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Cobalt silicide nanocables grown on Co films: synthesis and physical properties

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Abstract

Single-crystalline cobalt silicide/SiO_x nanocables have been grown on Co thin films on an SiO₂ layer by a self-catalysis process via vapor–liquid–solid mechanism. The nanocables consist of a core of CoSi nanowires and a silicon oxide shell with a length of several tens of micrometers. In the confined space in the oxide shell, the CoSi phase is stable and free from agglomeration in samples annealed in air ambient at 900 °C for 1 h. The nanocable structure came to a clear conclusion that the thermal stability of the silicide nanowires can be resolved by the shell encapsulation. Cobalt silicide nanowires were obtained from the nanocable structure. The electrical properties of the CoSi nanowires have been found to be compatible with their thin film counterpart and a high maximum current density of the nanowires has been measured. One way to obtain silicate nanowires has been demonstrated. The silicate compound, which is composed of cobalt, silicon and oxygen, was achieved. The Co silicide/oxide nanocables are potentially useful as a key component of silicate nanowires, interconnects and magnetic units in nanoelectronics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

At the present time in nanotechnology, one-dimensional nanocable heterostructures have drawn a great deal of research attention for their synthesis, formation mechanisms, properties and applications [1–10]. Meanwhile, a large number of epitaxial silicide nanowires (NWs) have been investigated due to their low resistivity, physical properties and excellent compatibility with silicon device processing [11–17]. With the advances in nanoelectronics, the synthesis and properties of free-standing silicide NWs and semiconductor/silicide heterostructures have received increasing attention [18–23]. The research on silicide NWs has been extended to a prosperous field on the magnetic, thermoelectric and field emission properties. The strategy of using the vapor transport method has been proved to be an effective approach to grow a variety of silicide phases. The success also opens up great opportunities to probe the physical properties in single-crystal form as well as to assess the size-dependent effects. In other words, the critical issue of whether

the properties of nanoscale silicides are varied with their dimension may be solved. Wu *et al* found that single-crystal and defect-free NiSi NWs have ideal resistivities and remarkably high failure current densities [11]. Lin and Higgins *et al* paid attention to the magnetic properties of the MnSi nanowires [24, 25]. Among these research results on silicide NWs, CoSi NWs has exhibited unusual magnetic properties and an electrical characteristic on resistivity [26–28]. In their reports, ferromagnetic NWs have great potential applications in future nanospintronics combined with the Si IC technology because of its compatibility. A previous report showed that the resistivity of the CoSi thin film on a (001)Si substrate and the bulk single-crystal CoSi is 350 and 180 μΩ cm, respectively [29, 30]. On the other hand, CoSi NWs were found to possess a resistivity ranging from 126.5 to 510 μΩ cm. In this paper single-crystalline CoSi/SiO_x nanocables (NCs) were grown on Co films on SiO₂ by a feasible method. The resistivity of CoSi NWs was measured to be about 325 μΩ cm. The CoSi/SiO_x NCs were found to be thermally stable, converted to Co₂SiO₄ and Co oxide NWs, respectively, after being annealed at 900, 1000 and 1100 °C in air ambient for 1 h. Analogous to the bulk cables, conducting

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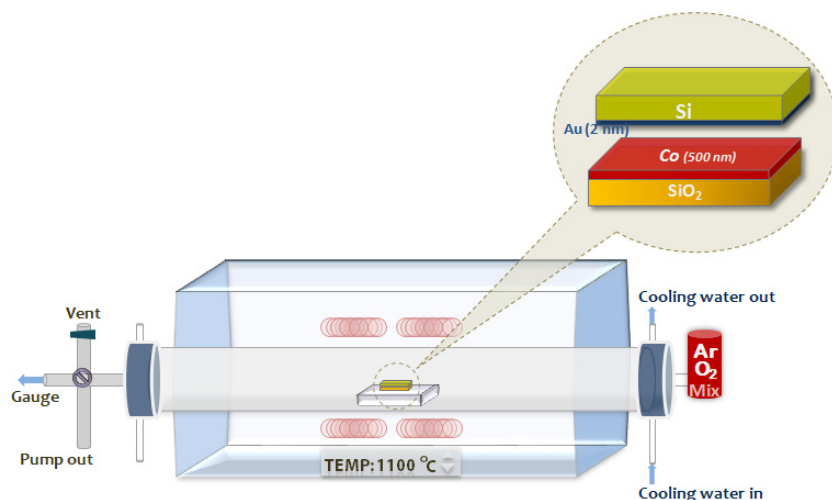


Figure 1. The configuration of the experimental set-up.

