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Growth of single-crystalline cobalt silicide nanowires with excellent physical properties

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With the miniaturization of electron devices, the minuscule structures are important to state-of-the-art science and technology. Therefore, the growth methods and properties of nanomaterials have been extensively studied recently. Here, we use chemical vapor transport (CVT) methods to synthesize single-crystalline cobalt silicide nanowires (NWs) by using $(\text{CoCl}_2 \cdot 6\text{H}_2\text{O})$ as a single-source precursor. By changing reaction temperature and ambient pressure, we can obtain different morphology of cobalt silicide NWs under the appropriate concentration of silicon and cobalt. The field emission measurement of CoSi NWs shows low turn-on field ($5.02 \text{ V}/\mu\text{m}$) and it is outstanding for magnetic properties that differ from the bulk CoSi. The CoSi nanowires with different diameters have diverse magnetic saturation (Ms) and coercive force (Hc). © 2011 American Institute of Physics. [doi:10.1063/1.3643007]

I. INTRODUCTION

As the trend of device miniaturization moves on, nanomaterials have attracted more and more attention because their property is distinct from their counterpart bulk materials. One-dimensional nanomaterials, such as nanorod, nanowire, nanotube, and nanobelt, are novel materials and have potential to be used in electronic devices, optoelectronics, thermoelectrics, spintronics, etc.^{1–3} Transition-metal silicide nanowires are the extremely broad set of refractory materials, and were widely researched for their unique physical properties, low resistivity, and excellent compatibility with contemporary silicon device processing.^{4–12} With the advancement in nanoelectronics, the synthesis and properties of the silicide and silicide/semiconductor nanoheterostructures have received increasing attention.^{13–17} For synthesis, high aspect ratios (length/diameter) transition silicide nanowires, we can use chemical vapor deposition (CVD)^{18,19} or chemical vapor transport (CVT)^{14,20} methods. To simplify the experimental process, metal chloride is widely used as precursor. Metal chloride is vaporizable at low pressure and easily reacts with silicon to form SiCl_4 and MSi_x , so we can use single-source precursors (SSPs) to form transition-metal silicide nanowires. The concentration of precursor's vapor is the only parameter that has influence on the morphology of nanowires. For instance, using FeCl_3 (Ref. 21) or CoCl_2 (Refs. 22 and 23) to be precursor, we can obtain FeSi and CoSi nanowires, respectively. Cobalt silicide nanowires, are the so-called "B20" metal monosilicides group, which has relatively good electronic characteristics,^{24,25} including low resistivity, good thermal stability, appropriate work function ($\sim 4.8 \text{ eV}$), and compatibility with the processing of Si devices. For these properties, cobalt silicide nanowires become one potential candidate for cold cathode materials and inter-

connect in electronic devices. Besides, the bulk CoSi is a diamagnetic semi-metal. However, the CoSi nanowire ensemble exhibits ambiguous magnetic property. In this article, the effects of reaction temperature and ambient pressure on the morphology of nanowires have been discussed. The field emission property and the room-temperature ferromagnetic properties were also demonstrated in this work.

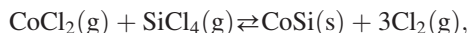
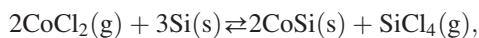
A. Experimental methods

Three-zone furnace was used to synthesize cobalt silicide nanowires via a chemical vapor deposition method. Single-crystal Si(001) substrates were cleaned in acetone, followed by immersing the substrates in diluted HF for 1 min to remove the oxide layer. Subsequently, the substrates were transferred to the furnace at the downstream. The cobalt chloride (CoCl_2) powder, as the precursor for cobalt silicide nanowires, was placed in an alumina boat at the upstream. The temperature of precursor and substrates were ramping to 600°C and $800\text{--}900^\circ\text{C}$, respectively. The ramping rate was $5^\circ\text{C}/\text{min}$ and the reaction time was 2 h. Ar was introduced into the furnace at the flow rate of 150 sccm. The structural characterization was examined by the x-ray diffraction (XRD). The morphology of nanowires was examined with a field emission scanning electron microscope (FESEM). Transmission electron microscope (TEM) was utilized for further investigation of atomic structures of nanowires. The field emission property was measured by the system equipped with a Keithley power supply. The magnetic property of cobalt silicide nanowires were measured by superconducting quantum interference device (SQUID).

