Korean J. Chem. Eng., **21**(6), 1240-1244 (2004)

Electrical Characterization of C-coated Nickel Silicide Nanowires Grown on Ni-loaded Si Substrate

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(*Received 3 March 2004 • accepted 30 August 2004*)

Abstract−Carbon-coated nickel silicide nanowires (C-coated NiSi NWs) were grown in a home-made chemical vapor deposition (CVD) reactor. The coating of semiconductor or metal nanowires with nano-sized carbon layer is effective to prevent the oxidation of the nanowires, resulting in the stabilization of electrical properties of nanodevices. The growth of the NiSi nanowires and the coating of the NWs with carbon layers simultaneously took place in the reaction. The current-voltage curve of individual NiSi nanowire showed highly linear behavior, indicating the good ohmic contact without the insulating layer. The resistivity of the NiSi nanowire was about 370 μΩ-cm at room temperature, decreased monotonically as the temperature was lowered, and became saturated at low temperatures, indicating the growth of metallic NiSi nanowires. Field emission measurements showed that the C-coated NiSi nanowires were an excellent field emitter with large emission current densities at very low electric field.

Key words: C-coated NiSi Nanowires, Catalytic CVD Growth, Electrical Properties of Nanowires

INTRODUCTION

Recently, one-dimensional nanostructured materials such as nanotubes or nanowires have been successfully synthesized and have received much attention due to their remarkable physical and electrical properties for potential applications in nanodevices [Derycke et al., 2002; Duan et al., 2002]. Carbon nanotubes (CNTs) have already been employed as the active channel of field-effect and single electron transistors [Martel et al., 1998; Bockrath et al., 1997]. Various semiconductor nanowires (NWs) have been also subjected to the fabrication of optical and electrical devices [Gudiksen et al., 2002; Lee et al., 2000]. Crystalline semiconductor NWs hold considerable technical benefits for device application because the NWs have a flexible ability in the doping process and hetero-junction growth. Recently, the modification of the NWs with other nanomaterials, like a filling of CNTs with metal [Pradhan et al., 1999] or a coating of semiconductor nanowires with graphitic layers [Zhang et al., 2000], has been considered to significantly improve chemical and physical properties of the NWs, resulting in an even more diverse range of applications. For example, the application of semiconductor NWs for an emission tip of field emission flat panel displays (FED) requires uniform and stable emission. But pure semiconductor NWs have not satisfied these demands. The encapsulation of the NWs with various materials has been explored to improve their emission properties [Chen et al., 2001; Yi et al., 2002].

In this work, we report a unique carbon layer coated nickel silicide nanowire (C-coated NiSi NW) formation over Ni catalyst loaded Si substrate in an RF-induction heating chemical vapor deposition reactor. For the electrical characterizations of the NiSi nanowires, the individual NiSi nanowire was assembled on a patterned substrate and the resistivity of individual NiSi nanowire was examined as a function of temperature. Field emission characteristics were also measured for the C-coated NiSi nanowires.

EXPERIMENT

C-coated nanowires were prepared in a radio-frequency induction heating chemical vapor deposition (RF-CVD) reactor, which was described in detail elsewhere [Nahm et al., 2001]. p-type Si(100) wafer with the resistivity of 20 Ω-cm (10×10 mm^2) was employed as a substrate for the growth of the nanowires. The Si substrate was sonicated for 3 min in acetone, dipped for 3 min in HF aqueous solution, rinsed in DI water, and flushed in an oxygen-free nitrogen flow. 0.01 M $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in ethyl alcohol solvent to make a mixed solution. The ultrasonically cleaned silicon wafer was dipped for three minutes into the mixed solution to load Ni catalyst on Si surface. The substrate was then oven dried at 80 °C for 5 h. The Ni catalyst-loaded Si substrate was mounted on the graphite susceptor and set up in the reactor. The reactor was evacuated to 10^{-4} Torr for 30 min and was then purged with hydrogen gas, more than five times, to eliminate residual gases in the reactor. The catalyst coated substrate was heated at 700 °C for 5 min under 1,000 sccm H_2 flow to activate Ni catalyst. The hydrogen flow was kept throughout the growth reaction. Si source (SiH_4) was introduced into the reactor with a flow rate of 3.0 sccm, followed by the heating of the substrate to the growth temperature (800 °C). The growth of Si nanowires was carried out as a function of the growth time (10-30 min). When the growth was over, SiH_4 flow was first stopped and then the substrate was cooled down to the room temperature under N_2 gas flow. The flow of N_2 gas was kept on for 2 h to wash out residual gases from the reactor.