CoSi NWs with protective SiO_x shells may find applications as interconnects and magnetic units in nanoelectronic devices.

2. Experimental procedures

2.1. Synthesis of cobalt silicide nanocables

Single-crystalline CoSi NCs were grown in the two-zone furnace (figure 1) with a designed process. (001)-oriented single-crystal silicon wafers with a resistivity of 1–30 Ω cm were used as substrates. The wafer was cleaned by a standard RCA process followed by dilute HF dipping and then loaded into an electron beam evaporation system. An Au film of 2 nm in thickness was deposited on the Si substrates in a vacuum of 6×10^{-5} Torr. Au and Si would form an Au–Si eutectic alloy at high temperature and serves as a source of Si vapor. 500 nm thick Co was sputtered on the thermally grown SiO_2 wafer. During the growth, these two substrates were placed face to face in a vacuum furnace with a base pressure better than 10^{-2} Torr. The samples with 500 nm thick Co were placed on the underside and the Si substrate coated with 2 nm Au was placed on the top. The furnace was pumped prior to the sealing off at both ends. The temperature of the system was raised from room temperature to 1100 °C and held at that temperature for 1 h. After the treatment, the furnace was cooled down to room temperature and the pressure of the chamber was 5 Torr.

2.2. Heat treatment of the nanocables

The heat treatment of the as-grown samples was conducted in a diffusion furnace at atmospheric pressure at various temperatures. CoSi NWs without the oxide shell were also conducted for comparison.

2.3. Characterizations and electrical property measurement

A field emission scanning electron microscope (FESEM) was used to examine the grown products and a JEOL-2010 transmission electron microscope (TEM) equipped with an energy dispersive spectrometer (EDS) was used to investigate

the microstructures and to determine the compositions of the samples. A Keithley 4200 was used to measure the electrical properties of the CoSi NWs.

3. Results and discussion

Figure 2(a) shows the SEM image of as-grown products on the Co/oxide substrate. Fluffy islands as well as long and straight NWs were grown on the surface of the substrate. From a combination of SEM and TEM/EDS analysis, the long and straight NWs were identified to be CoSi/ SiO_x NCs. The NCs were as long as several tens of micrometers. On the other hand, the fluffy islands are Co islands covered with thickets of SiO_x NWs, as shown in figure 2(b). TEM images in figure 2(c) show the structures of the NCs. Analysis of the high resolution image and the diffraction pattern corresponding to the core, as shown in figure 2(d), reveal that it is of cubic CoSi. Figure 2(e) shows the tip of the NC. There is a nanoparticle at the tip of the 100 nm diameter NC. EDS data, as shown in figure 2(f), indicate that the shell of the NC and the catalyst are composed of (Si, O) and Co, respectively. The presence of a catalytic Co particle at the tip indicates that the CoSi NWs were grown via a vapor–liquid–solid (VLS) mechanism through a self-catalysis process [31, 32].

CoSi NWs were obtained by the removal of the outer shell oxide by dipping in a dilute HF solution. From the comparison of the SEM images in figures 3(a) and 2(b), the oxide NWs on the cobalt islands can be removed. Figures 3(b) and (c) show that CoSi NWs are grown from the Co islands and even across two islands to form interconnects. The TEM image of the NW without the oxide shell in figure 3(d) and the inset electron diffraction pattern in figure 3(e) indicate that the growth direction is along [111]. The high resolution TEM image of the NW is shown in figure 3(e), where a CoSi nanowire of high crystallinity can be seen after the removal of the oxide; the outer amorphous region is a carbon film on the Cu grid as sample support. If the period for sonication was long enough, some small Co islands could be removed, as shown in figure 3(f).