II. RESULTS AND DISCUSSION

In the growth process, CoCl_2 was vaporized, transported by Ar gas, and reacted with silicon substrate. The plausible reactions to form CoSi NWs are (following of reversible pathway²²):

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We can control morphology and density of cobalt silicide NWs by tuning the reaction temperature and the ambient pressure in the furnace. Figures 1(a)–1(c) show the as-grown products at different growth temperatures. The nanoparticles are first formed at 800 °C, meaning that the critical supersaturation was not achieved to grow the NWs. With the increasing temperature at 850 °C, high-density NWs are formed on the substrate with diameter and length of 70 nm and 3–4 μm, respectively. For samples grown at 900 °C, micrometer-scaled clusters were deposited and short NWs were grown on the top. This means that a high supersaturation ratio was achieved, leading to bulk-like crystal growth because of the reduced surface energy at high temperature.^{21,26} For the study of the temperature effect, the ambient pressures were fixed at 1 Torr, which is based on our previous report for the growth of the CoSi nanostructures.^{12,23} The influence of ambient pressure on the aspect ratio and density of NWs has been studied. Figures 1(d)–1(f) show the as-grown products at different growth pressure, respectively, proving that aspect ratio and density were also controlled by the pressure. At a fixed temperature (600 °C at precursor and 800 °C at substrate) to study the ambient effect, the concentration of SiCl₄ vapor will increase at higher ambient pressure. When the vapor of CoCl₂ precursor concentration is fixed at constant temperature, [Co]/[Si] compositions are an inverse proportion to the ambient pressure. The nucleation

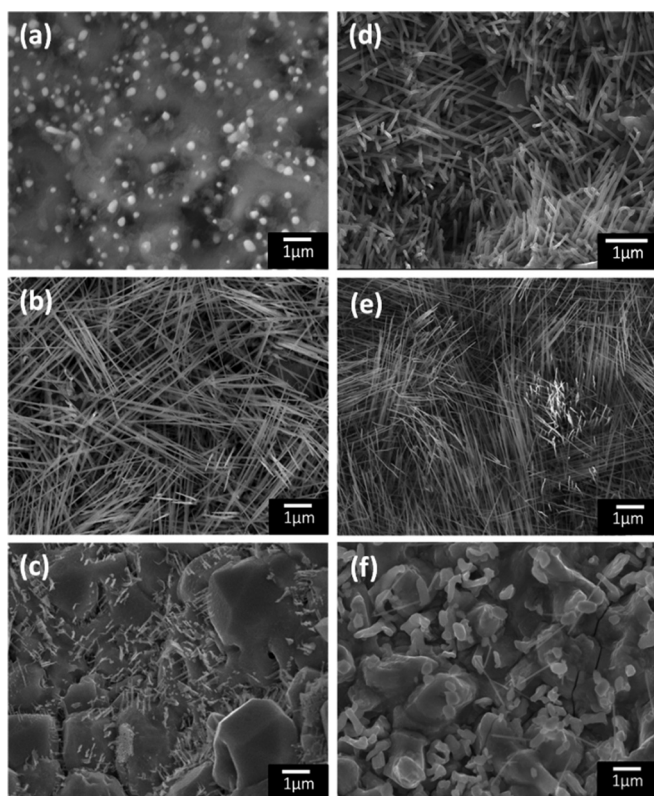


FIG. 1. Representative SEM image of CoSi NWs grown at (a) 800 °C, (b) 850 °C, and (c) 900 °C, respectively. SEM image of CoSi NWs grown at (d) 2 Torr, (e) 3 Torr, and (f) 4 Torr, respectively.

