Electrical Properties and Magnetic Response of Cobalt Germanosilicide Nanowires

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Recent studies have shown that semiconductor and magnetic behaviors in FeSi2 NWs as well as a high Curie temperature in Heusler alloy Fe2Si NWs have been reported.11–13 The signature of helimagnetic ordering in MnSi NWs was revealed via the magnetotransport study.14–16 Ternary Fe1−x−y−z Co2Si1−x−y−z Ge1−y−z NWs displayed diverse magnetic behaviors including ferromagnetic semiconductor and helical magnet effects with different Co concentrations.17,18 Bulk CoSi is a diamagnetic material; however, CoSi

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The effects of partial substitution of Ge for Si in cobalt germanosilicide (CoSi1−x−y−z Ge1−x−y−z) nanowires (NWs) on the electrical transport, magnetic properties, and magnetoresistance (MR) have been investigated. Cobalt germanosilicide NWs were synthesized by a spontaneous chemical vapor transport growth method. The Ge concentration can be selectively controlled from 0 to 15% and 0–50% for CoSi1−x−y−z Ge1−x−y−z and Co2Si1−x−y−z Ge1−y−z NWs, respectively, by varying the reaction temperature. Electrical measurements showed that the resistivities of CoSi1−x−y−z Ge1−y−z NWs are 90, 60, 30, and 23 μΩ-cm for x = 0, 0.01, 0.05, and 0.15, respectively. Therefore, the electrical resistivity of CoSi1−x−y−z Ge1−y−z NWs was found to decrease significantly with an increasing Ge concentration, which is believed to be a result of the band gap narrowing. On the other hand, the CoSi1−x−y−z Ge1−y−z NWs exhibited ferromagnetism at 300 K, which is attributed to the uncoordinated Co atoms on the NW surface and spin-glass behavior at low temperature. The highest MR response of CoSi1−x−y−z Ge1−y−z NWs occurred at x = 0.5, where a MR ratio of 11.7% can be obtained at 0–25 K with a magnetic field of 8 T. The enhanced physical properties of cobalt germanosilicide NWs with Ge substitution shall lead to promising application in the fabrication of nanodevices, including spintronics and serving as the gate and interconnect material.

KEYWORDS: cobalt germanosilicide · nanowires · electrical transport · magnetoresistance · spintronics

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NWs were discovered to exhibit a unique ferromagnetism at room temperature due to the presence of Co atoms with low coordination numbers on the surface.\textsuperscript{17} Amorphous Co\textsubscript{2}Ge exhibits a transition from paramagnetic state to spin-glass state at 41 K.\textsuperscript{41} It could be suggested that the homogeneous mixed alloy of ternary cobalt germanosilicide (CoSi\textsubscript{1−x}Ge\textsubscript{x} and Co\textsubscript{2}Si\textsubscript{1−x}Ge\textsubscript{x}) NWs may display peculiar magnetic characteristics and improve the electrical properties.

In our previous work,\textsuperscript{20} the composition of cobalt silicide nanostructures has been found to correlate with the reaction conditions. CoSi NWs can be obtained by a spontaneous chemical vapor transport (CVT) growth method with a growth temperature under 830 °C. Increasing the temperature to 880 °C can result in the formation of Co\textsubscript{2}Si NWs. In this paper, we further developed a synthetic process to achieve the production of the cobalt germanosilicide NWs, including CoSi\textsubscript{1−x}Ge\textsubscript{x} and Co\textsubscript{2}Si\textsubscript{1−x}Ge\textsubscript{x} phases, for the first time. In distinct growth temperature ranges, the Ge content in the cobalt germanosilicide NWs could be selectively controlled by varying the reaction temperature. From the electrical characteristics, the CoSi\textsubscript{1−x}Ge\textsubscript{x} NWs exhibit a low resistivity of 23 μΩ·cm with x = 0.15. Magnetic response of Co\textsubscript{2}Si\textsubscript{1−x}Ge\textsubscript{x} NWs verifies that these NWs possess physically distinctive signatures from both Co\textsubscript{2}Si and CoSi\textsubscript{1−x}Ge\textsubscript{x} (x ≤ 0.5 in our study), which leads to a significant increase in the magnetoresistance (MR) ratio.

