

Growth and Luminescence of Ternary Semiconductor ZnCdSe Nanowires by Metalorganic Chemical Vapor Deposition

X. T. Zhang, Z. Liu, Quan Li, and S. K. Hark*

Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong

Received: May 24, 2005; In Final Form: July 28, 2005

ZnCdSe alloy nanowires were successfully grown on the GaAs (100) substrate by metalorganic chemical vapor deposition using Au as a catalyst. The nanowires display two distinct types of morphology. The majority of them are straight, uniform in diameter, and have a smooth surface. However, a significant portion of them contain one or two constrictions along their length. The alloy is found to be rich in Zn; its composition, as determined from X-ray diffraction and energy-dispersive X-ray microanalysis, is close to $\text{Zn}_{0.9}\text{Cd}_{0.1}\text{Se}$. The peak energy of its room temperature near-band-edge photoluminescence is also consistent with this composition. X-ray diffraction pattern and transmission electron microscopy find both types of nanowires to be single crystalline, have the metastable wurtzite structure, and a growth direction along $\langle 1100 \rangle$. The presence of an Au–Cd–Zn alloy particle at the tip of the nanowires supports vapor–liquid–solid as the growth mechanism. The appearance of constrictions in some of the nanowires is found to be linked to the existence of structural defects, possibly stacking faults, during growth.

Introduction

One-dimensional (1D) semiconductor nanowires have attracted much attention due to their novel properties. Over the past decade, considerable efforts have been devoted to the synthesis of nanowires of elements or binary compounds, which do not allow a variation in their compositions. Semiconducting nanowires of group IV elements, III–V and II–VI compounds, and metal oxides have been synthesized.^{1–8} However, only a few studies on ternary compound semiconductor nanowires were reported, these include Zn_2SnO_4 ,⁹ ZnMgO ,¹⁰ ZnMnO ,¹¹ GaAsP ,⁵ InAsP ,⁵ InGaN ,¹² and AlGaAs .¹³ The synthesis of ternary nanowires with a predictable composition is more difficult than that of binary nanowires, because it often involves the complexities of multicomponent phase diagrams, differential segregations, and nonequilibrium phenomena.

ZnSe and CdSe are important wide-band-gap semiconductors that have become the focus of intense research in recent years. Their optical properties make them suitable for visible light-emitting diodes (LEDs), lasers, and other optoelectronic devices. Moreover, they can be mixed at any ratio to form an alloy. The alloy ZnCdSe is itself a very important semiconductor with potential applications in optoelectronics, because its compositional dependent band gap (1.66–2.7 eV) can be tuned to cover the entire visible range. Nanowires of ZnSe and CdSe can be obtained by many methods and have been reported;^{8,14–18} to the best of our knowledge, alloy nanowires of ZnCdSe have not been. In this paper, we show that ZnCdSe nanowires can be grown by metalorganic chemical vapor deposition (MOCVD). MOCVD is an accepted technique in the industrial productions of many optoelectronic materials, partly because it is rather easy to control the ratio of the flow rates and vapor pressures of precursors to achieve doping and to adjust the composition of the depositing materials.

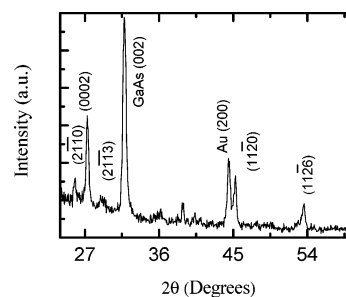


Figure 1. X-ray diffraction pattern of ZnCdSe alloy nanowires. Other than the (002) peak of the GaAs substrate and the (200) peak of the Au catalyst, all other peaks are indexed according to the wurtzite structure.

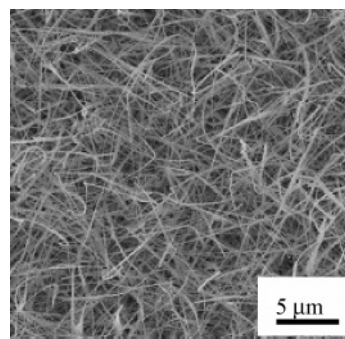


Figure 2. SEM image showing the dense, long, and fine ZnCdSe nanowires.

