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Single-crystalline δ -Ni₂Si nanowires with excellent physical properties

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Abstract

In this article, we report the synthesis of single-crystalline nickel silicide nanowires (NWs) via chemical vapor deposition method using NiCl₂·6H₂O as a single-source precursor. Various morphologies of δ -Ni₂Si NWs were successfully acquired by controlling the growth conditions. The growth mechanism of the δ -Ni₂Si NWs was thoroughly discussed and identified with microscopy studies. Field emission measurements show a low turn-on field (4.12 V/ μ m), and magnetic property measurements show a classic ferromagnetic characteristic, which demonstrates promising potential applications for field emitters, magnetic storage, and biological cell separation.

Keywords: CVD, Ni₂Si nanowires, Field emission, Ferromagnetic characteristic

Background

With the miniaturization of electronic devices, one-dimensional (1-D) nanostructures have attracted much attention due to their distinct physical properties compared with thin film and bulk materials. One-dimensional materials, such as nanorods, nanotubes, nanowires (NWs), and nanobelts, are promising to be utilized in spintronics, thermoelectric and electronic devices, etc. [1-5]. Metal silicides have been widely synthesized and utilized in the contemporary metal-oxide-semiconductor field-effect transistor as source/drain contact materials, interconnection [6], and Schottky barrier contacts. One-dimensional metal silicides have shown excellent field emission [7,8] and magnetic properties [9-11]. Hence, recently, the synthesis and study of 1-D metal silicide nanostructures and silicide/silicon or silicide/siliconoxide nanoheterostructures have been extensively investigated [9,12-18]. Among various silicides, Ni silicide NWs with low resistivity, low contact resistance, and excellent field emission properties [19,20] are considered as a promising material in the critical utilization for the future nanotechnology. Thus, plenty of methods have been reported to synthesize Ni silicide NWs. Wu et al. have formed NiSi NWs by the chemical reaction between coated

Ni metal layers and pre-fabricated Si NWs [13]. In addition, metal-induced growth, chemical vapor deposition (CVD), and chemical vapor transport method have been successfully applied to synthesize NiSi [21,22], Ni₃₁Si₁₂ [20], Ni₃Si [23], and Ni₂Si [24] NWs, and their physical properties have been investigated. For simplification of the whole processing, metal chloride compounds such as Fe(SiCl₃)₂(CO)₄ [9], CoCl₂ [11,25], or NiCl₂ [19] are commonly used as single-source precursors (SSPs) in synthesizing metal-silicide NWs. In this work, δ -Ni₂Si NWs were synthesized via CVD method with SSP of NiCl₂. The morphology and yield of δ -Ni₂Si NWs can be mastered through parameter control. The δ -Ni₂Si NWs were structurally characterized via high-resolution transmission electronic microscopy (HRTEM). The growth mechanisms of δ -Ni₂Si NWs and NiSi phases were identified through structural analysis by X-ray diffraction (XRD) and TEM. Electrical measurements showed an outstanding field emission property, and magnetic property measurements demonstrated a classic ferromagnetic behavior of the δ -Ni₂Si NWs.

Methods

The synthesis of the silicide NWs was carried out in the three-zone furnace via a chemical vapor deposition process. Commercial single-crystalline Si substrates were firstly cleaned in acetone for 10 min by ultrasonication. In order to remove the native oxide layer, substrates were dipped in dilute HF solutions for 30 s and then

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dried by nitrogen gas flow. The nickel chloride (NiCl_2) precursor was placed in an aluminum boat at the upstream and flown by carrier gas Ar at 30 sccm, while Si substrates were put at the downstream. The temperatures of the precursor and substrates were controlled at 600°C and 400°C , respectively, and held for 15 to 30 min with a $10^\circ\text{C}/\text{min}$ ramping rate. The vacuum pressure was controlled in the range of 6 to 15 Torr. The morphologies were investigated by field emission scanning electron microscopy. XRD and TEM were utilized in structural characterization. The noise of the atomic images was filtered by fast Fourier transform (FFT). The field emission property was measured using a Keithley power supply (Keithly Instruments Inc., Cleveland, OH, USA) with an anode probe of $180\ \mu\text{m}$ in diameter. A superconductive quantum interference device (SQUID; MPMS XL, SQUID Technology, Heddington, Wiltshire, UK) was utilized for magnetic property measurements.