**RESULTS AND DISCUSSION**

Cobalt germanosilicide NWs were synthesized in the same furnace at various reaction temperatures by the spontaneous CVT method. The scheme of the detailed setup for the synthesis of cobalt germanosilicide NWs is depicted in the Supporting Information S1. The morphologies and elemental compositions of the NWs synthesized on the sample in region A were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Figure 1. The SEM image reveals a high density of NWs of tens of micrometers in length. The low-magnification TEM image shows a clean and smooth surface of 80–100 nm in diameter. No catalyst and no secondary growth were observed. A selected area electron diffraction (SAED) pattern of a typical NW is shown in Figure 1c. The diffraction spots in the SAED pattern can be ascribed to the cubic B20-type CoSi and demonstrate that the NW growth is along the [\textbf{T10}] direction. The corresponding high-resolution TEM (HRTEM) image is shown in Figure 1d and reveals that the NW is single-crystalline and defect-free. The energy-dispersive X-ray spectrometry (EDS) study by TEM indicates that the Ge content of the individual CoSi\textsubscript{1−x}Ge\textsubscript{x} NWs (x = [Ge]/[Si] + [Ge]) is an average with a value of x = 0.15 ± 0.01, as shown in Supporting Information S2(a).

The average value was obtained from the EDS measurements of about 10 NWs. The Ge element was homogeneously distributed in the whole NWs from the analysis of EDS spectra obtained at different locations of the NWs. The Ge content in the CoSi\textsubscript{1−x}Ge\textsubscript{x} NWs could be controlled selectively by adjusting the reaction temperature of NW growth for x = 0, 0.01 ± 0.005, 0.05 ± 0.01, and 0.15 ± 0.01. The exact reaction temperatures measured with a thermocouple are 750, 770, 790, and 850 °C for x = 0, 0.01 ± 0.005, 0.05 ± 0.01, and 0.15 ± 0.01, respectively. All of them exhibit a similar morphology to that of CoSi\textsubscript{1−0.3}Ge\textsubscript{0.3} NWs.

![Figure 1](image)

The Ge concentration of CoSi\textsubscript{1−x}Ge\textsubscript{x} NWs was found to increase with the reaction temperature. This is the first report on the synthesis of cobalt germanosilicide NWs, even though the growth of many metal silicide NWs using metal halide precursors has been reported.\textsuperscript{10–14,17,20,21} Vapor–solid mechanisms and self-catalyst growth are usually proposed in the growth process utilizing this method.\textsuperscript{22} In a previous study on a ternary compound of CoSi\textsubscript{1−x}Ge\textsubscript{x}, the heat of formation was approximated from the relative crystal energies between CoSi and CoGe structures by a first-order approximation. It is suggested that the crystal energy of CoSi\textsubscript{1−x}Ge\textsubscript{x} alloys would increase if Si atoms are partially replaced by Ge atoms.\textsuperscript{23} The elevated reaction temperature could provide higher nucleation energy for CoSi\textsubscript{1−x}Ge\textsubscript{x} NWs, which is needed for maintaining a stable compound with higher Ge content.

The substrate in the region B was positioned at a comparatively high temperature zone (880 °C). The
diameters and lengths of the NWs produced in this region are 80–100 nm and tens of micrometers, respectively, as illustrated in Figure 2a. The TEM image, SAED pattern, and HRTEM image of a NW are shown in Figure 2b, c, and d, respectively. The SAED pattern can be identified as an orthorhombic Co2Si structure, and the regular spot pattern of the electron diffraction confirmed the single-crystalline nature of NWs. The result is consistent with the HRTEM image shown in Figure 2d. The TEM-EDS study in Supporting Information S2(b) indicates that the Ge content of the individual Co2Si1−xGex NWs has an average value of x = 0.5 ± 0.03. The average value was obtained from the EDS spectra of about 10 NWs. The Ge element was homogeneously distributed over the whole NWs from the analysis of the EDS spectra obtained from different places of the NWs. The Co2Si1−xGex NWs could be synthesized with a controlled Ge concentration by varying reaction temperature. The Ge concentrations (x) and temperature are 0, 0.1 ± 0.01, 0.5 ± 0.03 and 880, 900, and 950 °C, respectively. All have a similar morphology to the Co2Si0.5Ge0.5 NWs.