Experimental Section

The nanowires were grown on GaAs (100) substrates in a horizontal MOCVD reactor. Before growth, the substrates were steamed in 1,1,1-trichloroethane vapor for 30 min, rinsed with deionized water, and blown dry with N_2 gas. After the cleaning, they were sputter-coated with a thin film of Au, of ~ 1 nm coverage, and immediately loaded into the reactor. The Au-covered substrates were heated to 550 °C and maintained at

* To whom correspondence should be addressed. E-mail: skhark@phy.cuhk.edu.hk.

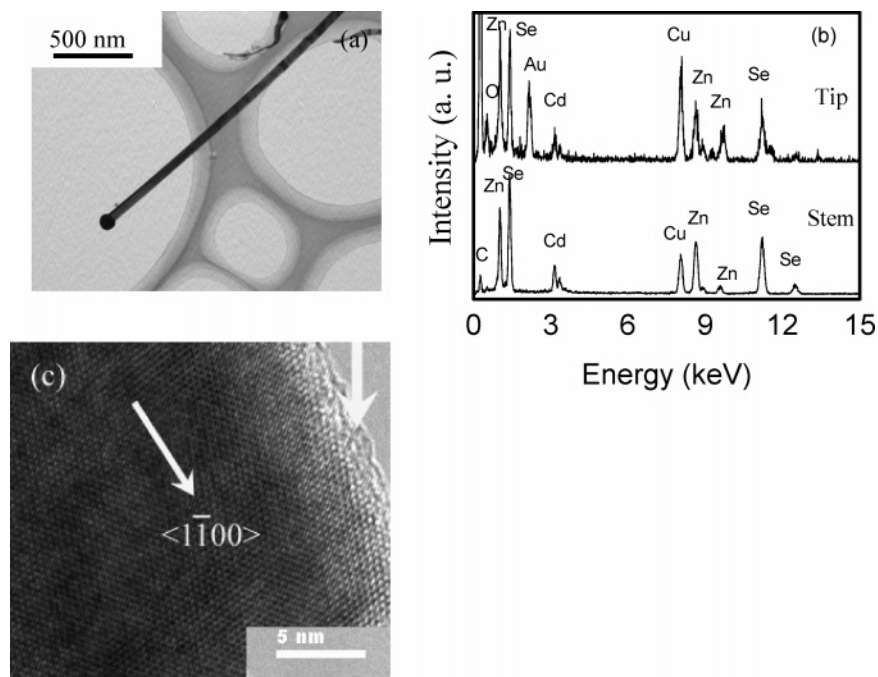


Figure 3. (a) TEM image of a ZnCdSe nanowire; (b) EDX nanoanalysis spectra obtained at the tip (upper curve) and at the stem (lower curve) of a nanowire; and (c) a high-resolution lattice image of the stem of a nanowire (the narrow white arrow indicates its growth direction and the fat arrow indicates the presence of a thin oxide layer).

this temperature for 10 min in a flowing hydrogen gas environment before precursors were introduced. Diethylzinc, dimethylcadmium, and diisopropylselenide at flow rates of 1.08, 4, and 7.2 sccm, respectively, were used as precursors. The temperature and reactor pressure were kept at 550 °C and 100 Torr during growth, which lasted for 1 h. The synthesized products were characterized by X-ray diffraction (XRD, Rigaku RU-300 with Cu K α radiation), scanning electron microscopy (SEM, LEO, 1450 VP), energy-dispersive X-ray microanalyses (EDX, Oxford Link II, UK), and high-resolution transmission electron microscopy (TEM, Philips Tecnai 20). Photoluminescence (PL) spectra of the nanowires were taken at room temperature using the 325 nm line of a He–Cd laser with an output power of about 2 mW focused by a 50 mm focal length lens as the excitation source.

Results and Discussion

Figure 1 shows an X-ray diffraction pattern of the as-synthesized alloy nanowires. The peaks in it can be indexed according to the wurtzite structure; and their positions are somewhere between those of wurtzite-structured ZnSe and CdSe. Applying Vegard's law, we determine the alloy as Zn_{0.9}-Cd_{0.1}Se from the position of the peaks. The morphology of the nanowires was examined by scanning electron microscopy, a typical image of which is shown in Figure 2. A high density of nanowires is clearly visible over the entire surface of the substrate. The morphology and structure of the nanowires were further studied by transmission electron microscopy (TEM). A low magnification TEM image is given in Figure 3a, which clearly shows a nanowire that has a particle attached at one end. It appears to have a smooth surface and a uniform circular cross-section. The length of the nanowires is typically about 20 to 30 μ m and the diameter ranges from 20 to 100 nm. In addition to those that are uniform in cross-section, nanowires that contain one or two constrictions were obtained at the same time (Figure 4a). To confirm their composition, EDX microanalyses of different spots on the nanowire were carried out.