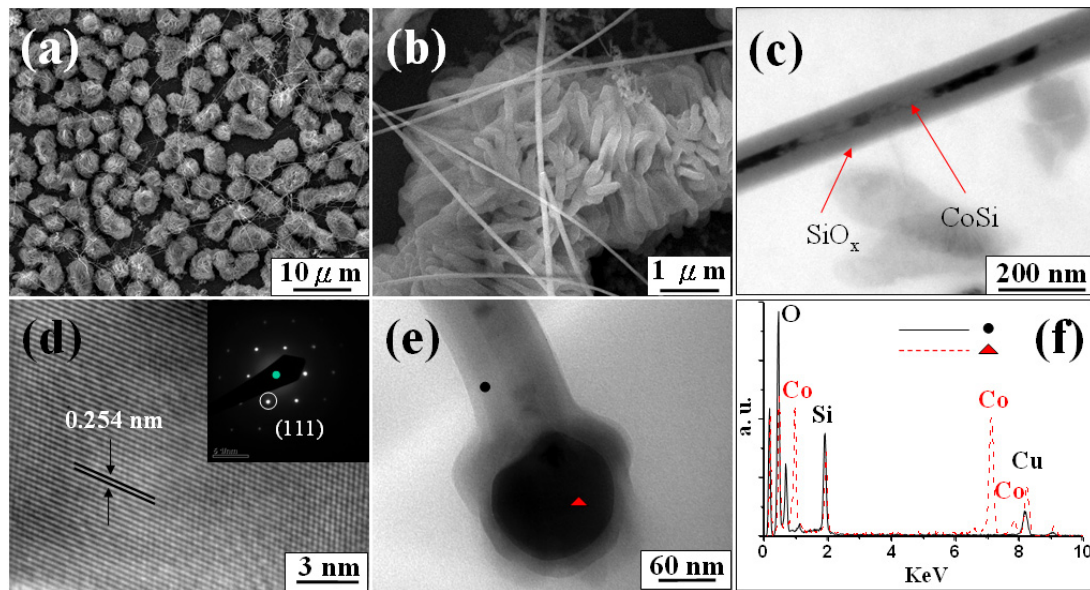


Figure 2. (a) Low magnification image of the as-grown samples, (b) high magnification image showing the appearance of the cobalt island, (c) TEM images of the CoSi NCs, (d) high resolution TEM image of the core, inset shows the corresponding diffraction pattern, (e) TEM image of the catalyst and (f) EDS diagram of the shell and the catalyst. The black solid EDS diagram indicates the composition of the shell and the red dashed EDS diagram indicates the composition of the catalyst.