The X-ray powder diffraction (XRD) measurements on the Co2Si1−xGex NWs samples were also performed for phase identification. The XRD patterns of Co2Si1−xGex NWs are displayed in Figure 3a, which indicate that all peaks can be ascribed to the Co2Si phase (JCPDS file: 89-4181). The peaks due to any other traceable impurity phase were not observed. With the increase of Ge concentration, it was found that the peaks shift to lower angles and the widths of peaks become broader. To scrutinize the peak shift, the Δ(2θ) in the (002) plane is 0.22° and 0.63° for x = 0.1 and 0.5, respectively. The variation of the lattice parameter as a function of Ge concentration is shown in Figure 3b. It is clearly seen that the lattice constant increases with Ge content, indicating that the Si sites are partially substituted by Ge atoms, according to Vegard’s law. The XRD data of CoSi1−xGex NWs are not shown. Because of the large peak widths, the concentration of Ge in the NWs could not be readily determined by the shift of the peak position.

Electrical transport properties of cobalt germanosilicide NWs with various Ge content have been measured by the four-terminal I−V method. The SEM image of a typical NW device is shown in the inset of Figure 4. The resistivity values were obtained from 4 to 5 NWs for each Ge concentration. The average resistivities and Ge contents of the CoSi1−xGex NWs are 90, 60, 30, and 23 μΩ·cm for x = 0, 0.01, 0.05, and 0.15, respectively, as illustrated in Figure 4. The detailed I−V curves of individual CoSi1−xGex NWs are shown in Supporting Information S3(a). The values match well with the reported value of CoSi NWs (126 μΩ·cm)17 and approach that reported for bulk single-crystalline CoSi2 (18 μΩ·cm),44 which is the lowest resistivity for cobalt silicides. A decrease in resistivity was observed with the increase in Ge content of CoSi1−xGex NWs. A previous

Figure 2. Structural characterization of Co2Si1−xGex NWs grown in region B. (a) Typical SEM image of Co2Si1−xGex NWs. (b) TEM image of a Co2Si1−xGex NW. (c) SAED pattern of a Co2Si1−xGex NW with the zone axis of [T11]. (d) HRTEM image of a Co2Si1−xGex NW. The marked spacings of 0.414 and 0.339 nm correspond to the [011] and [101] planes, respectively.

Figure 3. (a) XRD patterns of the Co2Si1−xGex NWs with x = 0, 0.1, and 0.5. (b) Lattice parameter versus Ge concentration as obtained from XRD.
study on the bulk CoSi$_{1-x}$Ge$_x$ has revealed the semimetallic characteristics of this compound, and the semimetallic nature is associated with the low density of states (DOS) at the Fermi level.$^9$ The Ge substitution for Si could narrow the band gap due to an increase of the DOS at the Fermi level. The reduction in the electrical resistivity with the increase in Ge content would correspond to the decrease of the band gap. The electrical transport measurements of Co$_2$Si$_{1-x}$Ge$_x$ NWs have been characterized, and the detailed data are shown in Supporting Information S3(b). The resistivities and Ge contents of the Co$_2$Si$_{1-x}$Ge$_x$ NWs are 180, 187, and 102 $\mu\Omega$-cm for $x = 0, 0.1,$ and $0.5,$ respectively, which match well with the value reported for single-crystalline Co$_2$Si NWs (200 $\mu\Omega$-cm)$^{21}$.

In situ annealing TEM was used to investigate the thermal stability property of CoSi$_{1-x}$Ge$_x$ NWs in real time. The samples were produced by scraping the as-grown NW samples on a TEM Mo grid (with carbon film windows). As seen in Supporting Information S4, the TEM images reveal that the morphology of the CoSi$_{0.85}$Ge$_{0.15}$ NW remained intact as the temperature was ramped to $950^\circ$C ($1000^\circ$C min$^{-1}$) and then held for 30 min. The structural information and composition of the annealed CoSi$_{0.85}$Ge$_{0.15}$ NWs were obtained from TEM analyses (Supporting Information S4). A SAED pattern obtained from an annealed NW shows regular spots, indicating the single-crystalline nature and can be indexed to the cubic CoSi structure. From the EDS spectrum (not shown), the ratio of Co:Si:Ge is approximately 1:0.85:0.15. The TEM analyses of SAED pattern and EDS spectra of several annealed NWs show the same structure and chemical composition as the

Figure 4. Resistivity versus Ge content curves of CoSi$_{1-x}$Ge$_x$ NWs. The resistivity of a NW decreases with increasing Ge concentration. The inset is a typical SEM image of the electrical device fabricated with the standard EBL processes.

