

Web of Science® – now with Conference Proceedings

[<< Back to results list](#)

◀ Record 2 of 240 ▶

Record from Web of Science®

Bismuth Seed-Assisted Liquid-Phase Synthesis of Germanium Telluride Nanowires

find it 

Print

E-mail

Add to Marked List

Save to EndNote® Web


Holdings ▾

Go

Save to EndNote®, RefMan, ProCite more options

Author(s): Lee MK (Lee, Myung-Ki)¹, Kim TG (Kim, Tae Geun)², Ju BK (Ju, Byeong-Kwon)², Sung YM (Sung, Yun-Mo)¹

Source: CRYSTAL GROWTH & DESIGN Volume: 9 Issue: 2 Pages: 938-941 Published: FEB 2009

Times Cited: 0 References: 34  Citation Map beta

Abstract: GeTe (GT) nanowires (NWs) were successfully synthesized using Bi seeds by a low-temperature solution-based process. Scanning electron microscopy (SEM) images show formation of straight and cylindrical shaped GT NWs together with spherical shaped Te particles. GT NWs were similar to 50-100 nm in diameter and similar to 2 μ m in length. X-ray diffraction (XRD) patterns of as-prepared samples show formation of hexagonal Te, orthorhombic GeTe, and amorphous phase in the samples. The [008] growth of orthorhombic GeTe NWs was identified using high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). Ostwald ripening was proposed as a growth mechanism of GT NWs. Differential scanning calorimetry (DSC) results on the samples reveal an apparently decreased melting point of GT.

Cited by: 0

This article has been cited 0 times
(from Web of Science).

[Create Citation Alert](#)

Related Records:

Find similar records based on shared
references (from Web of Science).

[\[view related records \]](#)

References: 34

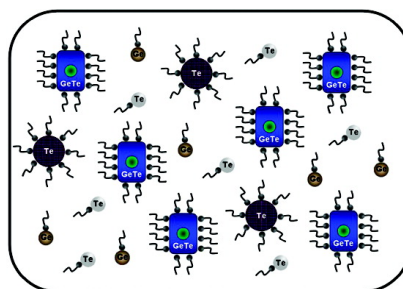
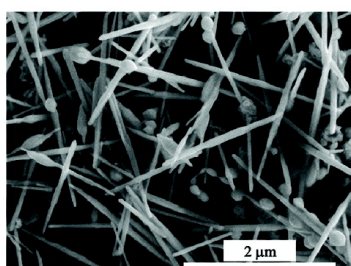
View the bibliography of this record
(from Web of Science).

Bismuth Seed-Assisted Liquid-Phase Synthesis of Germanium Telluride Nanowires

Myung-Ki Lee, Tae Geun Kim, Byeong-Kwon Ju, and Yun-Mo Sung

Cryst. Growth Des., 2009, 9 (2), 938-941 • DOI: 10.1021/cg800702d • Publication Date (Web): 18 December 2008

Downloaded from <http://pubs.acs.org> on March 12, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Bismuth Seed-Assisted Liquid-Phase Synthesis of Germanium Telluride Nanowires

Myung-Ki Lee,[†] Tae Geun Kim,[‡] Byeong-Kwon Ju,[‡] and Yun-Mo Sung^{*,†}

Nanomaterials Chemistry Laboratory (NMCL), Department of Materials Science & Engineering, Korea University, Seoul 136-713, South Korea, and Department of Electronic Engineering, Korea University, Seoul 136-713, South Korea

Received July 2, 2008; Revised Manuscript Received November 11, 2008

ABSTRACT: GeTe (GT) nanowires (NWs) were successfully synthesized using Bi seeds by a low-temperature solution-based process. Scanning electron microscopy (SEM) images show formation of straight and cylindrical shaped GT NWs together with spherical shaped Te particles. GT NWs were ~ 50 – 100 nm in diameter and ~ 2 μm in length. X-ray diffraction (XRD) patterns of as-prepared samples show formation of hexagonal Te, orthorhombic GeTe, and amorphous phase in the samples. The [008] growth of orthorhombic GeTe NWs was identified using high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). Ostwald ripening was proposed as a growth mechanism of GT NWs. Differential scanning calorimetry (DSC) results on the samples reveal an apparently decreased melting point of GT.