Two typical spectra are shown in Figure 3b. The upper spectrum was obtained from a spot at the tip, which clearly shows the characteristic peaks of Au, Zn, Cd, and Se. The lower spectrum was taken from a spot on the stem and it consists of mainly peaks of Zn, Cd, and Se. The Cu and C peaks in both spectra came from the TEM sample grid, and the weak O peak is probably a result of surface oxidation when the nanowires were exposed to air. The atomic percentages of Zn, Cd, and Se were measured to be about 44%, 8%, and 48%, respectively. Within experimental errors, this composition agrees with that determined by XRD. We note that bulk alloys of ZnCdSe would be zinc blende in structure at this composition.¹⁹ We think the significant contribution of surface free energy to the total free energy favors the wurtzite over the zinc blende structure for the small diameter nanowires. The high-resolution TEM lattice image of the ZnCdSe nanowire shown in Figure 3c confirms their single crystalline wurtzite structure. An amorphous layer, probably an oxide, about 1 nm thick is seen covering their surface. The lattice image along the [0001] zone axis shows that the nanowires grew along the $\langle 1100 \rangle$ direction.

The nanowires appear to grow via the VLS mechanism.^{5,12,13} In our experiments, the substrate was heated to and kept at 550 °C for 10 min prior to growth. This temperature is sufficiently high for nanosized liquid droplets of Au to form. The alloy particles found at the tip of the nanowires provide support to VLS as the most plausible mechanism of growth. Nanowires having a constricted waist were also studied by TEM. Figure 4a shows a nanowire of this kind. A high-resolution lattice image of the waist and its corresponding Fourier transform are shown in Figure 4, parts b and c, respectively. We see that the nanowire is single crystalline and grows along the same direction as those without a constriction. Careful examinations of 10 randomly selected nanowires that have constrictions revealed that there is always a discontinuity in their lattice planes in the waist region. To better show the discontinuity, we have performed inverse Fourier transform of spatially filtered diffraction pattern in Figure 4c. The resultant lattice

