Synthesis and Electrical Properties of Single Crystalline CrSi₂ Nanowires

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Free-standing CrSi₂ nanowires are synthesized by a vapor transport based method for the first time. High-quality CrSi₂ nanowires with a hexagonal cross section are produced by the reaction of a CrCl₂ precursor and a Si substrate without using any metal catalyst. We have studied the crystal structure and electrical transport properties of CrSi₂ nanowires. Transmission electron microscopy and X-ray diffraction studies confirm the single-crystalline nature of the CrSi₂ nanowires of a C40 type structure. Four-probe devices were fabricated by the focused ion beam equipped with a nanomanipulator. Measured resistivity of the nanowire is 0.012 Ω·cm, which is close to that of bulk single-crystalline CrSi₂.

1. Introduction

Transition metal silicides have attracted growing attention for their applications in the semiconductor technology. Metallic silicides such as NiSi, CoSi₂, and TiSi₂ have been used as interconnects in complementary metal-oxide-semiconductor (CMOS) devices owing to their low resistivities.1 Semiconducting silicides such as CrSi₂, β-FeSi₂, and ReSi₂ with a narrow energy gap (0.1−0.9 eV) have been the subject of extensive research because of their potential use in silicon-integrated optoelectronic devices.2 Among them, CrSi₂ has an energy gap of 0.30 eV and could find applications in the Schottky barrier solar cell technology.3,4 Because hexagonal CrSi₂ of a C40 type structure has a high melting point, oxidation resistance, and withstanding to stretching and deformation, it is regarded as one of the promising structural materials for the aerospace and energy generation industries.5 It is also a possible thermoelectric conversion element that can be utilized for generating electric power at high temperature.6 The figure of merit of the thermomodule of CrSi₂ has been measured as 2.8 × 10⁻⁴ deg⁻¹ at room temperature, which is close to the value of those observed for the most superior chalcogen compound thermoelements and representative metallic thermocouple elements such as alumel or chromel.7

One-dimensional nanostructures such as nanowires (NWs) and nanotubes show unique optical, electrical, and mechanical properties compared to their bulk counterparts owing to their reduced diameter and high aspect ratio.8 Syntheses of various free-standing transition metal silicide NWs have been recently reported. Schmitt et al. synthesized CoSi and FeSi NWs from a single source precursor by the MOCVD method and measured their electrical transport properties.9 Ouyang et al. reported the synthesis of FeSi NWs on a Si substrate using a FeCl₃ precursor.10 We have developed a synthetic method for selective growth of CoSi and Co₂Si NWs on a Si and sapphire substrate, respectively.11 Free-standing TaSi₂ NWs showing good field emission properties have been synthesized on the Si substrate covered with FeSi₂ or NiSi₂ thin films by Chueh et al.12 Still, there is no report on the synthesis of free-standing CrSi₂ NWs.

The lattice mismatch between (001) CrSi₂ and (111) Si is small, and the difference in atomic spacing is only about 0.14%.13 Hence, CrSi₂ NWs are expected to grow epitaxially on Si and to show better conductivity and better interface properties with Si. This could make CrSi₂ NWs versatile building blocks for future Si based applications. Here, we report the first synthesis of single-crystalline CrSi₂ NWs and the study of their crystal structure and electrical properties.

2. Experimental Section

We adopted a modified van-Arkel method for the synthesis.14 Single-crystalline CrSi₂ NWs were synthesized using a 1 in. diameter quartz tube in a horizontal hot-wall two zone furnace as shown in Scheme 1. The temperature of both of the zones was independently controlled. Anhydrous CrCl₂ powder (0.05 g, 99.999%, Sigma-Aldrich) was used as a chromium precursor and placed in a small alumina boat. The precursor was vaporized in heating zone A and the NWs grew on the Si substrate covered with a native silicon oxide layer in heating zone B. The carrier argon gas was supplied through a mass-flow controller at the rate of 300 sccm. A Si substrate for NW deposition was placed at approximately 10 cm (d value in Scheme 1) downstream from the location of precursor and also became the source of Si for silicide formation. Temperature of heating zone A and B was maintained at 750 and 900 °C, respectively, for 10 min of reaction time, while the pressure was maintained at 500 Torr during the reaction. No catalyst was used for the NW synthesis.