A field emission scanning electron microscopy (FE-SEM, HITACH S-4700) was used to observe the morphology of the grown

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nanowires. The crystal quality and microcrystal structure of the nanowires were evaluated by using field emission transmission electron microscopy (FETEM, TECNAI F30-UT FE-TEM accelerated by 300 KV). Chemical analysis of the nanowires was carried out by using energy-dispersive X-ray spectroscopy (EDS) installed on the TEM. Raman spectroscopy and X-ray diffraction (XRD, RIGAKU D/MAX-1200) were also employed to evaluate the crystal structure of the nanowires. Field emission measurement was performed in a base pressure of middle 10^{-7} torr. The distance between the anode and the nanowire cathode was maintained to be 145 μm. Field emission characteristics of the nanowires were evaluated by measuring emission current density as a function of applied field.

RESULTS AND DISCUSSION

Figs. 1(a), (b), and (c) show FE-SEM images for nanostructures grown on Ni catalyst loaded Si surface for 10, 20, and 30 min, respectively. The growth was carried out at 800 °C with 3 sccm SiH_4 under 1,000 sccm H_2 flow. The images show that the grown nanostructures are in the form of nanowires. At a 10 min growth time, the nanowires grow uniformly across the Si surface with high density. The nanowires grow straight with the length of more than 10 μm. The average diameter of the nanowires ranges in 20-40 nm. However, a metal tip, which usually appeared on the top of nanowires or nanotubes [Chen et al., 2002; Kim et al., 2003], is not present on the top of the nanowires as shown in the bottom right inset of Fig. 1(a). It seems that, with increasing the growth time, the density of the nanowires decreases, whereas the average diameters of the nanowires increase. The increased time induces the aggregation of catalyst particles on the substrate surface, resulting in the decrease of the density with the increase of the diameter. The nanowires grown for 10 min were employed to investigate the structure and electrical properties.

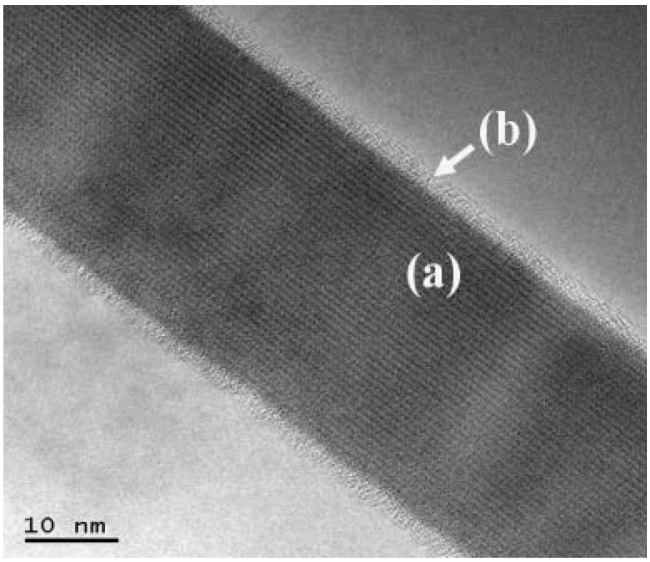

Fig. 2. HR-TEM image of a nanowire grown for 10 min.

