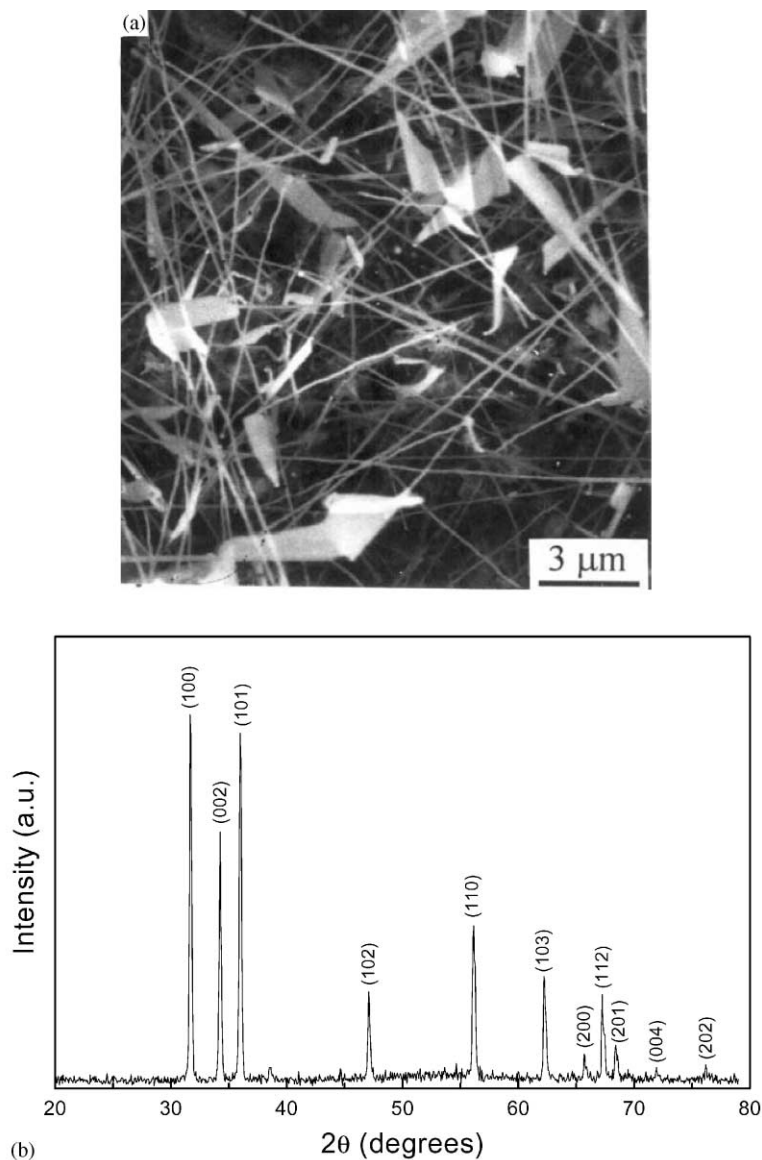


Fig. 1. The structure of ZnO nanowires (with wurtzite crystal structure). (a) Typical SEM image of the as-synthesized ZnO nanowires obtained from thermal evaporation of Zn powders containing Au nanoparticles as catalyst at 900°C. (b) XRD pattern recorded from the ZnO nanowires.

very difficult to decompose  $O_2$  into atomic oxygen at the conventional chemical vapor deposition (CVD) growth condition. Therefore, in this present case,  $O_2$  cannot decompose into atomic oxygen at 900°C. The presence of a small amount of  $O_2$  is not expected to change the Au–Zn phase

diagram, meanwhile they act as the oxygen source during the zinc oxide nanowires growth. Therefore, in this experimental process, the Zn vapor is rapidly generated at high temperature for the fast heating speed by vaporizing the zinc powders, and reacted with the Au catalyst to form alloy droplets.

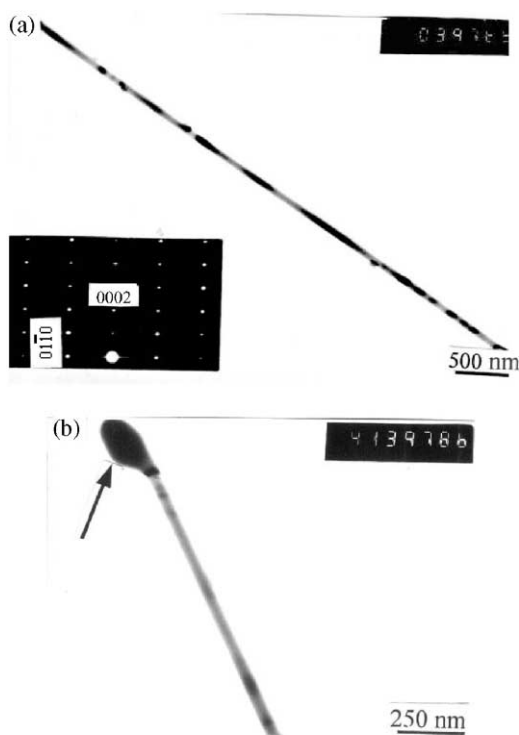


Fig. 2. Typical TEM images showing the general morphology of ZnO nanowires: (a) a ultralong ZnO nanowire, (b) a thin ZnO nanowire with a Zn/Au alloy tip, (inset) the corresponding highly diffusive pattern of electron diffraction from the nanowires.

