Directed growth of nickel silicide nanowires

C. A. Decker, R. Solanki,[a] J. L. Freeouf, and J. R. Carruthers
OGI School of Science and Engineering, Beaverton, Oregon 97006

D. R. Evans
Sharp Laboratories of America, Camas, Washington 98607

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Deposition of nickel silicide nanowires has been achieved in the temperature range of 320 to 420 °C by decomposition of silane on nickel surfaces. The substrates consisted of Ni foils and thin Ni films (~10–100 nm) evaporated on 1-μm-thick layers of SiO_2 predeposited on Si wafers. Nanowire growth between two metal pads was achieved with aid of an electric field. It was found that thinner diameter nanowires were produced at low temperatures and that the density of the nanowires was dependent on the reactor pressure. The current–voltage relationship of these nanowires has also been examined. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1650877]

Silicides constitute an important group of compounds that are used in modern silicon microelectronic and optoelectronic devices.[1,2] Applications of the silicides include electrical contacts, polycide gates, and local interconnects. As the dimensions of the microelectronic devices continue to shrink, nanoscale silicide structures will be required. Beyond 0.1 μm critical dimension, Ti and Co silicides that are currently employed will need to be replaced in order to reduce the linewidth dependence of resistance.[3–5] A potential replacement at this scale is Ni silicide, which offers lower contact resistance, stress, and process temperature, as well as less Si consumption.[5,6] We report here our initial results of growth of Ni silicide nanowires (NSNWs) for potential one-dimensional transport of carriers on future devices. A contiguous growth of Ni silicide and silicon NWs would reduce contact resistance to a minimum value and also potentially reduce dislocation generation due to the lattice misfit.

Growth of a variety of SNWs, ranging from Ti to rare-earth silicides, has been reported.[7–10] These NWs have been grown by first depositing an appropriate metal film on a Si surface, followed by heat treatment. Unlike this approach, we have grown NSNWs by thermal decomposition of silane on Ni surfaces. Due to a catalytic decomposition of silane on a Ni surface, growth of NSNWs occurs at a relatively low temperature.

NSNWs were grown in a reactor that consisted of a quartz tube placed in a tube furnace. During the growth, silane (10% silane, balance He) was flowed into the reactor and pumped out at the other end with a roughing pump. When not in use, the reactor was flushed with dry N_2. The substrates were placed on a Mo holder, whose temperature was monitored with a thermocouple. The substrates included Ni foil and electron-beam-evaporated Ni films (10–100 nm thick) on SiO_2-coated Si wafers.

The main growth parameters monitored were temperature, pressure in the reactor (controlled with a throttle valve), and silane flow rate. The best temperature range was determined to be between 370 to 420 °C. It is possible to achieve NW growth at lower temperatures (~320 °C) by first ramping up substrate temperature to about 420 °C and then reducing it for the actual growth. This suggests that specific silicide phase formation is required for the NW growth. At higher temperatures, the diameters of these structures increased, resulting in clumped wires that produced a rough surface.

NWs reported here were grown over a pressure range of 0.8 to 100 Torr. It was found that the pressure affected the NW density. As the pressure was increased, fewer NWs grew, and the NW structures were nonuniform and short, with larger diameters. NSNWs grown at 2.2 Torr and 420 °C are shown in Fig. 1. It can be seen that the diameters are about 17 nm and are fairly uniform. The NW growth rate under these conditions was 0.15 μm/min. The influence of the silane flow rate was examined over 10 to 100 sccm range and was found to produce no significant difference in the growth over this range.

The density of NWs was dependent on the substrates used. For example, when viewed with a field-emission scanning electron microscope (FE-SEM), a Ni foil surface appeared furry due to the high density of the NWs, whereas the e-beam-evaporated films produced scattered NWs. To better understand the difference between the two surfaces, they were examined using x-ray diffraction. As expected, the x-ray analysis of the Ni foil showed a rich spectrum with strong cubic Ni lines. As-deposited thin Ni films (10–100

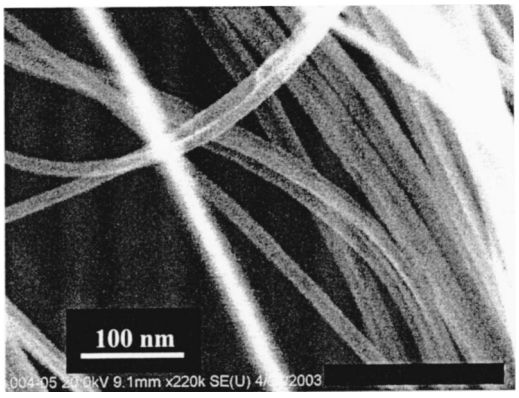

FIG. 1. SEM micrograph of the NSNWs.

[a]Electronic mail: solanki@ece.ogi.edu

nm), on the other hand, produced almost featureless spectra with a couple of small peaks of cubic Ni. Atomic force microscope scans also showed the expected difference in morphology of the two surfaces. However, the nucleation sites on the Ni films can be increased with a rapid thermal anneal (RTA) pulse; for example, 20 s at 700–800 °C. The RTA pulse increases the grain size of the Ni film, hence producing a rougher surface and more nucleation sites for growth of SNWs. Currently, we are exploring nonthermal means of increasing the density of NWs on deposited Ni films and have achieved encouraging results that will be discussed separately. However, at this time, the exact nature of the nucleation sites has not been determined.