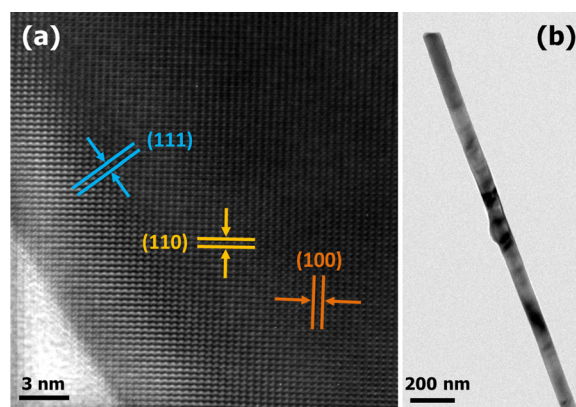


FIG. 2. (Color online) (a) High-resolution, and (b) low-magnification TEM images of CoSi NW grown at 850 °C.

rate of NWs will be proportional to the concentration of Si.²⁷ Thus, the density of CoSi nanowires increases as the pressure increases. However, it tends to form bulk morphology when pressure is too high. It can prove that both high temperature and pressure will induce the high supersaturation, and it can promote the bulk morphology growth. Furthermore, precursor species impinge on the substrate and nanowire sidewalls, attributing to axial and radial nanowire growth.²⁸ The concentration of Si only affects the length of nanowires. For higher ambient pressure, the aspect ratio become larger with decreasing [Co]/[Si] compositions.²⁷ In addition, the ambient pressure will not change the phase of the NWs. The high-resolution TEM image (Fig. 2(a)) of NWs grown at 850 °C shows that the NWs are cubic B20 type, single-crystalline cobalt silicide phase (CoSi), and grow along [111] direction (Fig. 2(b)). The XRD analysis of samples at reaction temperature of 800 °C–900 °C were shown in Fig. 3. At 800 °C, the diffraction peaks between 40° and 50° could be ascribed to be the orthorhombic Co₂Si phase. Although NWs did not grow at relative low temperature, the vapor of cobalt still reacts with the Si substrate to form the Co₂Si nanoparticles. At relative high temperature (850 °C and 900 °C), the cobalt

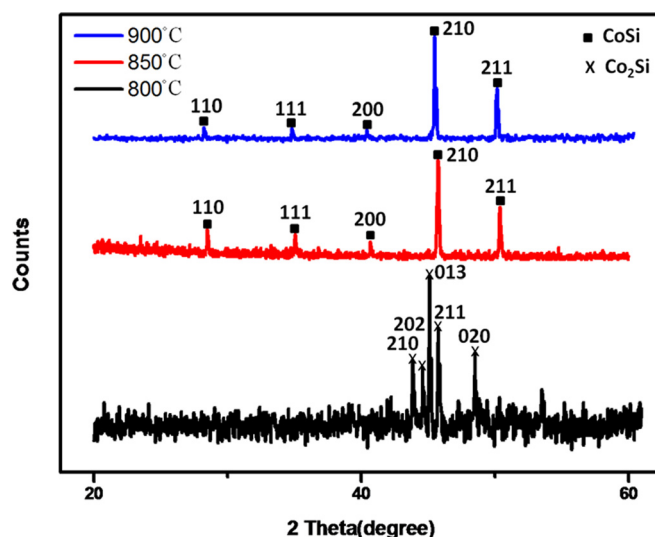


FIG. 3. (Color online) XRD pattern of samples grown at 800 °C, 850 °C, and 900 °C, respectively.

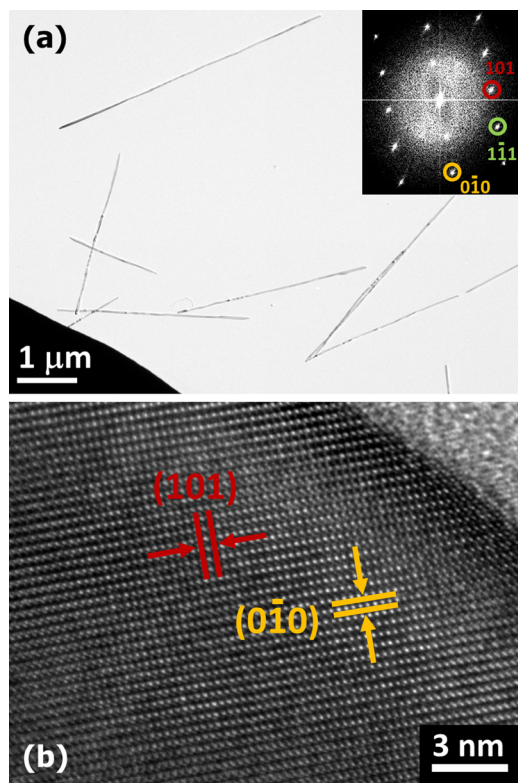


FIG. 4. (Color online) (a) Low-magnification, and (b) high-resolution TEM images of CoSi NWs grown at 3 Torr. The inset of (a) is the corresponding diffraction pattern.