1. Introduction

Chalcogenide materials such as germanium telluride (GeTe: GT) have attracted a great deal of attention due to their reversible phase change properties which are used in the fields of optical data storage (CD and DVD) and phase-change random access memory (PRAM).^{1–4} In particular, chalcogenide PRAM devices are being rapidly spread to industries, and they are replacing current dynamic random access memory (DRAM), static random access memory (SRAM), or flash memory due to their non-volatility, random access, low cost, etc.^{5–7} To achieve a high performance PRAM device, however, several requirements such as small cell size, high durability, low reset current, and low power consumption must be met. The major bottleneck of high performance PRAM is the high reset current that is needed to write data by transforming the low-resistivity crystalline state of a chalcogenide material to the high-resistivity amorphous state. Hence, the reduction of the reset current is a key issue which can allow fast amorphization of a chalcogenide material with less power consumption and thus fast memory switching. The reset current can be controlled by various factors such as chalcogenide alloy composition, cell structure and size, and so on. In accordance with the efforts to reduce reset current in PRAM devices, replacement of current thin film forms with a low-dimensional structure has been emerging as a breakthrough technology. Lankhorst et al.⁸ proposed the possibility of one-dimensional Ge₂Sb₇Te₅ (GST) PRAM devices fabricated by lithography techniques to reduce the reset current. Recently, Argawal et al.^{9,10} and Park et al.^{11,12} reported the vapor-phase growth of GST and GT nanowires (NWs), respectively, and demonstrated their PRAM applications. Also, more recently Yu et al.¹³ and Yu et al.¹⁴ demonstrated the reduced reset current in chalcogenide (GeTe and In₂Se₃) nanowire-based PRAM devices.

Through the decade, a variety of studies have been performed for one-dimensional nanostructures of II–VI and III–V semiconductors,^{15–17} metal oxides,^{18–20} and chalcogenides^{21–23}

due to their superior properties for high-performance device applications. Many synthetic routes have been developed for NW growth, and they can be classified into probably two categories, vapor-phase growth^{24,25} and liquid-phase growth.^{26,27} So far, the reported synthesis of phase-change NWs is based solely on the so-called vapor–liquid–solid (VLS) mechanism.^{9–12,23} Although high-density and high-quality NW arrays can form on a substrate through the VLS mechanism, it requires a high-temperature evaporation and vapor transport process using high-cost precursors. Furthermore, especially for PRAM device applications, vertically grown NW arrays are not necessary since individual NWs spread on a substrate can be used for PRAM device construction.

In contrast to the VLS mechanism, the liquid-phase process promises low-cost production arising from low reaction temperature (<300 °C) and low-cost precursors. Also, high throughput of NWs is possible. In particular, seed-assisted liquid-phase synthesis has a great advantage of accelerated nucleation and growth of NWs. In this study, we for the first time report high-yield synthesis of GT NWs through a Bi seed-assisted liquid-phase process at very low temperature.

2. Experimental Procedures

For the synthesis of GT NWs 0.1 mmol of germanium (VI) isopropoxide (Ge *i*Pr) and 0.1 mmol of Te powder (Aldrich, Milwaukee, WI) were dissolved in 5 mL of trioctylphosphine (TOP), respectively. By sputtering Bi target, a Bi thin layer was formed on a fluorine-doped tin oxide (FTO) glass plate. The glass plate was loaded in a three-neck flask containing 0.1 mL of Ge solution, and 6 mL of 1-octadecene (ODE) was added. As surfactants 1 mL of oleic acid and oleylamine was injected into the three neck flask under N₂ atmosphere and heated to 220 °C. The Bi layer on the FTO glass broke up into very fine Bi nanoparticles serving as seeds for the nucleation of GT NWs. The solution was continuously stirred during the reaction to maintain uniformity of concentration. The 0.1 mL of Te solution was injected into the flask, and the reaction between Ge and Te was continued for 4 h under gentle stirring. The solution was cooled to room temperature and toluene was added for cleaning. The solution was centrifuged at 3000 rpm for 3 min and NWs were collected. For the cleaning process, chloroform and toluene were alternatively used. Finally, GT NWs were dispersed in chloroform under N₂ atmosphere.