For the investigation of structure and chemical composition of the nanowires, HRTEM and EDX measurements were carried out for the nanowires grown at the same condition of Fig. 1. Fig. 2 shows HRTEM image for a nanowire. It exhibits the diameter of the nano-

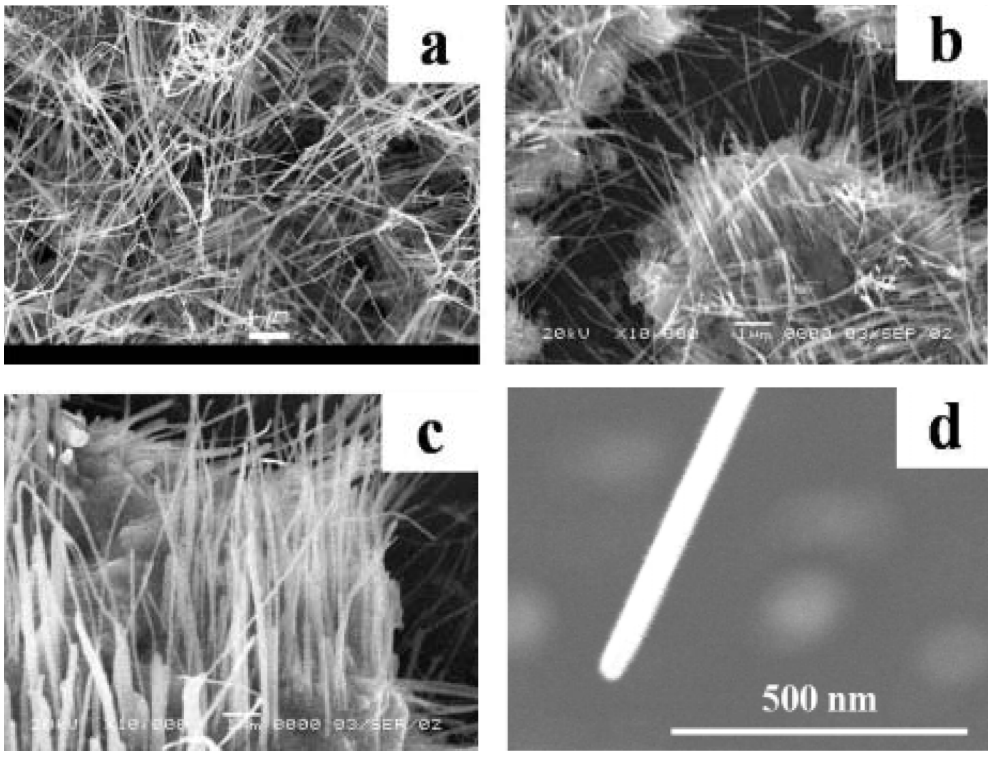

Fig. 1. FE-SEM images of NiSi nanowires grown on Ni catalyst loaded Si surface as a function of growth time: (a) 10 min, (b) 20 min, (c) 30 min, and (d) .a tip of a nanowire grown for 10 min.

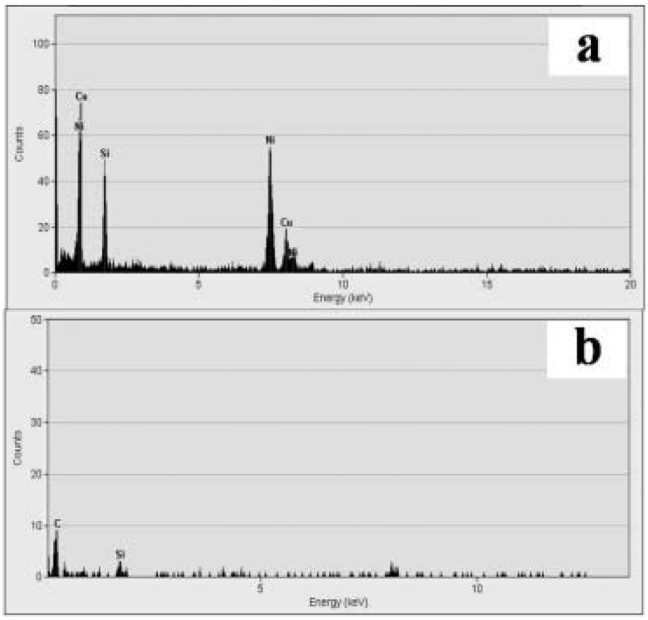

Fig. 3. EDS spectra for (a) the inner nanowire and (b) the outer cell of the nanowire.