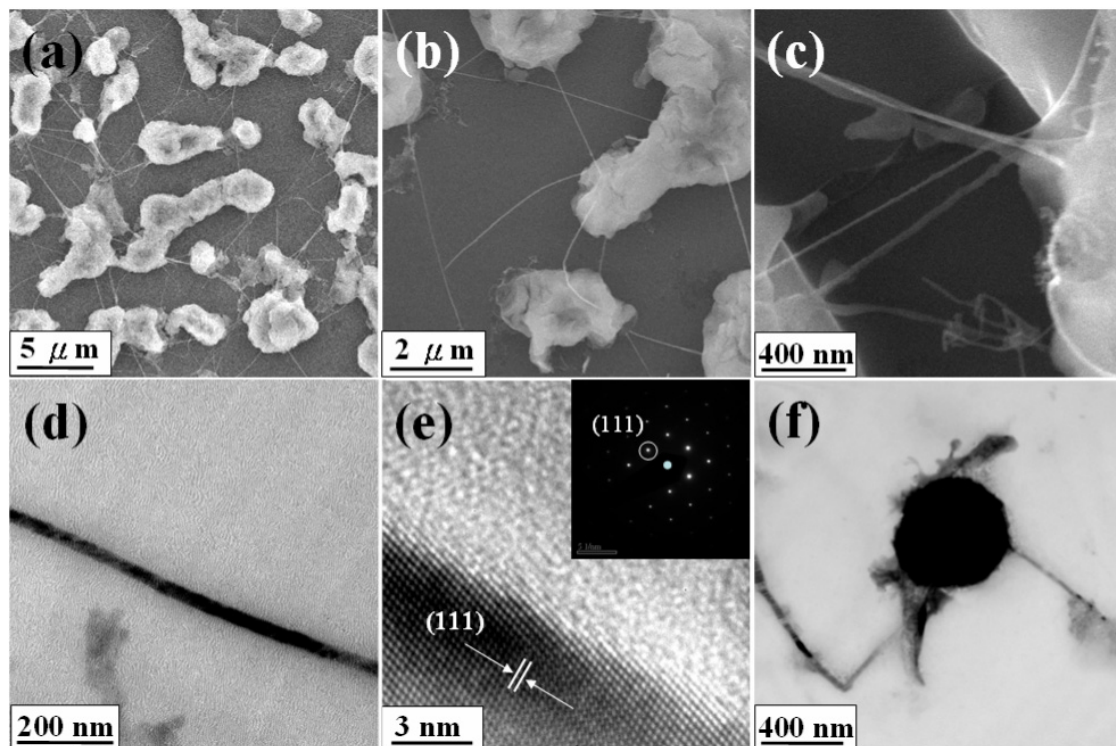


Figure 3. (a) Low magnification SEM image of CoSi NWs, (b) high magnification SEM image of the NWs and cobalt islands, showing the oxide sheath was removed and interconnects between islands, (c) high magnification SEM image of the connection of the NWs and Co islands, (d) TEM image of the CoSi NW, (e) high resolution TEM image of the NW, inset shows the corresponding diffraction pattern and (f) TEM image of the cobalt island connected with the NWs.

The as-grown CoSi NCs were annealed in a diffusion furnace in air ambient at various temperatures for 1 h. If the samples were annealed at or below 900 °C, the NCs maintain the morphology and the composition of the core was the same.

It means that the oxide shell protects the CoSi core from oxidation and agglomeration. In contrast, severe oxidation occurred for CoSi nanowires without an oxide shell exposed in air at 500 °C. The results indicate that the silicide core/oxide