The crystal structure of GT NWs was investigated by X-ray diffraction (XRD, Rigaku Model D/MAX-2500V/PC, $\lambda = 1.5418$ Å). Field emission scanning electron microscopy (FE-SEM, Hitachi S-4300)

* To whom correspondence should be addressed. E-mail: ymsung@korea.ac.kr; tel: 82-2-3290-3286; fax: 82-2-928-3584.

[†] Nanomaterials Chemistry Laboratory (NMCL), Department of Materials Science & Engineering.

[‡] Department of Electronic Engineering.

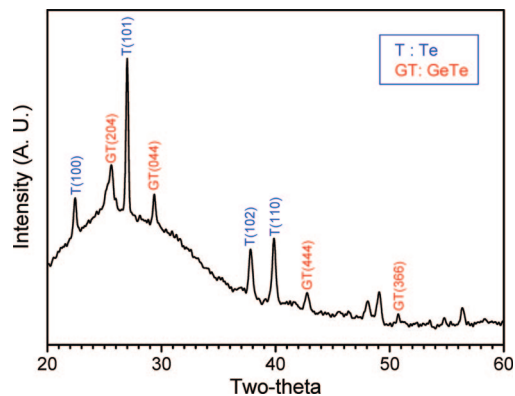


Figure 1. X-ray diffraction (XRD) pattern of GeTe nanowires.

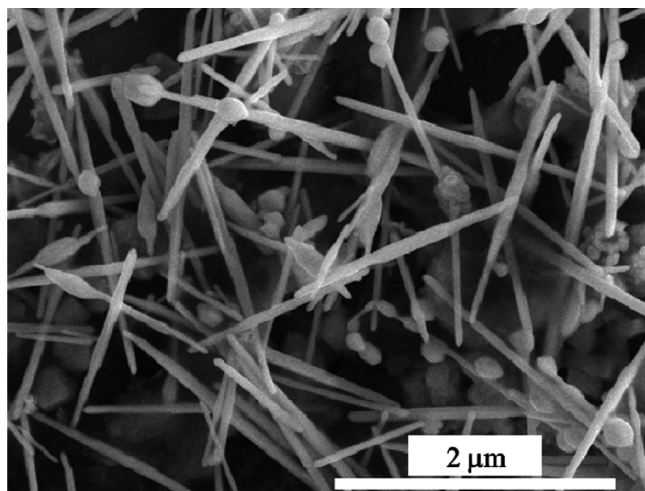


Figure 2. Scanning electron microscopy (SEM) image showing formation of GeTe nanowires and Te microparticles.

was used to examine the morphological features and distribution of NWs. Energy dispersive spectroscopy (EDS, Horiba EX-200) was applied to investigate the chemical composition of NWs. High resolution transmission electron microscopy (HRTEM, JEM 2100F, 200 kV) was used to examine crystallinity, and selected area electron diffraction (SAED) was conducted to confirm crystalline structure. Differential scanning calorimetry (DSC: Setaram TG-DTA/DSC 1600, Caluire, France) analysis was performed at a scanning rate of 15 °C/min to investigate the solid-state phase transition and melting behavior of samples.

3. Results and Discussion

The crystallinity of as-prepared samples was analyzed using X-ray diffraction (XRD) as shown in Figure 1. The appearance of GeTe (204), (044) (JCPDS No. 22-0312) and Te (100), (101) (JCPDS No. 03-0506) peaks confirms the formation of orthorhombic GeTe and hexagonal Te crystals. Also, a big hump ranging from ~20 to 40° was identified, indicating the existence of amorphous phase in the samples. Morphological features of the samples were investigated by FESEM as shown in Figure 2. FESEM samples were prepared by drying the solution containing NWs. The samples were identified to consist of two different structures: one is nanowires and the other is particles. EDS analysis on the samples confirms that NWs are stoichiometric GeTe and particles are pure Te. GT NWs were in a cylindrical structure and no facet was found. The diameter and length of GT NWs were ~50–100 nm and ~2 μm, respectively. Te particles were almost spherical and they were ~200–400

