Low temperature synthesis of ZnSe nanowires by self-catalytic liquid-solid growth

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ABSTRACT

Nanowire arrays of zinc selenide with zinc blende structures have been synthesized on the zinc foil via a simple thermal evaporation route at relatively low temperature ($\sim 400^\circ\text{C}$). A self-catalytic liquid–solid growth is proposed for the formation of the nanowires. The nanowires are usually 50–150 nm in diameter, and several microns in length. Room-temperature cathodoluminescence spectrum from zinc blende ZnSe nanowires shows a near band edge emission band peaked at around 462 nm and a broad deep-level emission band at around 580 nm, respectively.

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1. Introduction

Zinc selenide (ZnSe), which has a direct wide band gap of 2.7 eV and a large exciton binding energy of 21 meV, has attracted intensive attention for its applications such as blue light-emitting devices and laser diodes. Recently, a variety of nanostructured ZnSe materials including nanorods [1], nanoribbons [2], nanowheels [3], nanorings [4], nanopowders [5], and nanowires [6,7] have been reported due to their potential applications in constructing nanoscale optoelectronic devices.

The preparation of ZnSe nanostructures has been demonstrated by various methods, including vapour phase methods [8], hydrothermal process [9], and template-based methods [10]. Among them, vapour phase methods such as thermal evaporation and condensation [3,11], and evaporation of organic zinc precursors [7] have been used for producing ZnSe nanostructures. However, such methods often use metal catalysts such as Au [3,12] to assist and control the growth process. Hence, the remains of metals will influence the purity of the final products. Therefore, seeking self-catalytic growth techniques of ZnSe nanowires is important.

In this paper, we report the synthesis of ZnSe nanowire arrays on the zinc foil by the incorporation of selenium powder without using any other metal catalysts. The ZnSe nanowire arrays were characterized by different measurements. Meanwhile, possible growth mechanism of ZnSe nanowires was discussed.

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2. Experimental details

In a typical procedure, selenium powder and a zinc foil (8 mm $\times$ 10 mm $\times$ 0.25 mm) were kept in an alumina boat (the zinc foil was placed 1 cm downstream the selenium powder) and placed at the center of a quartz tube which was inserted into a horizontal tube furnace along the argon gas flow direction in sequence. The reaction chamber was sealed and pumped to and keep at a pressure 200 Torr throughout the experiment. Argon (purity: 99.9%) was introduced into the reaction chamber at a flow rate of 100 standard cubic centimetres per minute (sccm) as a carrier gas. Subsequently, the temperature of furnace was raised to 400°C at a rate of $40^\circ\text{C min}^{-1}$ and maintained at this temperature for 1.5 h. Finally, it was cooled to room temperature. After reaction, the products grew on the surface of the zinc foil as yellow films. There was still rest of Se vapour which did not react with zinc in the chamber. In order to collect the rest of the Se vapour, we constructed a home-made cold-trap system to solidify Se vapour in the downstream zone. After reaction, we can clearly see that the rest of the Se vapour was solidified and became gray-black solid Se bulk in the downstream zone. Hence, we can minimize the Se vapour pollution in the environment.

The morphology of as-prepared products was determined by field emission SEM (FE-SEM, JSM-6500F) equipped with EDX spectrometer. X-ray diffraction (XRD) patterns were obtained on a PANalytical X'Pert Pro diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 45 kV and 40 mA. Raman scattering spectrum was recorded using a Jobin-Yvon T64000 Raman-scattering spectrometer at room temperature in the backscattering geometry. The 514.5 nm line of a 100 mW Ar⁺ laser was used for the excitation source. The excitation power was 160 W cm^{-2} and the spot size of the laser light was focused to about $40 \mu\text{m}^2$. To study the optical properties of ZnSe nanowires, the cathodoluminescence (CL) spectrum was carried out using a temperature-controllable cathodoluminescence detector (Mono CL, Gatan) installed in the FE-SEM, which was performed at an accelerating voltage of 10 kV and the probe current of 20 nA. The areas under CL measurement were about $40 \mu\text{m} \times 40 \mu\text{m}$. The CL detector enables measurements of the CL spectra between 200 and 850 nm.

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Fig. 1. X-ray diffraction pattern of as-grown ZnSe nanowires.