Figure 5. (a–c) Plot of the magnetization, $M$, as a function of the magnetic field, $H$, obtained from the Co$_2$Si$_{1-x}$Ge$_x$ NWs with $x = 0, 0.1,$ and $0.5,$ respectively, at 10 and 300 K. (d) Plot of the $M$–$H$ curves obtained from the bulk Co$_2$Si$_{1-x}$Ge$_x$ alloys with various Ge concentrations ($x = 0, 0.1, 0.3,$ and $0.5$) at 10 K. (e and f) Plot of $M$ as a function of $T$ at an applied field of 100 Oe obtained from Co$_2$Si$_{1-x}$Ge$_x$ NWs with $x = 0$ and $0.5,$ respectively. Black and red lines represent the field-cooling (FC) and zero-field-cooling (ZFC) data, respectively.
unannealed NWs, indicating that the CoSi$_1$–Ge$_x$ NWs have a high thermal stability.

The magnetic properties of Co$_2$Si$_1$–Ge$_x$ NWs were measured with the superconducting quantum interference device (SQUID) magnetometer. Figure 5a–c show plots of the magnetization versus the applied magnetic field ($M$ versus $H$) at temperatures of 10 and 300 K for the NWs with $x = 0, 0.1,$ and 0.5. A ferromagnetism signature at room temperature was observed from the hysteresis loops with nonzero remnant magnetization and coercivity for the Co$_2$Si$_1$–Ge$_x$ NWs. The ferromagnetic behaviors in the NWs are attributed to the reduced coordination of the Co atoms on the Co$_2$Si$_1$–Ge$_x$ NWs surface, considering that the NW surface to volume ratio is high. The magnetic moment per surface Co atom of Co$_2$Si$_1$–Ge$_x$ NWs from the $M$/$H$ data was estimated, as shown in Supporting Information S5. The calculated average magnetic moments per surface Co atom of Co$_2$Si$_1$–Ge$_x$ NWs are 1.53, 1.20, and 1.85 for $x = 0, 0.1,$ and 0.5, respectively. These values are in general agreement with the reported magnetic moment of the Co atom of 1.72 $\mu_B$. For the $M$–$H$ curves of Co$_2$Si$_1$–Ge$_x$ NWs, the divergences of saturated magnetization at 10 and 300 K became larger with increasing Ge content. For comparison, alloys with the same composition of Co$_2$Si$_1$–Ge$_x$ NWs were prepared using an arc melting furnace in a water-cooled copper crucible under Ar atmosphere. The $M$–$H$ curves of bulk Co$_2$Si$_1$–Ge$_x$ samples were obtained, and a similar magnetic signature was also observed, as illustrated in Figure 5d. The saturation of the magnetization close to $H = 0$ becomes more abrupt with increasing Ge concentration. The features in the magnetic response resemble closely the spin-glass-like behavior, due to a spin disorder system (frustrated interaction) augmented by the stochastic disorder. In a previous study, the spin-glass behavior of bulk amorphous Co$_2$Ge was reported. This material exhibits a single transition from paramagnetic to the spin-glass state at 41 K ($T_f$, freezing temperature). The temperature dependences of magnetization for Co$_2$Si$_1$–Ge$_x$ NWs and Co$_2$Si$_1$–Ge$_x$ NWs have been measured during zero-field-cooling (ZFC) and field-cooling (FC) under an applied field of 100 Oe, as shown in Figure 5e and f, respectively. The ZFC and FC curves of Co$_2$Si$_1$–Ge$_x$ NWs show a steep decrease at temperatures below 50 K. However, these features are not observed in the FC or ZFC curves of Co$_2$Si$_1$–Ge$_x$ NWs.