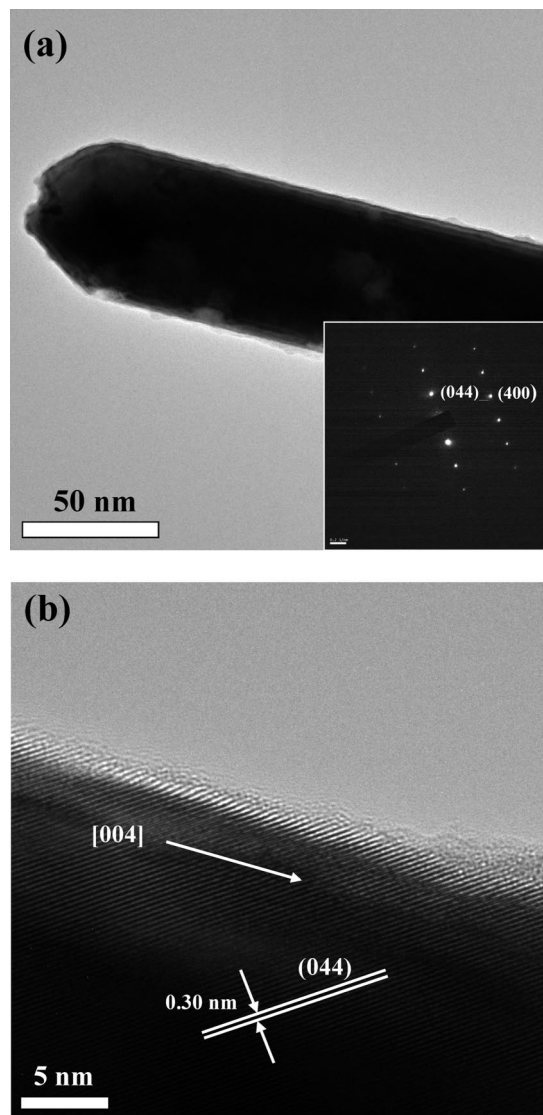


Figure 3. (a) Transmission electron microscopy (TEM) image of GeTe nanowires and (b) high-resolution TEM (HRTEM) image of GeTe nanowires showing lattice fringe image. The inset image is selected area electron diffraction (SAED) pattern.

nm in diameter. Bi particles were not detected in the samples, especially at the tips of GT NWs, implying that the NW growth is not based on the so-called solution–liquid–solid (SLS) mechanism.

Low magnification TEM images of GT NWs are shown in Figure 3a. NWs were very straight and cylindrical, while their surface was rough due to the remaining surfactant such as oleic acid and oleylamine. SAED patterns shown as an inset in Figure 3a confirms the [008] growth of orthorhombic GT NWs and their single crystallinity. In the case of reported VLS growth, the crystal structure of GT NWs was usually rhombohedral due to their high reaction temperature of ~400 °C. In this study, however, the orthorhombic GT NWs were synthesized by seed-assisted solution phase method at a very low temperature of ~200 °C. Figure 3b presents HRTEM image of GT NWs showing lattice fringe image. The lattice *d*-spacing of 0.3 nm indicates formation of (044) planes and the NW growth direction is [008]. Native oxide formation was not detected at the surface of GT NWs.

The formation mechanism of GT NWs under mild conditions was speculated, and the schematic diagram is presented in Figure