Results and discussion

Figure 1a,b,c,d shows the SEM images of samples grown at different pressures (6, 9, 12, 15 Torr, respectively), indicating that the geometry on the surface of substrates varied with the ambient condition. With lower partial pressure of the precursor, as shown in Figure 1a, Ni silicide NWs were not formed due to insufficient supply of the Ni source; however, small nanowhiskers can be observed on the surface. As the ambient pressure was raised to the range of 9 to 12 Torr (Figure 1b,c), NWs with high aspect ratios were obtained for proper concentrations of precursors and growth conditions. The diameter of the NWs slightly increased with the increase of

the ambient pressure (from 30 to 50 nm to 40 to 70 nm). This may be attributed to the fact that higher precursor concentration is more suitable for the formation of $\delta\text{-Ni}_2\text{Si}$ system. Furthermore, when the pressure was higher than 15 Torr, the concentration of the Ni source was oversaturated and the morphology of the product turned into islands instead of NWs. Those islands may result from the condition change to decrease the surface energy of the system by transforming into bulk-like structures, as shown in Figure 1d. Thus, the diameter of the NWs can be controlled under specific pressure range and the ambient pressure plays an important role in maintaining the morphology of the NWs.

Figure 2a,b shows a series of SEM images of NWs with different growth times at a constant gas flow rate (30 sccm) and ambient pressure (9 Torr). The yield and density increased prominently when the growth time was raised from 15 to 30 min. The XRD analysis of different reaction time is shown in Figure 2c. The characteristic peaks were examined and identified to be orthorhombic $\delta\text{-Ni}_2\text{Si}$ and NiSi according to the JCPDF data base. From Figures 1 and 2, SEM images indicate that there were two types of microstructures (NWs and islands) in the products. In order to identify each phase of the microstructures of the as-grown products, structural analysis of the NWs has been performed. Figure 3a

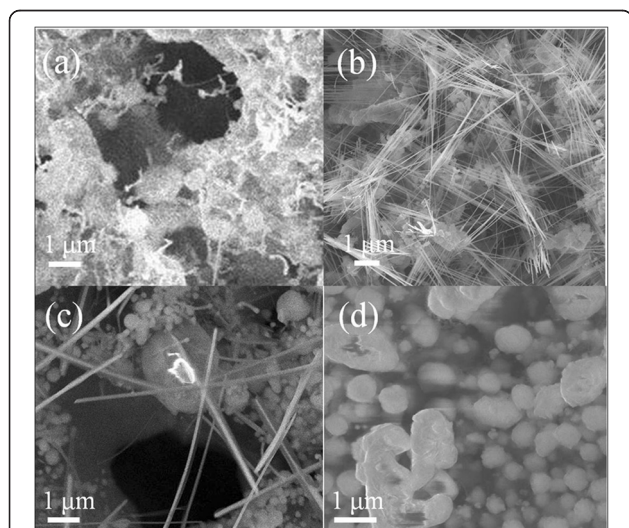


Figure 1 SEM images of as-synthesized NWs at vacuum pressures of (a) 6, (b) 9, (c) 12, and (d) 15 Torr. The temperature was fixed at 400°C , reaction time was 30 min, and carrier gas flow rate was held at 30 sccm.