silicide changes the phase from Co_2Si to CoSi, which is the most stable phase in the CoCl₂ and Si substrate reaction system in thermodynamics. And this is the only phase can be synthesized under this situation. The reaction of Co on Si has been reported and the silicidation temperature of Co_2Si is lower than the other phase.^{29,30} The crystal structure of CoSi NWs grown at 3 Torr were also examined by TEM. Figures 4(a) and 4(b) depict the low-magnification and high-resolution TEM images of the NW, respectively. The inset in Fig. 4(a) is the corresponding diffraction pattern, demonstrating that these NWs were also characterized as CoSi phase. The growth processes of CoSi nanowires required three steps as shown in Fig. 5. First, the cobalt chloride vapor will react with Si substrate and then cobalt will deposit to form the Co_2Si thin film by interdiffusion at lower temperature with nanoparticles on the surface. Next, with the increase of the temperature, the Co_2Si thin film with nanoparticles on the top would transform to CoSi, which is the thermodynamically most stable phase in the reaction of Si substrate and

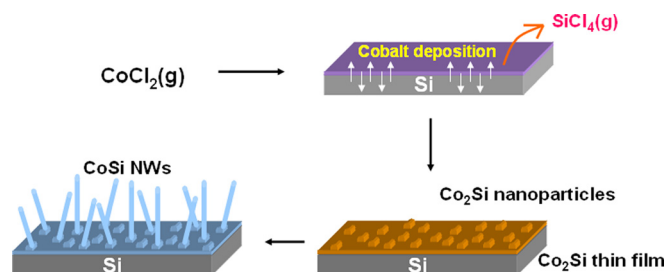


FIG. 5. (Color online) Proposed growth steps of CoSi NWs.

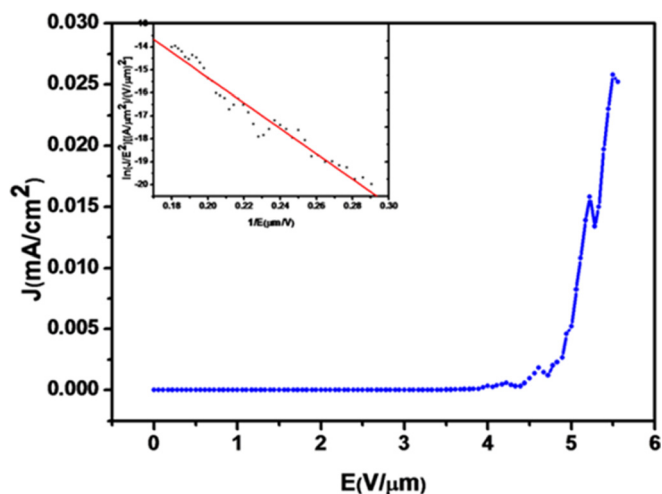


FIG. 6. (Color online) Field emission curves of CoSi NWs. The inset shows the corresponding $\ln(J/E^2)-1/E$ plot.

CoCl_2 .²⁷ Finally, the single crystalline CoSi NWs grow by self-catalyzing. In our results, there is no catalyst on the top of the NWs. This result corresponded with those of other metal silicide NWs, including Ti_5Si_3 , FeSi, and CrSi_2 silicide NWs, which were also grown on the silicon substrate by metal-chloride precursors. Then the most stable phase of the NWs appeared because it was comparably easy to nucleate. When CoSi nanoparticles become larger, the concentration of the critical supersaturation becomes much higher and it would be harder to precipitate NWs. Therefore, the metal silicide NWs would grow when the nanoparticles were small, whereas the concentration of precursor and temperature were in an appropriate condition for the growth of NWs. Based on our observations, we believe that the mechanism of the NW synthesis is by vapor-liquid-solid (VLS) method and self-catalytic process.