3. Results and discussion

The ZnSe nanowires were characterized by XRD to confirm the crystalline phase of the nanowires. Fig. 1 shows the representative XRD pattern of ZnSe nanowires synthesized at 400 °C revealing cubic zinc blende phase of ZnSe with a lattice constant of $a = 0.56$ nm, which matches well with those in JCPDS (Joint Committee on Powder Diffraction Standards, Card No. 37-1463). Zn signals in the XRD pattern were original from the uncovered portion of the Zn foil. The sharp XRD peaks imply good crystallinity. The chemical composition and stoichiometry of the ZnSe nanowires were investigated through EDX. The EDX spectrum recorded (not shown here) on a single ZnSe nanowire reveals the presence of only Zn and Se as the elementary components in the nanowire. Quantitative analysis shows that the atomic ratio of Zn to Se is very close to 1:1 stoichiometry.

Fig. 2a shows the general morphology, observed by scanning electron microscopy (SEM), and reveals that the deposited ZnSe nanowires were vertically aligned and grown in high density on the entire surface of the zinc foil. The average density of the nanowires was about 10^9 cm⁻². The typical diameters and lengths of the nanowires are in the range of 50–150 nm and 1–10 μm, respectively. Fig. 2b is a magnified SEM image of ZnSe nanowires, indicating that there are spherical particles terminating at the ends of the nanowires. The existence of spherical particles at the tip of nanowires provides a firm evidence for the self-catalytic liquid–solid mechanism [13].

On the basis of our experimental data presented here, the growth mechanism of the ZnSe nanowires were proposed as follows. Since there are no nanosized transition-metal or noble-metal catalyst particles introduced in our reactants, which are usually found to attach to or embed in the ends of the nanostructures fabricated by conventional VLS methods. Spherical particles can be clearly observed at the tip of the nanowires in our product. Therefore, the formation of ZnSe nanowires in our experiments suggests a self-catalytic liquid–solid mechanism proposed by Dang et al. [13], contrasting with the conventional VLS growth. The growth of ZnSe nanowires can be separated into four steps: (i) formation of nanoscale Zn droplets on the Zn surface at temperature close to its melting point, (ii) dissolution of further zinc and selenium vapour species into molten Zn, (iii) phase segregation to create multiple nuclei on the substrate, and (iv) homoepitaxial growth of these nuclei into one-dimensional structure [14].

To further explore the crystalline quality of the ZnSe nanowires, a microscopic confocal Raman spectrometer was used to obtain the Raman data of ZnSe nanostructures by focusing the laser fac-

Fig. 2. (a) Low and (b) high magnification scanning electron microscope (SEM) images of vertically aligned ZnSe nanowires grown on zinc substrate.

ula on different locations. It was found that different areas show similar Raman profiles. Fig. 3 shows the typical Raman spectrum of a high purity sample. Two Raman peaks at 203 and 250 cm⁻¹ can be attributed to the transverse optic (TO) and longitudinal optic (LO) phonon modes of ZnSe, respectively. No vibration modes due to impurities are observed. From previous reports [15–17], the LO phonon frequency of single-crystalline ZnSe is 255 cm⁻¹ at room temperature. For ZnSe polycrystalline nanoparticles, the TO and LO phonon frequencies are 210 and 255 cm⁻¹, respectively, and the broad Raman peaks may be attributed to the high surface-to-volume ratio of small particles. Compared with the previous results,

Fig. 3. Raman scattering spectrum acquired from ZnSe nanowires at room temperature.

Fig. 4. Cathodoluminescence spectrum of ZnSe nanowires.

the LO and TO phonon peaks of the ZnSe nanowires are both shifted toward lower frequencies, which are probably due to the effects of small size and high surface area.

To investigate the optical properties of the ZnSe nanowires, the CL measurement was conducted at an acceleration voltage of 10 kV. Fig. 4 shows the typical room temperature CL spectrum of the as-grown nanowires. Generally, two bands appeared in the CL spectrum of the ZnSe nanowires, a weak narrow band at 462 nm and a strong broad band at 580 nm. The weak narrow band is due to the recombination of free excitons through an exciton–exciton collision process also known as near-band-edge (NBE) emission and the visible deep-level-emission is because of the existence of non-stoichiometric defects, dislocations, and/or stacking faults [2,18,19]. Compared with the luminescence spectra of ZnSe nanostructures reported previously [2,3], we found that most of the spectra only contain a broad defect emission and the band edge emission is hardly observed. This behavior reflects good crystalline quality of our grown ZnSe nanowires.