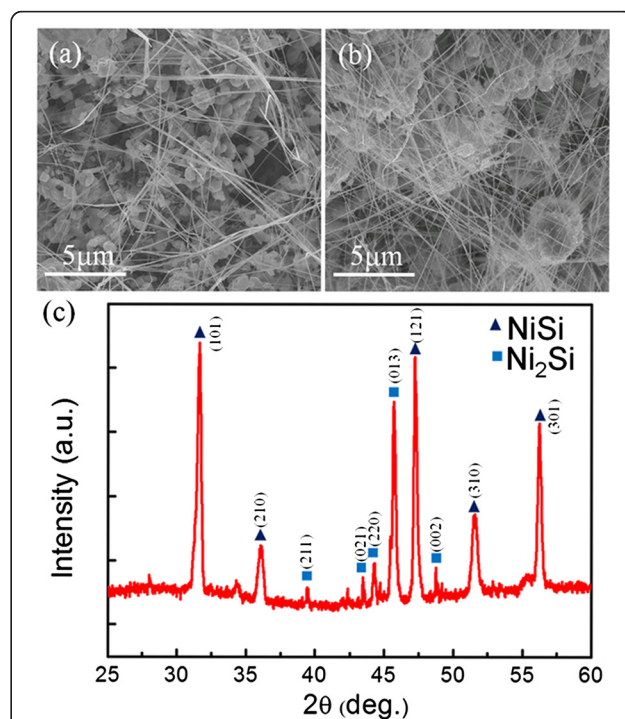
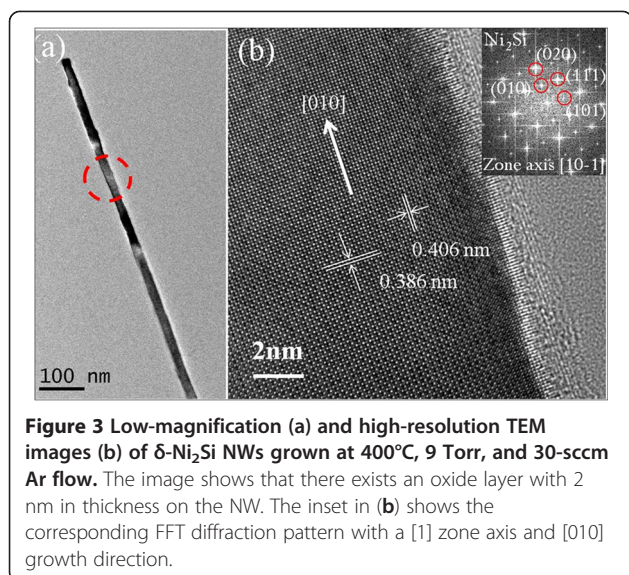
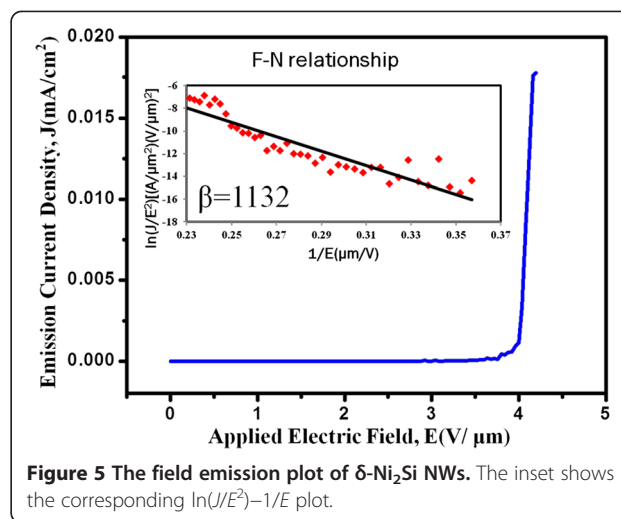
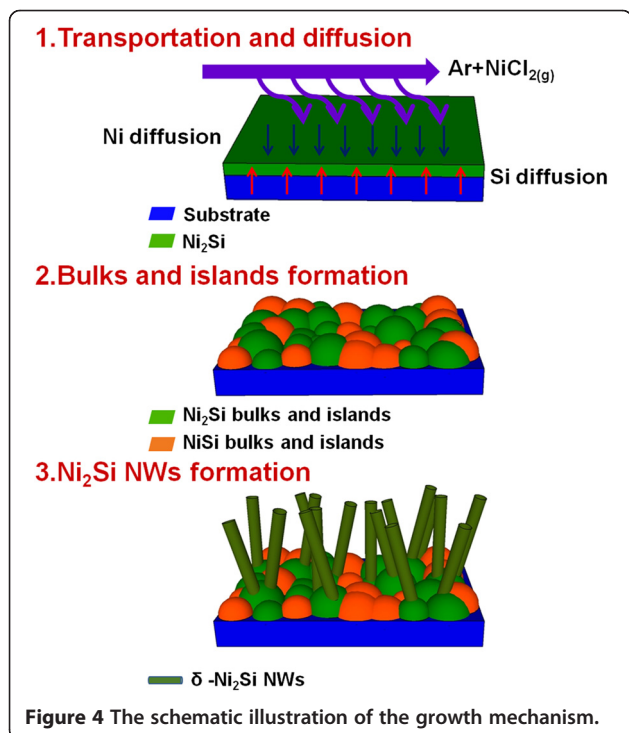


