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Vertically well-aligned epitaxial Ni$_3$Si$_{12}$ nanowire arrays with excellent field emission properties

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Vertically well-aligned single crystal Ni$_3$Si$_{12}$ nanowire (NW) arrays were epitaxially grown on Ni$_3$Si$_{12}$ films preferentially formed on Ni foil substrates with a simple vapor phase deposition method in one step. The Ni$_3$Si$_{12}$ NWs are several micrometers in length and 50–80 nm in diameter. The resistivities of the Ni$_3$Si$_{12}$ NWs were measured to be 51 µΩ cm by four-terminal electrical measurement. The NWs can carry very high currents and possess excellent field emission properties. The growth of vertically well-aligned Ni$_3$Si$_{12}$ NW arrays shall lead to significant advantages in the fabrication of vertical Si nanodevices. © 2008 American Institute of Physics.

As the microelectronic devices entering into nanoera, the requirements of the metallization in complementary metal oxide semiconductor (MOS) device integration are important to develop new approach for future applications.¹–⁵ Among metal silicides, the low resistivity NiSi is currently the most promising material because of its electrical properties and appropriate work function. On the other hand, Ni-rich silicides, such as Ni$_2$Si and Ni$_3$Si$_{12}$, have gained much attention for use in fully silicided gates because of their higher work functions (~4.8 eV) which can effectively improve the p-type MOS device performance.⁶

Nanotechnology has been considered to be one of the most important enabling technologies for the future generation devices. Several growth methods have been adopted to form vertical nickel silicide nanowires (NWs). Freestanding NiSi NWs were first synthesized from chemical vapor deposition process by Decker et al.⁷ Wu et al.⁸ coated evaporated nickel film onto freestanding silicon NWs to form NiSi with an annealing process. In addition, Ni$_2$Si,⁹ Ni$_3$Si$_{12}$,¹² Ni$_3$Si$_{11}$,¹³ and Ni$_3$Si$_{14}$⁴ NWs were synthesized by pyrolysis of silane gas,⁷,¹⁰,¹¹,¹³ sputtering silicon onto Ni surfaces⁹ by metal-induced growth (MIG) or using iodine as transport agent in chemical vapor transport methods.¹²,¹⁴ Recently, a new method by nanococontact reaction between Ni and Si NWs to form NiSi NWs¹⁵ has been reported. In addition, Ni silicide NWs were obtained by means of solid-state reactions of the Si NWs with subsequently deposited Ni films.¹⁶

The vertical metal silicide NWs are grown almost exclusively in a random fashion. Oriented growth of NiSi NWs was achieved only with the MIG method on Ni film coated on SiO$_2$ layer. The growth of 1–2 µm NWs was induced during the sputtering of Si. However, the growth mechanism was not elucidated.⁹ In the present work, vertically well-aligned Ni$_3$Si$_{12}$ NW arrays of more than 7 µm in length were grown. It is worthwhile to mention that self-assembled epitaxial metal silicide NWs on the silicon surface have been extensively investigated.¹

Pure Ni foils (99.9% purity), cleaned in acetone, de-ionized water, hexane, and dilute HNO$_3$, consecutively, were used as the substrates. After the cleaning process, the Ni foils were placed in an alumina boat and inserted into a quartz tube furnace pumped down to about 1.0×10⁻⁵ torr in pressure. The flows of 100 SCCM (SCCM denotes cubic centimeter per minute at STP) Ar and 25 SCCM H$_2$ were kept constant and introduced as the carrier gas with the pressure in the quartz tube fixed at 1 torr. The upstream and downstream ends of the furnace were heated from room temperature to reach 1100 and 750 °C, respectively. Silicon powders (99.9%) in an alumina boat were positioned at the 1100 °C zone upstream in the quartz tube as the source. Ni foils were located downstream at the end of 750 °C zone. The reaction time was set to be 3 h unless otherwise mentioned. The furnace was then allowed to cool down to room temperature.

A field emission scanning electron microscope (FESEM) (JEOL 6500F with an accelerating voltage of 15 kV) was used to examine the morphology of Ni$_3$Si$_{12}$ NWs. Transmission electron microscopy (TEM) analysis was carried out to verify the crystal structures of NWs in a JEOL JEM 2010 TEM operating at 200 kV. Energy dispersive spectroscopy (EDS) was conducted in the TEM to determine the composition of a single NW. Agilent B1500A semiconductor device analyzer (SDA) with probe station (LakeShore TTP4) and Keithley 4200 SDA with a four-probe inside a FESEM (JEOL 7000F)¹⁷ were used for the electrical measurements.