X-ray diffraction (XRD) patterns of the specimen were recorded on a Rigaku D/max-rc (12 kW) diffractometer operated at 40 kV and 80 mA with filtered 0.15405 nm CuKα radiation. Field emission scanning electron microscope (FESEM) images of CrSi₂ NWs were taken on a Phillips XL30S. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images, and selected area electron diffraction (SAED) patterns
were taken on a JEOL JEM-2100F transmission electron microscope operated at 200 kV. After nanostructures were dispersed in ethanol, a drop of the solution was put on the holey carbon coated copper grid for the preparation of TEM analysis.

The devices for electrical transport properties of individual CrSi$_2$ NWs were fabricated by focused ion beam (FIB) technique. One of the most critical steps in the characterization of individual NWs had been the dispersion and manipulation of the NWs. We used a dual beam columns focused ion beam (FEI NOVA 200) equipped with a nanomanipulator (Zyvex S100) for the manipulation of NWs. The FIB had a site-specific deposition capability that allowed deposition without the limitation of position, geometry, and shape of structure patterning. The nanomanipulator, which was equipped with a FIB, provided precise control and manipulation for individual NWs with 10 nm accuracy. The nanomanipulator had ranges of movement 12 mm in $X$, $Y$, and $Z$ axes, respectively, with a 100 nm resolution for coarse movement and 100 nm in $X$ and $Z$, 10 nm in $Y$ axes with better than 10 nm resolution to probe the electrodes directly.

3. Results and Discussion

The morphology of the CrSi$_2$ NWs was examined by SEM and TEM. Figure 1a shows a SEM image of straight NWs on the Si substrate. High magnification SEM (insets in Figure 1a) images reveal the hexagonal cross section of the sidewall facets along with a pyramidal pointed tip of the NWs. Similar features are also observed in other hexagonal semiconducting NWs such as ZnO and GaN.$^{15,16}$ The NWs are tens of micrometers long and 60 to 120 nm in diameter.

Figure 1b shows a typical XRD pattern of the CrSi$_2$ NWs grown on a Si substrate. All the observed peaks in the spectrum were successfully indexed to the hexagonal crystal structure of CrSi$_2$ (JCPDS card no. 35-0781) with lattice parameters $a = 4.4281$ Å and $c = 6.3691$ Å of a space group $P6_22$. No peak of any other phases is detected. The intense and sharp diffraction peaks suggest that the as-synthesized product is highly crystalline. We note that, while in the bulk the intensity of (003) peak is 34% of the most intense (111) peak, in this XRD pattern the intensity of (003) peak is 46% of the (111) peak. This difference in peak intensities as compared to bulk values could be partly due to the directional growth of the free-standing NWs.

The elemental composition of the NWs was investigated by TEM-EDS using HRTEM. Figure 2 shows a TEM-EDS spectrum of an individual CrSi$_2$ NW. The analysis of a TEM-EDS spectrum confirms that the NWs contain only Cr and Si, approximately in a ratio of 1:2 within instrumental accuracy. The TEM image in Figure 3a shows straight and smooth NWs with no secondary growth or extra structural features. The SAED study shows a regular spot pattern, which reveals the single-crystalline nature of the NWs. The spots can be fully indexed to the hexagonal C40 type CrSi$_2$ and demonstrate that the NW growth is along the [001] direction down the [010] zone axis.
the present study, the formation of CrSi2 NWs could be rationalized from the Cr–Si phase diagram. CrSi2 is a congruently melting solid in the Cr–Si phase diagram, while CrSi is not. In the reactions of thin films composed of Cr and Si, it has been found that CrSi2 phase nucleates first regardless of the initial compositions of the films. This suggests that CrSi2 is the most thermodynamically favorable phase for the nucleation among various phases of chromium silicides. Thus, CrSi2 is the most likely phase to appear when NWs are synthesized by the direct reaction of CrCl2 vapor with a Si substrate.

In related reactions for the formation of cobalt silicide NWs, we have observed that CoSi NWs are formed on a Si substrate and Co2Si NWs are formed on a sapphire substrate placed over a silicon wafer. This shows that the silicide NWs can be formed not only by the direct reaction of a halide precursor with a Si substrate (a reaction on a Si substrate) but also through a gas-phase reaction of the metal halide vapor with the gaseous SiCl4 (a reaction on a sapphire substrate) depending on the reaction conditions. In light of the above discussion, we propose the following two plausible reaction pathways for the formation of CrSi2 NWs:

\[
2\text{CrCl}_2(g) + 5\text{Si}(s) \leftrightarrow 2\text{CrSi}_2(s) + 3\text{Cl}_2(g) \quad (1)
\]

\[
\text{CrCl}_2(g) + 2\text{SiCl}_4(g) \leftrightarrow \text{CrSi}_2(s) + 3\text{Cl}_2(g) \quad (2)
\]

The reaction pathway 1, however, would be the dominating reaction on a Si substrate, as is obvious by the reaction mechanism itself. The synthesis of Cr-rich silicide NWs on a sapphire substrate through the reaction pathway 2 by controlling the composition of the gaseous reactants is underway.