AC magnetization measurements of bulk Co$_2$Si$_1$–Ge$_x$ were performed at a frequency of 109 Hz under different magnetic fields of 5, 30, and 90 Oe. Figure 6a shows that the freezing temperature ($T_f$) of bulk Co$_2$Si$_1$–Ge$_x$ is shifted to lower temperature and the intensity of susceptibility ($\chi'$) is decreased with increasing magnetic field (5, 30, and 90 Oe) at 109 Hz. The results are similar to spin-glass behavior of amorphous Co$_2$Ge that was reported by Zhou et al. However, the freezing temperature of amorphous Co$_2$Ge ($T_f$ is 41 K) is higher than our single-crystalline Co$_2$Si$_1$–Ge$_x$ system ($T_f \sim 25$ K). The interaction of the crystalline Co$_2$Si$_1$–Ge$_x$ ternary system needs more detailed magnetic property study. MR measurements for individual
Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs were carried out with an applied magnetic field. To prepare a MR device, the NWs were dispersed on a SiO<sub>2</sub>/Si substrate and the 30/120 nm Cr/Au contacts to an individual NW were defined with electron beam lithography (EBL). Figure 6b is the temperature-dependent MR of Co<sub>2</sub>Si<sub>1</sub>-Ge<sub>x</sub> NWs (x = 0.1 and 0.5), which also shows a maximum value at 10–25 K. The results were consistent with the ac magnetization measurements of bulk Co<sub>2</sub>Si<sub>0.5</sub>Ge<sub>0.5</sub> in Figure 6a. The MR versus applied magnetic field (up to 8 T) curves at temperatures of 100, 50, 25, 10, 5, and 2 K for Co<sub>2</sub>Si<sub>0.5</sub>Ge<sub>0.5</sub> NWs are plotted in Figure 6c. The MR curves at 5 and 2 K show a quick saturation as the applied field exceeds 2 T and a negative MR was observed at all temperatures. These MR features are similar to the reports of Co<sub>2</sub>Si nanobelts.19 Figure 6d shows the MR data of Co<sub>2</sub>Si<sub>1</sub>-Ge<sub>x</sub> NWs with x = 0, 0.1, and 0.5 at 25 K. Maximum MR ratios of 1.21%, 2.07%, and 11.7% were observed with increasing Ge content (x = 0, 0.1, and 0.5, respectively) under the magnetic field of 8 T. Generally, MR effects in silicide nanostructures can be attributed to the interaction of conducting electrons with spins of localized dangling bonds. The Si was substituted by Ge in Co<sub>2</sub>Si<sub>1</sub>-Ge<sub>x</sub> NWs, as mentioned above, and could augment the stochastic disorder spin due to the spin-glass behavior from the Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> (x ≤ 0.5) compound. This may explain the relatively large MR values of Co<sub>2</sub>Si<sub>1</sub>-Ge<sub>x</sub> NWs compared to those reported in a previous study for Co<sub>2</sub>Si NWs.20 The physical properties observed for Co<sub>2</sub>Si<sub>1</sub>-Ge<sub>x</sub> NWs verify that these NWs possess physically distinctive features from Co<sub>2</sub>Si and Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> (x ≤ 0.5). The measurements of magnetic properties for Co<sub>2</sub>Si<sub>1</sub>-Ge<sub>x</sub> NWs have been carried out. As seen in Supporting Information S6, the room-temperature ferromagnetic properties were also observed in Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs, but the spin-glass behavior was not present in Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs with the Ge substitution. Therefore, almost no MR effect (the MR data are not shown) in Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs was observed. The room-temperature ferromagnetic behavior and the large MR response of Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs suggest that Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs have great potentials in versatile applications for Si/Ge-based spintronics.

**SUMMARY AND CONCLUSIONS**

In summary, cobalt germanosilicide (Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> and Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub>) NWs have been synthesized via a spontaneous CVT growth method in one step. The Ge concentration can be selectively controlled from 0 to 15% and 0–50% for Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> and Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs, respectively, by varying the reaction temperature. The elemental components are uniformly distributed along the free-standing NWs. The resistivity of Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs was found to decrease with increasing Ge content, and the structure remained intact at high temperature (950 °C). The reduction in electrical resistivity with the increase in Ge content would correspond to the decrease in the magnitude of the band gap resulting from the Ge substitution with Si. The room-temperature ferromagnetism and the reentrant spin-glass-like behavior of Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs were discovered. The large MR performance of 11.7% at 10–25 K indicates that Co<sub>2</sub>Si<sub>x</sub>-Ge<sub>x</sub> NWs have great potential in spintronics applications. The superior electrical characteristics and MR properties indicate that the cobalt germanosilicide NWs could play an important role in versatile applications for Si/Ge-based nanodevices.

**REFERENCES AND NOTES**


**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.


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