wires ranges from 30 to 40 nm, in good agreement with the FE-SEM data. It is worthwhile to see nanowires are coated with a layer with thickness of 1.5-1.7 nm. The chemical composition of the center and wall of the nanowires were analyzed by using EDX spectroscopy. Figs. 3(a) and (b) reveal that the inner nanowire is composed of Si and Ni, while the outer thin layer is amorphous carbon. It seems that Cu results from TEM sample preparation. This means our samples are NiSi nanowires coated with thin carbon layers. Since no carbon source was supplied to the growth system, it is suggested that carbon atoms came from graphite susceptor and contributed to the coating of the NiSi nanowires. The growth of NiSi nanowires is also evidenced by measuring lattice spacing of the nanowire from the HRTEM image. The lattice spacing of our samples is 0.82 nm, which is much larger than that of Si nanowires (0.3 nm) [Carim et al., 2001]. This value fits well with the lattice spacing of c-axis for NiSi whose lattice constants, a and c, are 7.654 and 8.451 Å, respectively [Osawa et al., 1939]. Although the growth mechanism of the NiSi nanowires is currently ambiguous in this work, it is likely that Ni metal catalyst is a source of Ni in producing the NiSi nanowires.

For the electrical characterizations of the NiSi nanowires, we have measured the current-voltage curve and the resistivity of individual NiSi nanowire as a function of temperature. The individual NiSi nanowire was assembled on a metal electrode patterned Si substrate. The patterns for electrical leads were generated by using electron beam lithography onto the selected individual NiSi nanowire and then 20 nm of Ti and 50 nm of Au were deposited on the contact area by thermal evaporation. We have done the chemical etching to remove the insulation layer between nanowire and metal electrodes before the electrode deposition. Fig. 4 shows an FE-SEM

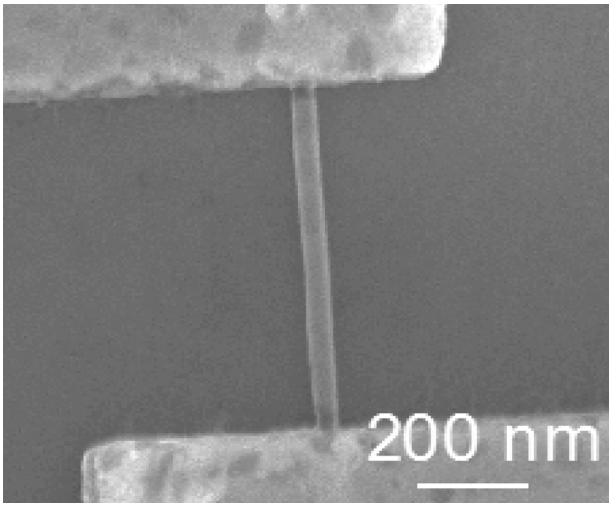

Fig. 4. FE-SEM image for an NiSi nanowire assembled on a metal electrode patterned Si substrate.

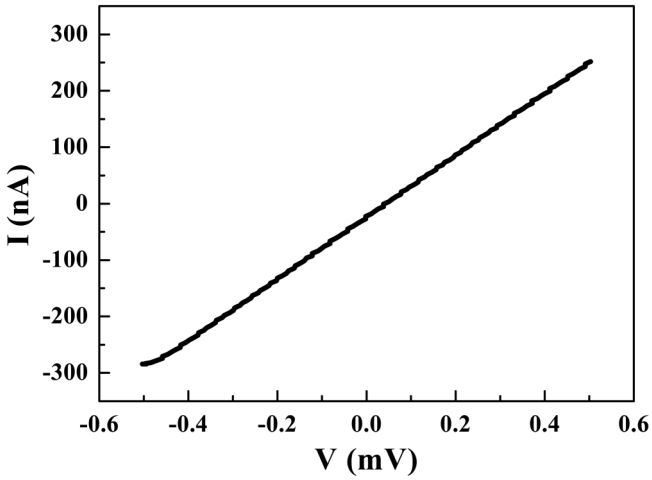

Fig. 5. A plot of current vs. applied voltage for the nanowire. The voltage probe distance and diameter of nanowire were about 885 nm and 40 nm, respectively.