CoSi NWs also have outstanding field emission properties because of their metallic property and special 1D geometry. Figure 6 is the plot of the current density (J) as a function of the applied field (E) and the $\ln(J/E^2)-1/E$ plot in the inset. The sample was measured with a $180\text{-}\mu\text{m}$ separation between the anode and emitting surface in a vacuum chamber pumped to $\sim 10^{-5}$ Torr. The turn-on field is about

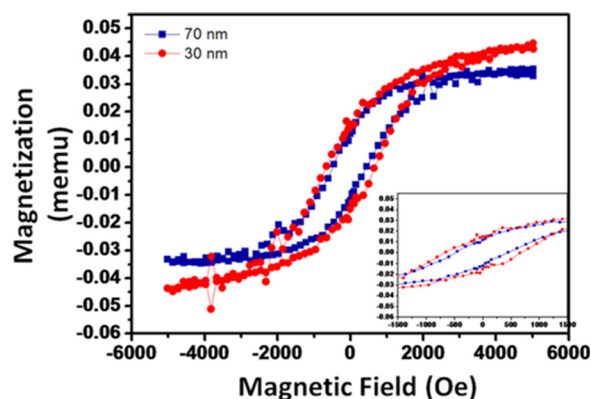


FIG. 7. (Color online) Plot of M - H curve at 2 K for two different diameters of NWs.

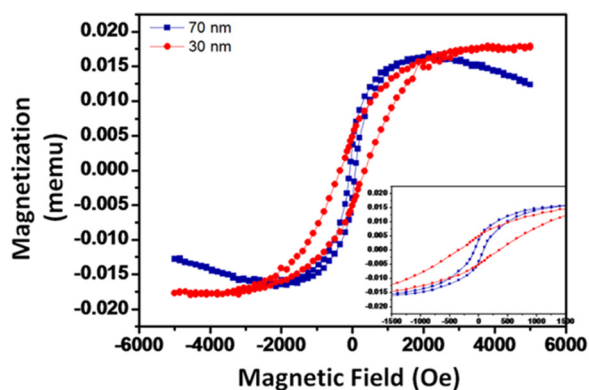


FIG. 8. (Color online) Plot of M - H curve at 300 K for two different diameters of NWs.

5.02 V/ μm . According to the Fowler–Nordheim (F–N) plot and the Fowler–Nordheim equation:

$$J = (A\beta^2 E^2 / \varphi) \exp(-B\varphi^{3/2} / \beta E),$$

where J is the current density, E is the applied electric field, and φ is the work function, respectively. For CoSi, φ is 4.7 eV, A and B are constants, corresponding to 1.56×10^{-10} [A(eV)/V $^{-2}$] and 6.83×10^9 [V(eV) $^{-3/2}$ m $^{-1}$], respectively. We could obtain that the field enhancement β is 1265 from the slope of $\ln(J/E^2) = \ln(A\beta^2/\varphi) - B\varphi^{3/2}/\beta E$, proving that CoSi NWs are promising emitters.

The magnetization of CoSi NWs was investigated by SQUID at different temperatures, as shown in Figs. 7 and 8. Insets in Figs. 7 and 8 highlight the hysteresis loops. The M - H curves show the hysteresis loops for CoSi nanowires, indicating that CoSi NWs is ferromagnetic and is different from bulk CoSi, which is a diamagnetic material. The ferromagnetic property was attributed to the not fully coordinated surface spins, which induce the ferromagnetic property on the surface of CoSi NWs.²² Comparing Fig. 7 with Fig. 8, the saturation magnetization M_s is getting higher at lower temperature (2 K) because the magnetic moments were not affected by thermal vibration at lower temperature. Moreover, the ferromagnetic property was affected by the diameter of NWs. The CoSi NWs with smaller diameter and larger aspect ratio have relatively high saturated magnetization (M_s) because the specific surface ratio is proportional to the aspect ratio, and the magnetic property of CoSi NWs is induced by uncoordinated surface spins. Furthermore, the coercivity is inverse to the diameter of nanowires because of the reduction in macroscopic interactions between the nanomagnets and the enhancement of the switching field of the individual nanowire.³¹

III. CONCLUSIONS

Cubic B20 type cobalt monosilicide NWs could be obtained by CVT method. By controlling the reaction temperature and pressure, cobalt silicide nanowires with different size and density can be obtained. The as-prepared CoSi nanowires, owing to their sharp tips, display good field emission

property. The magnetic properties were also demonstrated in this work. The CoSi nanowire ensemble exhibits room temperature ferromagnetic property with diverse M_s and coercive force (H_c) at different diameters, which was induced by the reduced coordination of the surface Co atoms.

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