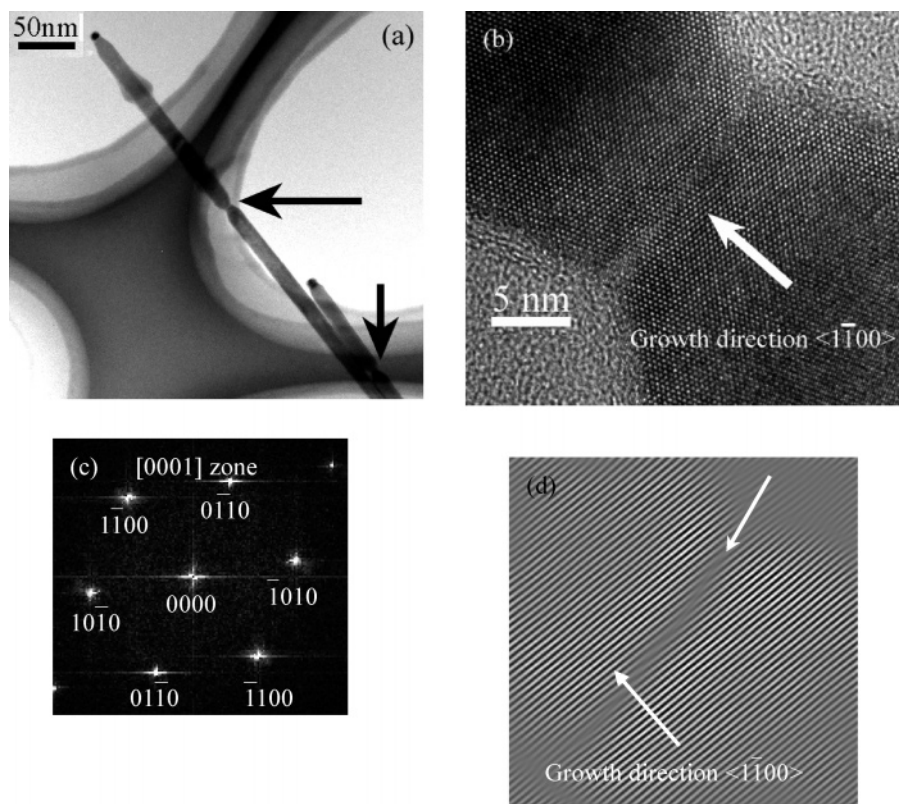


Figure 4. (a) TEM image of two ZnCdSe nanowires, the constrictions of which are indicated by arrows; (b) HRTEM image of a constricted waist, showing a discontinuity in the lattice planes at the waist; (c) Fourier transform of the lattice image of part b; and (d) inverse Fourier transform of the $(1\bar{1}00)$ and $(\bar{1}100)$ pair of diffraction spots in part c, showing the less-than-one-plane shift of the lattice planes across the discontinuity (indicated by an arrow).

image of Figure 4d, which is obtained by only transforming the $(1\bar{1}00)$ and $(\bar{1}100)$ pair of diffraction spots, shows that the lattice planes on the adjoining sides of the waist are shifted by less than one plane. For the other adjoining pairs of diffraction spots, the layer planes are continuous across the constriction. The exact mechanism by which the discontinuity arises is not clear at this time, but it appears that stacking faults and their associated partial dislocations play an important role. Modulation in the diameter of nanowires and whiskers had been observed in the VLS growth process and was attributed to a disturbance of vapor pressures or temperature or both during their growth. In the VLS growth of Si nanowires, the modulation was intentionally induced by sudden and large changes in temperature (about 100 °C) or vapor pressure.²⁰ Recently, modulation of the diameter of Zn_2SnO_4 nanowires was observed even without any externally induced disturbance.⁹ Nevertheless, disturbance in the concentrations of vapors that occurs naturally was suggested as the major factor that causes the change. In the VLS growth of nanowires, the interfacial area between the liquid and the solid phase controls the diameter of the nanowires. This area is in turn limited by the volume of the liquid droplet, which is itself a function of temperature and vapor pressures. The latter affect the volume through the concentrations of dissolved matter in the liquid. The modulation in the diameter of the nanowires therefore reflects the fluctuations in temperature and/or vapor pressures during growth. We do not think temperature or pressure fluctuation is the cause for the constrictions in our MOCVD grown nanowires. First of all, there are always less than two constrictions in our nanowires, indicating that the formation of a constriction is a random and rare event, unlike the modulation in diameter. Second, the temperature, flow rates, and pressure in our system were always maintained to

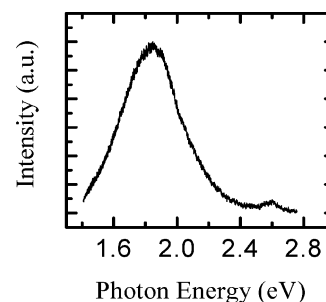


Figure 5. A photoluminescence spectrum of ZnCdSe nanowires measured at room temperature. The NBE peak, though weak, is clearly seen at 2.6 eV.

better than 1% by dynamic feedback controls. These insignificant fluctuations could not affect the volume of the gold droplets. Growth data recorded during growth also rules out any sudden and large change in the growth parameters. More importantly, the coexistence of nanowires with and without constrictions essentially rules out any fluctuations in growth parameters as their cause, which should affect all nanowires. We suspect the appearance of the constriction is a result of the influence on growth by stacking faults.

Figure 5 shows a representative photoluminescence (PL) spectrum of the ZnCdSe nanowires at room temperature. It consists of two luminescence bands centered at 2.60 and 1.84 eV, respectively. We attribute them to the near-band-edge (NBE) and deep-level emissions of the nanowires. The calculated E_g is ~ 2.576 eV for $x = 0.9$, from the relationship between the band gap and composition ($E_g = 1.66 + 0.73x + 0.32x^2$) of bulk $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ alloy.²¹ This agrees well with the observed NBE PL peak energy within experimental errors.