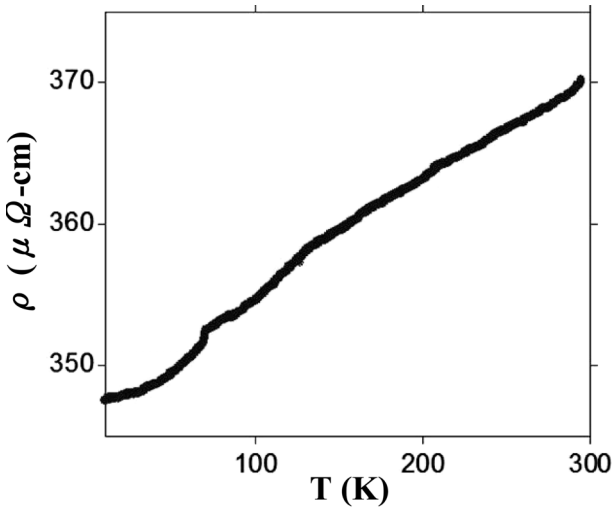

Fig. 6. Temperature dependence of resistivity of individual nanowire. The voltage probe distance and diameter of nanowire were about 885 nm and 40 nm, respectively.

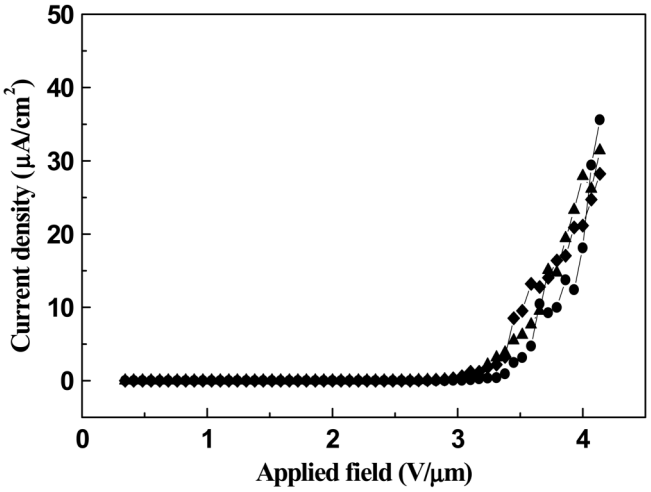

Fig. 7. Field emission I-V characteristics of C-coated SiNWs.

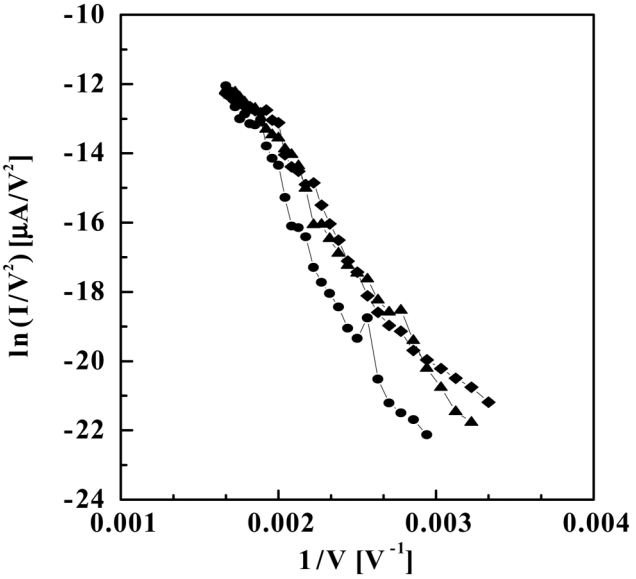

Fig. 8. Fowler-Nordheim plots for C-coated SiNWs.

image for a NiSi nanowire aligned on the patterned substrate. The voltage probe distance and diameter of nanowire were about 885 nm and 40 nm, respectively. The current flow through the NiSi nanowire was measured as a function of applied voltage. Shown in Fig. 5 is the current-voltage curve for the nanowire. The current-voltage curve shows highly linear behavior. This means that the good ohmic contact between the nanowire and metal electrode is achieved without any insulating layer.