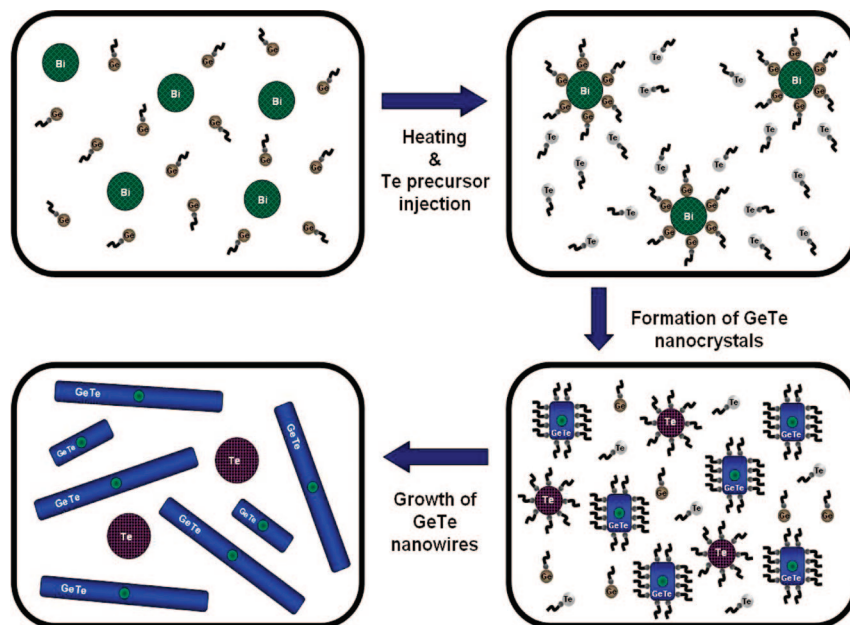


Figure 4. Schematic showing the mechanism for the formation of GeTe nanowires and Te microparticles.

4. The reaction temperature, precursor concentration, reaction time, and existence of seeds seem to play important roles in the formation of NWs. On the basis of the experimental results, the possible mechanism for GT NW growth is not SLS but a seed-assisted solution-phase one. In the typical SLS growth of NWs, metal catalysts exist at the tip of NWs.^{28–30} However, in our samples catalysts did not exist either at the surface or at the tips of NWs. The seed-assisted liquid-phase growth of NWs has been reported. For instance, silver NWs were successfully synthesized using a seed-assisted solution-base method by Sun et al.³¹ Platinum nanoparticles act as seeds and supply nucleation sites for the heterogeneous nucleation and growth of Ag NWs of 30–40 nm in diameter and $\sim 50 \mu\text{m}$ in length. Most probably the same mechanism works for our synthesis. At a reaction temperature of 220 °C, the Bi thin layer on the FTO glass breaks up into many several nanometer-scale Bi particles serving as seeds. At the initial step of synthesis Bi seeds act as heterogeneous nucleation sites for GeTe nanoparticles, forming a Bi@GeTe core@shell structure. Once the liquid-phase solution containing Ge and Te precursors and the solid-phase GeTe reach chemical equilibrium, Ge and Te attachment to GeTe nanoparticles for further growth is terminated. Instead, as a following step, larger GeTe nanoparticles grow at the expense of smaller ones through the so-called Oswald ripening process when the temperature is maintained at 220 °C.³² This heating can supply energy to the system enough to overcome the energy barrier for ripening.³³ By dissolution of small size GT nanocrystals Ge and Te can diffuse through the solution and arrive at the surface of large nanoparticles, resulting in ripening of large nanoparticles. With the confinement of surfactants, oleic acid and oleylamine, large GeTe nanoparticles can grow and elongate into one-dimensional NWs with a uniform diameter. The surfactants could preferably attach to the crystal planes exposed at the cylindrical surface of NWs and allow Ge and Te ion attachment only through both tip faces of NWs. In the absence of Bi seeds, only Te nanorods (NRs) or NWs were synthesized without formation of GT NWs in the same reaction system. Chalcogenide elements including Te and Se have been well-known for their strong tendency to grow into one-dimensional nanorods or nanowires due to their intrinsic helical chain structure formation. They can readily form a one-dimensional

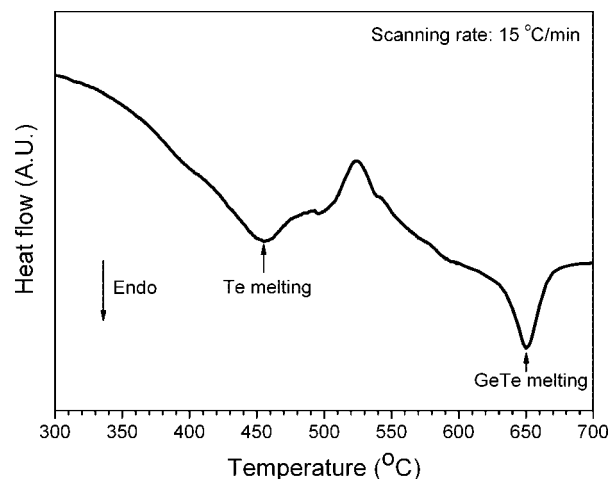


Figure 5. Differential scanning calorimetry (DSC) scan curve for the sample containing GeTe nanowires and Te microparticles.