As the droplets become supersaturated, ZnO nanowires are formed, by the reaction between Zn and O<sub>2</sub>.

The room temperature PL of the ZnO nanowires was examined and shown in Fig. 3. The excited wavelength was 380 nm and a 430 nm filter was used. The PL spectrum pattern has a strong green emission band peaking around 520 nm. In the past several decades, the green luminescence mechanisms of ZnO have been studied, and various models have been proposed [19,20]. Vanheusden et al. [21] proved that the singly ionized oxygen vacancy is responsible for the green emission in the ZnO and the emission results from the recombination of a photogenerated hole with an electron occupying the oxygen vacancy. Huang et al. [17] have reported that the progressive increase of the green light emission intensity

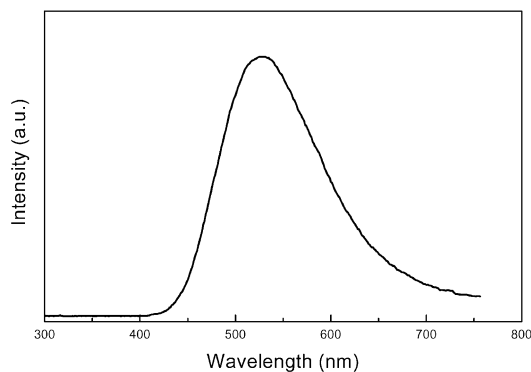


Fig. 3. PL spectrum of the ZnO nanowires.

relative to the UV emission as the wire diameter decreases, which suggests that there is a great fraction of oxygen vacancies in the nanowires. We believe that nanowires with high ratios (length/diameter) should have more surface and sub-surface oxygen vacancies. It was therefore reasonable to believe that the green light emission from the ZnO nanowires in our work could be attributed to the above-mentioned single ionized oxygen vacancy.

#### 4. Conclusions

In summary, we have successfully synthesized ZnO nanowires in bulk quantities by simple physical evaporation. SEM and TEM observations show that the ZnO nanowires have diameters of about 30–60 nm and lengths up to several tens of micrometers. PL measurement taken on the bulk nanowires shows a green light emission, which was attributed to the single ionized oxygen vacancy formed in the nanowires. The availability of the ZnO nanowires is expected to enable fascinating opportunities such as probing confinement, dynamics and transport of excitons in one dimension, and creating optically active nanostructured materials.

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## References

- [1] J.T. Hu, T.W. Odom, C.M. Lieber, *Acc. Chem. Res.* 32 (1999) 435.
- [2] Y. Zhang, K. Suenaga, C. Colliex, S. Iijima, *Science* 281 (1998) 973.
- [3] A.M. Morales, C.M. Lieber, *Science* 279 (1998) 208.
- [4] D.P. Yu, C.S. Lee, I. Bello, X.S. Sun, Y.H. Tang, G.W. Zhou, Z.G. Bai, Z. Zhang, S.Q. Feng, *Solid State Commun.* 105 (1998) 403.
- [5] C.R. Martin, *Science* 266 (1994) 1961.
- [6] Y. Li, Y. Ding, Z. Wang, *Adv. Mater.* 11 (1999) 844.
- [7] P. Yang, C.M. Lieber, *Science* 273 (1996) 1836.
- [8] J. Zhu, S. Fan, *J. Mater. Res.* 14 (1999) 1175.
- [9] M. Yazawa, M. Koguchi, A. Mute, M. Ozawa, K. Hiruma, *Appl. Phys. Lett.* 61 (1992) 2051.
- [10] P. Yang, C.M. Lieber, US Patent 5897945.
- [11] C.H. Liang, L.D. Zhang, G.W. Meng, Y.W. Wang, Z.Q. Chu, *J. Non-Cryst. Solids* 277 (2000) 63.
- [12] Z.G. Bai, D.P. Yu, H.Z. Zhang, Y. Ding, X.Z. Gai, Q.L. Hang, G.C. Xiong, S.Q. Feng, *Chem. Phys. Lett.* 303 (1999) 311.
- [13] Y.C. Choi, W.S. Kim, Y.S. Park, S.M. Lee, D.J. Bae, Y.H. Lee, G.S. Park, W.B. Choi, N.S. Lee, J.M. Kim, *Adv. Mater.* 12 (2000) 746.
- [14] N. Riehl, H. Ortman, *J. Electrochem. Soc.* 60 (1956) 149.
- [15] S.D. Sharma, S.C. Kashyap, *J. Appl. Phys.* 42 (1971) 5302.
- [16] Y. Li, G.W. Meng, L.D. Zhang, F. Philipp, *Appl. Phys. Lett.* 76 (2000) 2011.
- [17] M.H. Huang, Y.Y. Wu, H.N. Feick, N. Tran, E. Weber, P.D. Yang, *Adv. Mater.* 13 (2001) 113.
- [18] S. Link, M.A. El-Sayed, *J. Phys. Chem. B* 103 (1999) 4212.
- [19] F.A. Kroger, H.J. Vink, *J. Chem. Phys.* 22 (1954) 250.
- [20] E.G. Bylander, *J. Appl. Phys.* 49 (1978) 1188.
- [21] K. Vanheusden, W.L. Warren, C.H. Seager, D.K. Tallant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* 79 (1996) 7983.