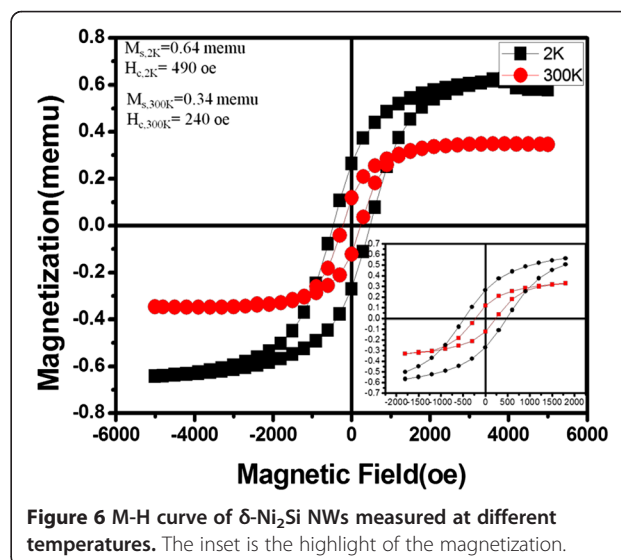
Figure 2 $\delta\text{-Ni}_2\text{Si}$ NWs grown at (a) 15 and (b) 30 min, and (c) corresponding XRD analysis of products. The temperature was fixed at 400°C , ambient pressure was 9 Torr, and the carrier gas flow rate was 30 sccm.



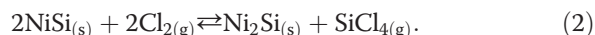
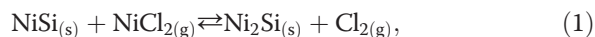
is the low-magnification TEM image of the NW with 30 nm in diameter. HRTEM image (Figure 3b) shows the NW of [010] growth direction with 2-nm-thick native oxide. FFT diffraction pattern of the lattice-resolved image is shown in the inset of Figure 3b, which represents the reciprocal lattice planes with [1] zone axis. The phase of the NW has been identified to be δ -Ni₂Si, constructed with the orthorhombic structure by lattice parameters of $a = 0.706$ nm, $b = 0.5$ nm, and $c = 0.373$ nm. Therefore, the as-deposited layer would be ascribed to NiSi.



The schematic illustration of the growth mechanism is in Figure 4. In the Ni-Si binary alloy system, it has been investigated that Ni atoms are the dominant diffusion species during the growth of orthorhombic δ -Ni₂Si and NiSi [26]. The reaction and phase transformation between δ -Ni₂Si and NiSi have also been reported [25]. Based on these previous studies, the reaction of the as-deposited Ni metal film occurred to form δ -Ni₂Si with a diffusion-controlled kinetics at 300°C to 400°C [27,28]. Then, partial transformation from δ -Ni₂Si into NiSi thin-film structures could happen if the thickness of the Ni is below 40 nm because NiSi would form on Si substrates with a low Si/NiSi interface energy [26,29]. Then, the continuous supply of Ni atoms may induce further growth of δ -Ni₂Si phase NWs via surface diffusion kinetics [30] on the remnant δ -Ni₂Si phase grains or NiSi bulks. There are two plausible and reversible formation



paths of δ -Ni₂Si, which can be described in the following equations [11,24,31]:



The two equations correspond well with the experiment results: higher ambient pressure will enhance the reaction to form Ni₂Si according to LeChatelier's principle, contributing to the formation and agglomeration of larger amount of δ -Ni₂Si NWs and islands at the surface.