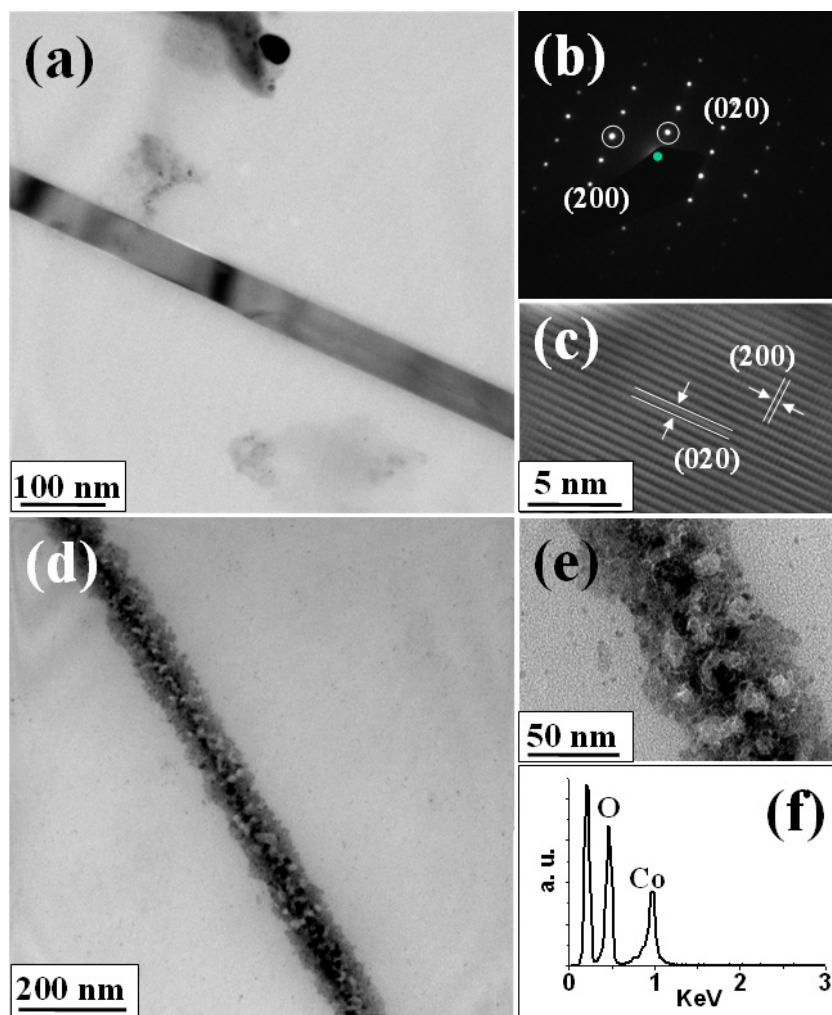


Figure 4. (a) TEM images of the Co_2SiO_4 NW, (b) corresponding diffraction pattern, (c) high resolution TEM image of the NW after filtering of the noise, (d) TEM image of the cobalt oxide NW, (e) high magnification TEM image of the NW, showing the size of the grains and (f) EDS diagram indicating the composition of the NW.

shell structure is important for wire protection and composition stability in the VLSI thermal processes. If the samples were annealed at 1000°C for 1 h, a new silicate NW appeared. CoSi NCs were found to transform to orthorhombic Co_2SiO_4 at 1000°C of annealing. The TEM image of the silicate NW with HF dipping for the removal of the oxide shell and the corresponding diffraction pattern are shown in figures 4(a) and (b), respectively. The high resolution TEM image after filtering of the noise is shown in figure 4(c). This result demonstrates that the silicate compound, which is composed of cobalt, silicon and oxygen, can be achieved in the presence of an oxide shell. This also suggests that single-crystal silicate NWs can be obtained by the transformation of the silicide NCs. If the samples were annealed at 1100°C for 1 h, the CoSi core would have been destroyed. Figure 4(d) shows the TEM image of the annealed sample. The NW became polycrystalline with rough surfaces. This demonstrates that oxygen in the furnace could break through the shell oxide and react with the core severely. Figure 4(e) is the high magnification TEM image of figure 4(d). The diameter of the nanocrystals within is about 5–10 nm in size. The EDS

spectrum in figure 4(f) shows the composition has changed to cobalt oxide.

The electrical properties of samples were measured with a Keithley 4200 multi-probe electrical measurement system attached to a JEOL-7000 FESEM. Pt was deposited as the contact metal in a focused-ion-beam (FIB) system. Before loaded into the chamber, the sample was dipped in a dilute HF solution to etch the oxide shell and was processed by sonication to remove some of the NWs. After two tungsten probes touched the contact pads, the I – V curves were obtained from the two probes [33]. The linear behavior of the I – V measurement, as shown in figure 5(a), at room temperature confirms the contacts between the electrodes and NWs are ohmic. In addition, the metallic CoSi NWs were measured to possess a resistivity of about $326 \mu\Omega \text{ cm}$, which is close to its thin film counterpart. The durability and reliability of the NWs were tested by applying high voltages. The I – V plot is shown in figure 5(b). The NW can endure a current up to 3.03 mA at 7.5 V and a maximum current density (J_{max}) of $1.6 \times 10^8 \text{ A cm}^{-2}$ was estimated, as shown in figure 5(b). The high J_{max} is comparable to that reported for the NiSi NWs

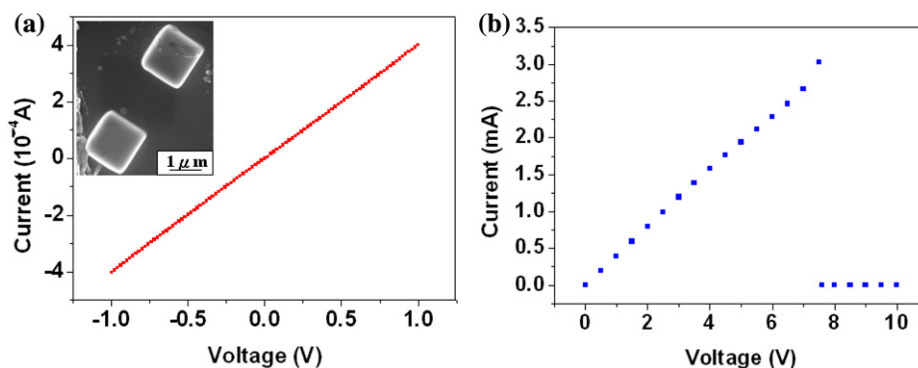
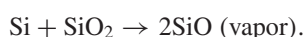


Figure 5. (a) I - V curve of the CoSi NW, inset shows the SEM images of the measurement configuration and (b) I - V curve recorded at high applied voltage.