Conclusion

In conclusion, straight and fine alloy ZnCdSe nanowires and nanowires having one or two constrictions were successfully grown by MOCVD. Their shapes and structures were studied by SEM, XRD, and HRTEM and the results obtained show that they are rich in Zn, single crystalline, and wurtzite structured. They grow along the $\langle 1100 \rangle$ direction, apparently via the VLS mechanism. The appearance of constrictions on the nanowires is found to be connected with the presence of stacking faults during growth. We can safely rule out fluctuations in growth conditions as its cause.

Acknowledgment. The work described in this paper was partially supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 401003) and a CUHK direct grant (Project code 2060277).

References and Notes

- (1) Holmes, J. D.; Johnston, K. P.; Doty, R. C.; Korgel, B. A. *Science* **2000**, 287, 1471.
- (2) Jie, J. S.; Wang, G. Z.; Han, X. H.; Hou, J. G. *J. Phys. Chem. B* **2004**, 108, 17027.
- (3) Huang, M. H.; Wu, Y.; Feick, H.; Weber, E.; Yang, P. *Adv. Mater.* **2001**, 13, 113.
- (4) Park, W. I.; Kim, D. H.; Jung, S. W.; Yi, G. C. *Appl. Phys. Lett.* **2002**, 80, 4232.
- (5) Duan, X.; Lieber, C. M. *Adv. Mater.* **2000**, 12, 298.
- (6) Li, Y.; Meng, G. W.; Zhang, L. D.; Phillipp, F. *Appl. Phys. Lett.* **2000**, 76, 2011.
- (7) Wu, Y.; Yang, P. *Chem. Mater.* **2000**, 12, 605.
- (8) Zhang, X. T.; Ip, K. M.; Liu, Z.; Leung, Y. P.; Li, Q.; Hark, S. K. *Appl. Phys. Lett.* **2004**, 84, 2641.
- (9) Jie, J. S.; Wang, G. Z.; Han, X. H.; Fang, J. P.; Yu, Q. X.; Liao, Y.; Xu, B.; Wang, Q. T.; Hou, J. G. *J. Phys. Chem. B* **2004**, 108, 8249.
- (10) Park, W. I.; Yi, G. C.; Kim, M.; Pennycook, S. I. *Adv. Mater.* **2003**, 15, 526.
- (11) Zheng, R. K.; Liu, H.; Zhang, X. X.; Djurišić, A. B. *Appl. Phys. Lett.* **2004**, 85, 2589.
- (12) Kim, H. M.; Lee, W. C.; Kang, T. W.; Chung, K. S.; Yoon, C. S.; Kim, C. K. *Chem. Phys. Lett.* **2003**, 380, 181.
- (13) Wu, Z. H.; Sun, M.; Mei, X. Y.; Ruda, H. E. *Appl. Phys. Lett.* **2004**, 85, 657.
- (14) Chan, Y. F.; Duan, X. F.; Chan, S. K.; Sou, I. K.; Zhang, X. X.; Wang, N. *Appl. Phys. Lett.* **2003**, 83, 2665.
- (15) Zhang, X. T.; Liu, Z.; Leung, Y. P.; Li, Q.; Hark, S. K. *Appl. Phys. Lett.* **2003**, 83, 5533.
- (16) Zhang, X. T.; Liu, Z.; Ip, K. M.; Leung, Y. P.; Li, Q.; Hark, S. K. *J. Appl. Phys.* **2004**, 95, 5752.
- (17) Urbiet, A.; Fernandez, P.; Piqueras, J. *Appl. Phys. Lett.* **2004**, 85, 5968.
- (18) Shan, C. X.; Liu, Z.; Ng, C. M.; Hark, S. K. *Appl. Phys. Lett.* **2005**, May 30 (To be published).
- (19) Nasibov, A. S.; Korostelin, Y. V.; Shapkin, P. V.; Suslina, L. G.; Fedorov, D. L.; Markov, L. S. *Solid State Commun.* **1989**, 71, 867.
- (20) Levitt, A. P. *Whisker Technology*; Wiley-Interscience, a Division of John Wiley & Sons: New York, 1970; p 108.
- (21) Lunz, U.; Kuhn, J.; Goschenhofer, F.; Schüssler, U.; Einfeldt, S.; Becker, C. R.; Landwehr, G. *J. Appl. Phys.* **1996**, 80, 6861.