X-ray diffraction spectra (not shown) of the samples grown at the 750 °C zone indicate that all the diffraction

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FIG. 1. SEM image of well-aligned Ni$_3$Si$_{12}$ NW arrays.
peaks can be ascribed to hexagonal Ni$_3$Si$_{12}$ [space group $P321(150)$, the lattice constants $a=0.6671$ nm and $c=1.2288$ nm (Ref. 18)] NWs and Ni substrate. No diffraction peaks from any other nickel silicide phase and impurities were detected. The diffraction peaks are strong and sharp indicating the high degree of crystallinity of as-grown samples. Figure 1 shows a SEM image of the Ni$_3$Si$_{12}$ NWs which were uniformly grown at the 750 °C zone on grains of Ni$_3$Si$_{12}$ thin film formed on the Ni foil substrate. The length and diameter of Ni$_3$Si$_{12}$ NWs are 3–5 µm and 50–80 nm, respectively. As the growth time was prolonged to 6 h, the length and diameter of Ni$_3$Si$_{12}$ NWs were increased to 6–7 µm and 120–130 nm, respectively. If the growth temperature was raised to 850 °C, vertically aligned Ni$_2$Si NWs were grown instead.

Figure 2(a) shows TEM image of a single 80 nm Ni$_3$Si$_{12}$ NW. The growth direction of Ni$_3$Si$_{12}$ NW is [100]. High resolution TEM (HRTEM) image in Fig. 2(b) reveals that the NW is single crystaline and defect-free. From the analysis of the EDS spectrum (not shown), the ratio of Ni and Si is close to 2.8:1.

The cross section TEM image in Fig. 3(a) of a sample prepared with the aid of focused ion-beam (FIB) apparatus and corresponding selected area electron diffraction (SAED) patterns confirms that the NW and underlying film are of the same phase and growth direction of Ni$_3$Si$_{12}$. Figure 3(b) shows the cross section TEM image of the Ni$_3$Si$_{12}$/Ni interface and the corresponding SAED patterns of Ni$_3$Si$_{12}$ thin film and Ni substrate. The crystallographic orientation relationships between Ni$_3$Si$_{12}$ and Ni are

$$[010]_{\text{Ni}_3\text{Si}_{12}} \parallel [112]_{\text{Ni}}$$

and

$$\langle 006 \rangle_{\text{Ni}_3\text{Si}_{12}} \parallel (11 - 1)_{\text{Ni}}.$$
ration between the anode and emitting surface. The turn-on field was defined as the applied field attained to a current density of 1 μA cm⁻² and was found to be about 1.0 V μm⁻¹. In accordance with the Fowler–Nordheim (FN) relationship, FE current from a metal or semiconductor is attributed to the tunneling of electrons from the material into vacuum through a potential barrier under the influence of an applied field. The FN plot is shown in the inset of Fig. 5. The field enhancement factor β was calculated to be about 3190 for Ni₃₁Si₁₂ NWs from the slope of the ln(J/E²)–1/E plot with a work function value of about 4.80 eV for Ni₃₁Si₁₂ NWs.¹⁹ The high FE performance is ascribed to the aligned geometry, especially the long Ni₃₁Si₁₂ NWs. In addition, epitaxy between Ni silicide NWs, Ni silicide films, and the metal substrates (Ni foil) also assists the electron transport on the side of emitting surface to enhance the FE performance.

The Si vapor from the source zone would react with the substrate of Ni foil to form single crystal Ni silicide (Ni₃₁Si₁₂) films [Fig. 3(a)] first at the end zone in the furnace. The Ni₃₁Si₁₂ films would in turn serve as the catalytic surfaces to assist Si vapor to condense and grow Ni₃₁Si₁₂ NWs epitaxially on thin films.²⁰,²¹ The phase formation of Ni silicides was found to depend on the ratio of Ni and Si.²² Ni atoms are known to be the dominant diffusing species in the Ni-Si reactions.¹⁵ Consequently, Ni atoms from the Ni substrate can be considered as the excess component. As a result, Ni-rich silicide phases (Ni₂Si, Ni₃₁Si₁₂, and Ni₅Si₂) are prone to form. On the other hand, the supply of Si vapor would diminish with the distance from the Si source. It correlates well with the finding that Ni₂Si and Ni₃₁Si₁₂ phases were formed at the zones close and farther away from the source zone downstream, respectively.

The directional growth of NiSi NWs to form nanobridges over trenches has previously been achieved by the MIG method on Ni film coated on SiO₂ layer. The growth of 1–2 μm NiSi NWs was induced on 1–3 μm Ni grains during the sputtering of Si.⁹ In the present work, vertically well-aligned Ni₃₁Si₁₂ NW arrays of more than 7 μm in length over ~30 μm in diameter areas were grown at the specific temperature zones. The clarification of epitaxial growth mechanism shall further facilitate the practical applications of the grown Ni₃₁Si₁₂ NWs in nanoelectronics devices.

In summary, vertically well-aligned single crystal Ni₃₁Si₁₂ NW arrays have been successfully synthesized with a simple vapor transport and condensation method. Highly oriented and large area arrays of NWs were epitaxially grown on Ni₃₁Si₁₂ films which were in turn preferentially formed on Ni foil substrates at the 750 °C zone. The length and width of Ni silicide NWs were found to increase with the growth time. The extent of the growth of NWs is correlated with the size of underlying Ni grains. The NWs can carry very high currents and possess excellent FE properties. The results show that the well-aligned single crystal Ni₃₁Si₁₂ NWs are potentially useful as high performance field emitters.

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