nanostructure without the aid of catalysts.³⁴ However, to form GT nanowires we definitely have to depend upon the catalysts. Also, when Ge and Te solutions were simultaneously injected to the Bi seeds only Te NWs or NRs were synthesized due to the lower-free energy of Te segregation compared to that of Ge–Te bonding. This is the reason that we supplied Ge-containing solution to Bicoated FTO substrates first and then injected Te solution into the reaction system later. As mentioned above in the typical VLS experiments the crystal structure of GT NWs was rhombohedral due to their high reaction temperature. However, in this study GT NWs in the metastable orthorhombic phase were obtained instead most probably due to the low temperature synthesis. The orthorhombic is a low-temperature phase having lower symmetry than the rhombohedral. The reason that Te particles were synthesized in the samples lies in the strong tendency of tellurium formation arising from low free energy of Te segregation.³⁴

The thermal behavior of samples containing GT NWs and Te particles was investigated using DSC as shown in Figure 5. Two endothermic peaks exist at 456 and 650 °C, respectively,

and one exothermic one exists at 524 °C. The first and the second endothermic peaks were identified as corresponding to melting of Te particles and that of GT NWs, respectively. The melting point of GT was dropped most probably due to the small diameter of NWs. The phase transformation of orthorhombic to rhombohedral known to occur at ~460 °C could not be detected probably overlapping with the huge melting peak of Te. The transformation from a low-temperature solid phase to a high-temperature one is also an endothermic reaction, and the enthalpy change is relatively small compared to melting. The reduced melting temperature of GT NWs compared to its bulk melting temperature of 725 °C could arise from the small dimensionality of NWs. This lowered melting temperature could be very desirable for reducing the reset current of a NW PRAM device, and hence it can accelerate the speed of memory switching. Also, the small dimensionality of GT NWs can contribute to the increase of integrated density of devices. In studies in the near future, Te nanoparticles will be removed by centrifugation or selective chemical etching for purification of GT NWs.

4. Conclusions

In this study, GT NWs were successfully synthesized with high yield using a Bi seed-assisted liquid-phase process at a very low temperature. The strong tendency to form Te particles arising from lower free energy of Te segregation was overcome by subsequently injecting Ge and Te precursor to Bi seed-bearing solution. GT NWs were very straight and they were in a cylindrical shape. Also, GT NWs were highly crystalline with orthorhombic structure. Instead of a solution–liquid–solid (SLS) mechanism, Ostwald ripening was proposed as the growth mechanism of GT NWs. DSC scan results show the apparently reduced melting point of GeTe phase. This high-quality, high-yield, and low-cost synthesis of GT NWs could contribute to the fabrication of nanostructured PRAM devices with low reset current, fast memory switching, and high integrated density. Also, this method can be extended to the synthesis of ternary chalcogenide compound NWs such as Ge₂Sb₂Te₅ (GST).

Acknowledgment. This work was supported by the IT R&D program of MKE/IITA [2006-S-078-03, Environmental Sensing and Alerting System with Nano-wire and Nano-tube]. This work was also supported by the Components and Materials Technology Development Program funded by the Ministry of Knowledge Economy, Republic of Korea (MKE, Korea) in 2008.