Due to the metallic property and special 1-D geometry, investigation of field emission properties has been conducted. Figure 5 shows the plot of the current density (J) as a function of the applied field (E) and the inset is the $\ln(J/E^2)-1/E$ plot. The sample of δ -Ni₂Si NWs was measured at 10^{-6} Torr with a separation of 250 μm . According to the Folwer-Nordheim relationship, the field emission behavior can be described by the following equation:

$$J = (A\beta^2 E^2 / \psi) \exp(-B\psi^{3/2} / \beta E). \quad (3)$$

The turn-on field was defined as the applied field attained to a current density of 10 $\mu\text{A}/\text{cm}^2$ and was found to be 4.12 V/ μm for our Ni₂Si NWs. The field enhancement factor was calculated to be about 1,132 from the slope of the $\ln(J/E^2)-1/E$ plot with the work function of 4.8 eV [32] for Ni₂Si NWs. Based on the measurements, Ni₂Si NWs exhibited remarkable potential applications as a field emitter like other silicide NWs [20,25,33].

The saturated magnetization (M_S) and coercivity (H_C) of δ -Ni₂Si NWs were measured using SQUID at 2 and 300 K, respectively. Figure 6 shows the hysteresis loop of the as-grown NWs of 30 nm in diameter with the applied magnetic field perpendicular to the substrates. The inset highlighted the hysteresis loop, which demonstrates a classic ferromagnetic characteristic. The H_C was measured to be 490 and 240 Oe at 2 and 300 K, respectively, and M_S was about 0.64 and 0.46 memu, correspondingly. For the magnetization per unit volume (emu/cm^3), normalization has been introduced through cross-sectional and plane-view SEM images (not shown here) to estimate the density of NWs and the average volume of δ -Ni₂Si NWs. The estimated values are 2.28 emu/cm^3 for 2 K and 1.211 emu/cm^3 for 300 K, respectively. With the normalized value, we may build up a database of the magnetic property of Ni₂Si NWs, which may be utilized in applications such as cell separation in biology [34].

Conclusions

δ -Ni₂Si phase NWs have been successfully synthesized through CVD using a single precursor, NiCl₂·6H₂O. The influence of the chamber pressure on the product morphology has been discussed. SEM, TEM, and XRD studies were conducted to analyze the growth mechanism and reaction paths. Electrical measurements show that the field emission property of the δ -Ni₂Si NWs makes them attractive choices for emitting materials. Magnetic measurements via SQUID at different temperatures show the ferromagnetic property of the δ -Ni₂Si NWs, and normalization has been applied to calculate the value of magnetization per unit volume. This work has demonstrated future applications of Ni₂Si NWs on biologic cell separation, field emitters, and magnetic storage.

Abbreviations

CVD: Chemical vapor deposition; FFT: Fast Fourier transform; H_C : Coercivity; HRTEM: High-resolution transmission electronic microscopy; M_S : Saturated magnetization; NWs: Nanowires; Oe: Oersted; SQUID: Superconductive quantum interference device; SSPs: Single-source precursors.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

WLC synthesized the Ni₂Si nanowires. WLC and YTH performed the field emission and magnetization experiments. JYC and CWH analyzed the diffraction data and atomic structure via TEM. CHC analyzed the structure through XRD spectra and demonstrated the illustration of growth mechanism. WLC and WWW conceived the study and designed the research. PHY supported the field emission experiments. WLC, KCL, CLH, and WWW wrote the paper. All authors read and approved the final manuscript.

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