Fig. 6 shows the temperature dependence of the resistivity of the individual NiSi nanowire. The resistivity of our grown NiSi nanowire is about 370 μΩ-cm at room temperature, which is 5-10 times larger than that of high quality $NiSi_2$ thin films [Hensel et al., 1984; Zhang et al., 2002]. The resistivity of the NiSi nanowire decreases monotonically as the temperature is lowered and becomes saturated at low temperatures. This kind of temperature dependence is the typical behavior expected for the resistivity of a normal metal. Silicide materials are also known as good metal, which is consistent with our experimental result.

Field emission characteristics were also measured for the C-coated NiSi nanowires. Fig. 7 shows the field emission current density measured from the NiSi nanowires cathode as a function of the applied electric field. Relatively smooth and consistent I-V curves are obtained. The turn-on field of the C-coated NiSi nanowires, which is defined as the field required to reach the current of 0.01 mA/cm^2, is estimated to be ~3.6 V/μm. This is higher than typical carbon nanotubes turn-on field (e.g. 1-2 V/μm for SWNT). But the value is comparable to turn-on fields observed for other types of field emitters such as silicon tip [Shang et al., 2002], nanowires [Wong et al., 1999; Chen et al., 2001] and nanotube [Rinzler et al., 1995].

The corresponding straight lines of Fowler-Nordheim (F-N) plot shown in Fig. 8 indicates that the electron emission is proceeded by field emission. The field enhancement factor, β, was calculated from the slope of the F-N plot and the work function of Si (about 4.6 eV).[7] The calculated field enhancing factor β is ~1,500. This relatively low turn-on field for the NiSi nanowires in comparison with the conventional Si tip may be caused by amorphous carbon layer on the NiSi nanowires. It has been suggested in many reports that thin dielectric layer coating improves field emission characteristics of emitter [Yi et al., 2002].

The growth mechanism of the NiSi nanowires is not well understood at present. In this growth system, SiH_4 gas diluted with H_2 is only supplied to the reactor. It is very likely that carbon and nickel atoms are originating from graphite susceptor and Ni catalyst, respectively. At present it is not clear how the growth of the NiSi nanowires progresses in the reaction. For the moment, we guess that Ni metal either acts as a catalyst or participates into the NiSi growth reaction as an element of the product. At the initial stage of the nanowire growth, the Ni catalysts provide nucleation sites for the nanowire growth, but they participate in the growth reaction to form NiSi nanowires. The fact that Ni metal tip was not observed from the nanowires after growth as shown in Fig. 2 partially supports the participation of Ni in the production of NiSi nanowire. However, the carbon atoms out-diffused from graphite susceptor seem not to take part in the growth at the initial stage of the nanowire growth, but they participate in the growth reaction at the later stage. We believe that further detailed experimental study is necessary in the future to clearly understand the growth mechanism of the C-coated NiSi nanowires.

CONCLUSION

C-coated NiSi nanowires were prepared in an RF-CVD reactor. The NiSi nanowires were coated with a layer with thickness of 1.5-1.7 nm. The average length of the C-coated NiSi nanowires was about 10 μm and the average diameter of the nanowires ranged in 20-40 nm. The resistivity of individual NiSi nanowire monotonically decreased with the decrease of the temperature from 370 μΩ-cm at room temperature and became saturated at low temperatures. This indicates the growth of metallic NiSi nanowires. Field emission measurements also showed that the C-coated NiSi nanowires would be employed as an excellent field emitter with very low electric field (~3.6 V/μm) and large emission properties (β=~1,500).

ACKNOWLEDGMENT

This work was supported partly by KOSEF through the Research Center for Energy Conversion and Storage and partly by Wonkwang University 2002.

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