References

- (1) Ovshinsky, S. R. *Phys. Rev. Lett.* **1968**, *21*, 1450.
- (2) Yoon, S. M.; Lee, N. Y.; Ryu, S. O.; Choi, K. J.; Park, Y. S.; Lee, S. Y.; Yu, B. G.; Kang, M. J.; Choi, S. Y.; Wuttig, M. *IEEE Electron Device Lett.* **2006**, *27*, 445.
- (3) Abrutis, A.; Plausinaitiene, V.; Skapas, M.; Wiemer, C.; Salicio, O.; Pirovano, A.; Varesi, E.; Rushworth, S.; Gawelda, W.; Siegel, J. *Chem. Mater.* **2008**, *20*, 3557.
- (4) Kolobov, A. V.; Fons, P.; Frenkel, A. L.; Ankudinov, A. L.; Tominaga, J.; Uruga, T. *Nat. Mater.* **2004**, *3*, 703.
- (5) Pirovano, A.; Lacaíta, A. L.; Benvenuti, A.; Pellizzer, F.; Bez, R. *IEEE Trans. Electron Devices* **2004**, *51*, 452.
- (6) Kang, D. H.; Ahn, D. H.; Kim, K. B.; Webb, J. F.; Yi, K. W. *J. Appl. Phys.* **2003**, *94*, 3536.
- (7) Senkader, S.; Wright, C. D. *J. Appl. Phys.* **2004**, *95*, 504.
- (8) Lankhorst, M. H. R.; Ketelaars, B. W. S. M. M.; Wolters, R. A. M. *Nat. Mater.* **2005**, *4*, 347.
- (9) Jung, Y.; Lee, S.-H.; Ko, D.-K.; Agarwal, R. *J. Am. Chem. Soc.* **2006**, *128*, 14026.
- (10) Lee, S.-H.; Ko, D.-K.; Jung, Y.; Agarwal, R. *Appl. Phys. Lett.* **2006**, *89*, 223116.
- (11) Yu, D.; Wu, J. Q.; Gu, Q.; Park, H. K. *J. Am. Chem. Soc.* **2006**, *128*, 8148.
- (12) Lee, J. S.; Brittan, S.; Yu, D.; Park, H. *J. Am. Chem. Soc.* **2008**, *130*, 6252.
- (13) Yu, D.; Brittan, S.; Lee, J. S.; Falk, A.; Park, H. *Nano Lett.* **2008**, DOI: 10.1021/nl802261s.
- (14) Yu, B.; Sun, X. H.; Ju, S.; Janes, D. B.; Meyyappan, M. *IEEE Trans. Nanotechnol.* **2008**, *7*, 496.
- (15) Duan, X. F.; Huang, Y.; Cui, Y.; Wang, J. F.; Lieber, C. M. *Nature* **2001**, *409*, 66.
- (16) Gudiksen, M. S.; Lathon, L. J.; Wang, J.; Smith, D. C.; Lieber, C. M. *Nature* **2002**, *415*, 617.
- (17) Ouyang, L.; Maher, K. N.; Yu, C. L.; McCarthy, J.; Park, H. *J. Am. Chem. Soc.* **2007**, *129*, 617.
- (18) Huang, M. H.; Mao, S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind, H.; Webber, E.; Russo, R.; Yang, P. D. *Science* **2001**, *292*, 1897.
- (19) Lee, J.-C.; Kim, T. G.; Choi, H.-J.; Sung, Y.-M. *Cryst. Growth Des.* **2007**, *7*, 2588.
- (20) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.
- (21) Cho, K. S.; Talapin, D. V.; Gaschler, W.; Murray, C. B. *J. Am. Chem. Soc.* **2005**, *127*, 7140.
- (22) Hor, Y. S.; Welp, U.; Xiao, Z. L.; Patel, U.; Mitchell, J. F.; Kwok, W. K.; Crabtree, G. W. *Appl. Phys. Lett.* **2005**, *87*, 142506.
- (23) Sun, X.; Yu, B.; Ng, G.; Meyyappan, M. *J. Phys. Chem. C* **2007**, *111*, 2421.
- (24) Park, W. I.; Kim, D. H.; Jung, S. W.; Yi, G. C. *Appl. Phys. Lett.* **2002**, *80*, 4232.
- (25) Wu, J. J.; Liu, S. C. *Adv. Mater.* **2002**, *14*, 215.
- (26) Holmes, J. D.; Johnston, K. P.; Doty, R. C.; Korgel, B. A. *Science* **2000**, *287*, 1471.
- (27) Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80.
- (28) Wang, X.; Zhuang, J.; Peng, Q.; Li, Y. D. *Nature* **2005**, *437*, 121.
- (29) Gates, B.; Yin, Y. D.; Xia, Y. N. *J. Am. Chem. Soc.* **2000**, *122*, 12582.
- (30) Grebinski, J. W.; Hull, K. L.; Zhang, J.; Kosel, T. H.; Kuno, M. *Chem. Mater.* **2004**, *16*, 5260.
- (31) Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. *Nano Lett.* **2002**, *2*, 165.
- (32) Li, R. F.; Luo, Z. T.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2006**, *128*, 6280.
- (33) Sung, Y.-M.; Kwak, W.-C.; Kim, T. G. *Cryst. Growth Des.* **2008**, *8*, 1186.
- (34) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15*, 353.