The possible NW growth mechanism is derived from various experiments conducted in different conditions. Because no catalytic metal particles or thin films are employed in the synthesis, VLS growth is unlikely. SEM and TEM studies also do not show the presence of any metal catalyst on the NW tips. The vapor pressure of a precursor turned out to be a very critical factor in the formation of CrSi2 NWs. When either the temperature of the precursor heating zone was increased or pressure of the system was decreased, microparticles were produced instead of NWs as shown in Figure 4a. The optimum conditions for the formation of NWs are determined by the degree of supersaturation of the metal silicide vapor, which is dependent on the balance between the rate of silicide vapor formation reaction and the substrate temperature. Note that the Si substrate plays a dual role, as a source of Si and as a substrate where the silicide vapor condensates and forms NWs. In the present case, the CrSi2 NWs are dominantly formed through reaction 1, of which the reaction rate depends on the precursor vapor pressure and the substrate temperature. These observations are also in accordance with the well-known vapor–solid mechanism for a NW synthesis in which low degree of supersaturation favors nucleation of NWs and bulk particles are formed at a higher degree of supersaturation.

The NW growth was found to be independent of a surface orientation. We observed no change in the density or structure of the synthesized CrSi2 NWs on either the Si (111) or Si (100) substrates. When the Si substrates were treated with 2% HF solution in order to remove the oxide layer before the reaction, no significant change in the density or the growth of the NWs could be observed. No NWs were formed, however, when the reaction occurred on a Si substrate covered with a thick oxide layer.

Figure 4b shows a SEM image of bundles of directionally grown CrSi2 NWs. A tilted SEM image of the sample (inset in Figure 3. (a) Representative TEM image and SAED pattern of CrSi2 NW. The SAED pattern is indexed for a hexagonal CrSi2 NW down the [010] zone axis. (b) Representative HRTEM image. The labeled distances of 0.66 and 0.40 nm correspond to the (001) and (100) planes, respectively, and the arrow shows the [001] growth direction. Inset in Figure 2b shows the two-dimensional fast Fourier transform (FFT) from the HRTEM.

Figure 4. (a) Representative SEM image of CrSi2 bulk structures. Inset shows a magnified image of the microstructures. Scale bar represents 2 μm. (b) Representative SEM image of bundles of directionally grown CrSi2 NWs. Inset shows a tilted SEM image of directionally grown CrSi2 NWs. Scale bar represents 1 μm.
The lower resistivity observed in the present work is in general agreement with these previous reports. The maximum current transport of CrSi$_2$ NW was investigated by a two-probe device. The measured current at a relatively high source-drain voltage of 10.5 V is 334 $\mu$A. This high current suggests the single-crystalline nature of the NWs. Note that we observed sudden decrease in current from 334 $\mu$A to 154 $\mu$A at 10.5 V [point (1) in Figure 5b]. Inset in Figure 5b shows a SEM image of a NW at point (1). The diameter at the center of the NW indicated by a circle is thinner than those of other parts. The current drop at point (1) may be explained by partial melting of the NW at localized hotspots, which makes the NW thinner and increases the resistivity. Complete breakdown of the NW occurred at 13 V [point (2) in Figure 5b]. Note that the resistivity of FeSi NWs is 1/100 of that of CrSi$_2$ NWs, but maximum current density of both NWs are similar. Among the reported free-standing silicide NWs, CrSi$_2$ NW shows the highest thermal stability.

4. Conclusion

We have successfully synthesized free-standing single-crystalline CrSi$_2$ NWs. High quality CrSi$_2$ NWs are produced by the vapor transport based method with no metal catalyst. The NWs have a very clean surface and show straight morphology. The disilicide NWs are formed by a direct reaction of CrCl$_2$ vapor and a Si substrate in a single step synthesis. Directional growth of the NWs is also found in the same reaction condition, and appears to proceed by nucleation of silicide particles or thin films and further self-seeded growth. To investigate electrical transport properties of a single NW, we fabricated two- and four-probe devices using a focused ion beam (FIB) system. The electrical resistivity of the NWs is found to be close to that of single-crystalline bulk. The maximum current transport study of CrSi$_2$ NWs shows partial melting of the CrSi$_2$ NW due to localized hotspots.

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References and Notes