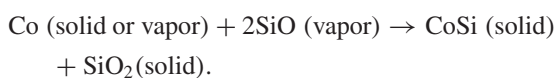
(3×10^8 A cm $^{-2}$). For the previous work on the thin film resistivity with an average grain size of about 60 nm, there were more than 20000 grain boundaries between the two probes with a spacing of about 0.16 cm. The high resistivity measured for a thin film (350 $\mu\Omega$ cm) may be attributed to the presence of grain boundaries while the CoSi NWs (326 $\mu\Omega$ cm) produced in the present study may be attributed to the contact resistance or NW surfaces. Based on all the experimental results, the inner CoSi can maintain good structural stability even at high temperatures. On the other hand, it has been demonstrated that, as the oxide is removed, the resistivity would be similar to that of CoSi NWs. Additionally, for NCs different from NWs in the structure, the oxide shell of NCs is also important in the applications in nanoelectronics, playing a different role in nanodevices. However, with the synthesis method here, both CoSi NWs and NCs can be efficiently obtained.

From the presence of Co particles at the tip of the CoSi NWs, it can be inferred that the CoSi NWs were grown via a VLS mechanism through a self-catalysis process. Meanwhile, these silicon oxide NWs on the Co islands indicated that silicon NWs were grown on the Co islands and then oxidized by the residual oxygen. Also, the existence of the SiO $_2$ NWs shows that the residual oxygen and Si vapor supplied from the Au-coated substrate were the key components during the growth. Without Au, there would not have been enough Si vapor for the formation of the SiO $_2$ shell. From the configuration of the NCs, the pathways of the growth of NCs are as follows,

First, the Si vapor from Au-Si eutectic alloys reacts with the residual oxygen and/or the exposed SiO $_2$ surface to form SiO vapor:



The SiO vapor is then attached to the Co islands, via the VLS mechanism. Through self-catalysis, the NCs are grown:



In the reactions between Co thin films and Si, CoSi forms at about 400 °C, and is transformed to CoSi $_2$ at higher

temperatures. In the present investigation, SiO vapor reacts with Co islands to grow CoSi/SiO $_x$ NCs. The silicon oxide shell serves to protect CoSi from agglomeration at a temperature as high as 1100 °C in vacuum [34]. In air ambient, the shell could also keep the core intact even after annealing at 900 °C. The high stability of the core-shell structure should be advantageous for applications as interconnects and magnetic units in nanoelectronics devices.

4. Conclusions

In conclusion, single-crystalline CoSi/oxide NCs have been synthesized by a VLS mechanism and Co self-catalysis. The shell of the NC consists of amorphous silicon oxide and the inner core is pure CoSi NW. The oxide shell can protect the wire from deterioration. The electrical properties of the CoSi NWs have been measured and the maximum current density has been found to be more than 10^8 A cm $^{-2}$. The growth mechanism of the CoSi NCs is attributed to the self-catalytic VLS mechanism. The Co $_2$ SiO $_4$ silicate compound was achieved in the presence of an oxide shell. This result implies that the silicate NWs can be obtained by oxide coating and thermal annealing of silicide NWs. With these outstanding properties of the CoSi NCs and the potential applications of magnetic CoSi NWs in Si-based spintronics, we propose that the silicide core/oxide shell structure may play a crucial role as silicate, interconnects and magnetic units in nanoelectronics.

Acknowledgments

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References

- [1] Cao L M, Tian H, Zhang Z, Feng M, Zhan Z J, Wang W K and Zhang X Y 2008 *Cryst. Growth Des.* **8** 4350
- [2] Yan K Y, Xue Q Z, Xia D, Chen H J, Xie J and Dong M D 2009 *ACS Nano* **3** 2235
- [3] Zhang Y, Suenaga K, Colliex C and Iijima S 1998 *Science* **281** 973