4. Conclusions

In summary, cubic zinc blende ZnSe nanowires have been synthesized on the zinc foil by thermal evaporation of selenium

powder without the use of additional metal catalysts or additives at low temperature. General morphology of the synthesized ZnSe nanowires indicated that the grown products have diameter in the range of 50–150 nm with lengths of 1–10 μm . Raman scattering and room temperature CL spectra substantiated that the synthesized ZnSe nanowires are good in crystal quality with a zinc blende cubic phase containing few structural defects and exhibiting good optical properties. The obtained ZnSe nanowires therefore are highly favorable for the fabrication of optoelectronic devices due to their good crystallinity and visible luminescence properties and low production cost.

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References

- [1] Z. Liu, S.K. Hark, *Nanotechnology* 17 (2006) 1355.
- [2] Y. Jiang, X.M. Meng, W.C. Yiu, J. Liu, J.X. Ding, C.S. Lee, S.T. Lee, *J. Phys. Chem. B* 108 (2004) 2784.
- [3] L. Jin, W.C.H. Choy, Y.P. Leung, T.I. Yuk, H.C. Ong, J.B. Wang, *J. Appl. Phys.* 102 (2007) 044302.
- [4] Y.P. Leung, W.C.H. Choy, I. Markov, G.K.H. Pang, H.C. Ong, T.I. Yuk, *Appl. Phys. Lett.* 88 (2006) 183110.
- [5] S.V. Pol, V.G. Pol, J.M. Calderon-Moreno, S. Cheylan, A. Gedanken, *Langmuir* 24 (2008) 10462.
- [6] X.T. Zhang, Z. Liu, Y.P. Leung, Q. Li, S.K. Hark, *Appl. Phys. Lett.* 83 (2003) 5533.
- [7] C. Ye, X. Fang, Y. Wang, P. Yan, J. Zhao, L. Zhang, *Appl. Phys. A* 79 (2004) 113.
- [8] D.Y. Xia, L. Dai, W.J. Xu, L.P. You, B.R. Zhang, G.Z. Ran, G.G. Qin, *Chin. Phys. Lett.* 23 (2006) 1317.
- [9] C. Jiang, W. Zhang, G. Zou, W. Yu, Y. Qian, *Nanotechnology* 16 (2005) 551.
- [10] S. Ramanathan, S. Patibandla, S. Bandyopadhyay, J. Anderson, J.D. Edwards, *Nanotechnology* 19 (2008) 195601.
- [11] U. Philipose, P. Sun, T. Xu, H.E. Ruda, L. Yang, K.L. Kavanagh, *J. Appl. Phys.* 101 (2007) 014326.
- [12] Y.Q. Wang, U. Philipose, T. Xu, H.E. Ruda, K.L. Kavanagh, *Semicond. Sci. Technol.* 22 (2007) 175.
- [13] H.Y. Dang, J. Wang, S.S. Fan, *Nanotechnology* 14 (2003) 738.
- [14] S. Biswas, T. Ghoshal, S. Kar, S. Chakrabarti, S. Chaudhuri, *Cryst. Growth Des.* 8 (2008) 2171.
- [15] T.J. Mountziaris, J.D. Peck, S. Stoltz, W.Y. Yu, A. Petrou, P.G. Mattocks, *Appl. Phys. Lett.* 68 (1996) 2270.
- [16] B. Schreder, A. Materny, W. Kiefer, G. Bacher, A. Forchel, G.J. Landwehr, *Raman Spectrosc.* 31 (2000) 959.
- [17] D. Sarigiannis, J.D. Peck, G. Kioseoglou, A. Petrou, T.J. Mountziaris, *Appl. Phys. Lett.* 80 (2002) 4024.
- [18] Y.C. Zhu, Y. Bando, *Chem. Phys. Lett.* 377 (2003) 367.
- [19] X.T. Zhang, Z. Liu, K.M. Ip, Y.P. Leung, Q. Li, S.K. Hark, *J. Appl. Phys.* 95 (2004) 5752.