- [4] Zhan J H, Bando Y, Hu J Q, Li Y B and Golberg D 2004 *Chem. Mater.* **16** 5158
- [5] Xie Y, Qiao Z P, Chen M, Liu X M and Qian Y T 1999 *Adv. Mater.* **11** 1512
- [6] Enyashin A N and Ivanovskii A L 2005 *Nanotechnology* **16** 1304
- [7] Daly B, Arnold D C, Kulkarni J S, Kazakova O, Shaw M T, Nikitenko S, Erts D, Morris M A and Holmes J D 2006 *Small* **2** 1299
- [8] Crowley T A, Daly B, Morris M A, Erts D, Kazakova O, Boland J J, Wu B and Holmes J D 2005 *J. Mater. Chem.* **15** 2408
- [9] Luo Y and Wang L W 2010 *ACS Nano* **4** 91
- [10] Xu J, Lee C S, Tang Y B, Chen X, Chen Z H, Zhang W J, Lee S T, Zhang W X and Yang Z H 2010 *ACS Nano* **4** 1845
- [11] Wu Y, Xiang J, Yang C, Lu W and Lieber C M 2004 *Nature* **430** 61
- [12] Liu B Z, Wang Y F, Dilts S, Mayer T S and Mohny S E 2007 *Nano Lett.* **7** 818
- [13] Hsu H C, Wu W W, Hsu H F and Chen L J 2007 *Nano Lett.* **7** 885
- [14] Schmitt A L, Bierman M J, Schmeisser D, Himpsel F J and Jin S 2006 *Nano Lett.* **6** 1617
- [15] Lu K C, Wu W W, Wu H W, Tanner C M, Chang J P, Chen L J and Tu K N 2007 *Nano Lett.* **7** 2389
- [16] Chou Y C, Wu W W, Cheng S L, Yoo B Y, Myung N, Chen L J and Tu K N 2008 *Nano Lett.* **8** 2194
- [17] Lin Y C, Lu K C, Wu W W, Bai J W, Chen L J, Tu K N and Huang Y 2008 *Nano Lett.* **8** 913
- [18] Schmitt A L, Higgins J M, Szczech J R and Jin S 2010 *J. Mater. Chem.* **20** 223
- [19] Chou Y C, Wu W W, Chen L J and Tu K N 2009 *Nano Lett.* **9** 2337
- [20] Song Y P, Schmitt A L and Jin S 2007 *Nano Lett.* **7** 965
- [21] Chueh Y L, Ko M T, Chou L J, Chen L J, Wu C S and Chen C D 2006 *Nano Lett.* **6** 1637
- [22] Zhou F, Szczech J, Pettes M T, Moore A L, Jin S and Shi L 2007 *Nano Lett.* **7** 1649
- [23] Seo K, Varadwaj K S K, Cha D, In J, Kim J, Park J and Kim B 2007 *J. Phys. Chem. C* **111** 9072
- [24] Lin Y C, Chen Y, Shailos A and Huang Y 2010 *Nano Lett.* **8** 913
- [25] Higgins J M, Ding R H, Degrave L P and Jin S 2010 *Nano Lett.* **10** 1605
- [26] Schmitt A L, Zhu L, Schmeisser D, Himpsel F J and Jin S 2006 *J. Phys. Chem. B* **110** 18142
- [27] Tsai C I, Yeh P H, Wang C Y, Wu H W, Chen U S, Lu M Y, Wu W W, Chen L J and Wang Z L 2009 *Cryst. Growth Des.* **9** 4514
- [28] Seo K, Varadwaj K S K, Mohanty P, Lee S, Jo Y, Jung M H, Kim J and Kim B 2007 *Nano Lett.* **7** 1240
- [29] Lur W and Chen L J 1988 *J. Appl. Phys.* **64** 3505
- [30] Ren W L, Li C C, Zhang L T, Ito K and Wu J S 2005 *J. Alloys Compounds* **392** 50
- [31] Kim J and Anderson W A 2006 *Nano Lett.* **6** 1356
- [32] Kim J, Anderson W A, Song Y J and Kim G B 2005 *Appl. Phys. Lett.* **86** 253101
- [33] Hsin C L, He J H, Lee C Y, Wu W W, Yeh P H, Chen L J and Wang Z L 2007 *Nano Lett.* **7** 1799
- [34] Walter D and Karyasa I W 2005 *Z. Anorg. Allg. Chem.* **631** 1285