Transmission electron microscopy (TEM) provided detailed structural information of these NWs. The TEM samples were produced by scraping a copper grid (with a holey carbon film) on a Ni surface with NWs or by directly growing the NWs on Ni TEM grids. The NWs grown on the Ni grids were not as easy to view since they tended to vibrate in the electron beam. Composition and electron diffraction analyses were performed on the NWs supported on Cu grids. These NWs were found to be single crystal and were surrounded by a thin amorphous film, which most likely is an oxide layer. Depending on growth conditions, single-phase NiSi, Ni_2Si, and Ni_3Si_2 NWs were detected.

Currently, the most common technique (from gas phase precursors) employed to produce NWs utilizes the vapor-liquid-solid mechanism.[11,12] In this process, the excess species is precipitated out of a eutectic droplet in the form of a NW. In our case, Ni-Si eutectic temperatures are above 1000 °C;[13] hence, a different mechanism has to be responsible for the NW growth. We propose the following mechanism composed of three sequential processes: (a) decomposition of silane into silicon on a Ni surface, (b) diffusing of Ni into silicon, and (c) formation of NSNWs.

It has been shown that decomposition of silane can occur at temperatures below 0 °C on a clean (111) surface of single-crystal Ni due a catalytic reaction.[14] For NW growth at about 370 °C, we expect decomposition of silane and deposition of a thin layer of amorphous silicon. One should note that this reaction on a Ni surface occurs well below silane thermal decomposition temperature of about 500 °C that is used for chemical vapor deposition of amorphous silicon. More recently, catalytic decomposition of disilane at about 200 °C has been utilized to grow SNWs on Ni crystals along (111) terraces that serve as templates.[15]

Nickel is known to be a fast diffuser in silicon.[16] Once a thin Si film is deposited on the Ni surface, the Ni atoms will diffuse into this film and start forming a silicide. Considering chemical potentials at a nickel silicide/Si interface, diffusion creates a forward driving force for Ni atoms through the silicide and there is an opposing force for diffusion of Si atoms into the silicide.[16] Based on published diffusion parameters,[2] we obtained the diffusion rate of Ni in Si to be about 0.6 μm/min at 400 °C. If we consider this to be the upper limit of the NW growth rate, it compares reasonably well to our measured growth rate of 0.15 μm/min and implies that the silicon NWs are completely saturated with Ni that are then converted to Ni silicide. Ni at the leading edge of the NWs lead to further decomposition of silane and repeat of the whole cycle.

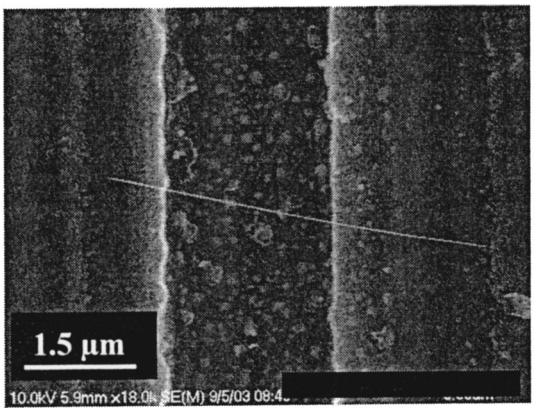

FIG. 2. NW growth across a trench for electrical characterization.

Electrical properties of the NSNWs were examined by first depositing bar-bell-shaped, 30-nm-thick Ni films using a shadow mask. The center bar (~1 mm long, 100 μm wide) was connected at each end to contact pads. A 3-μm-wide trench was etched in the center bar with a focused ion beam (FIB) to create a gap between the two pads. The residual Ga, as well as Ga ions implanted into SiO_2 from the FIB process (to produce the trench), was removed with a chemical etch. NSNWs were then grown across the gap in the presence of an ac or dc electric field of up to 5 V/μm. There was not a significant difference in growth between ac and dc fields. FIB was then utilized to disconnect all the NWs, except one spanning across the gap, as shown in Fig. 2. The $I-V$ profile of seven NWs (of different lengths) was first recorded, as shown in Fig. 3. All except one NW were then disconnected using FIB and its $I-V$ profile was measured at room temperature, also shown in Fig. 3. Without any NWs, the leakage current across the trench was in the picoampere range. The curve is a little asymmetrical, probably due to slightly different contacts at the two ends of the NW. The transport in this relatively long conductor is most likely dominated by scattering within the NW. From the slope at $V=0$, we estimated the upper limit of the contact resistivity between the SNW and metal contact to be about $10^{-4}\ \Omega\ \mathrm{cm}^2$.

In summary, growth of single-crystal nickel silicide nanowires has been achieved on nickel foils and thin-film surfaces at temperatures as low as 370 °C. The diameter of the NWs depends on the growth temperature, with low

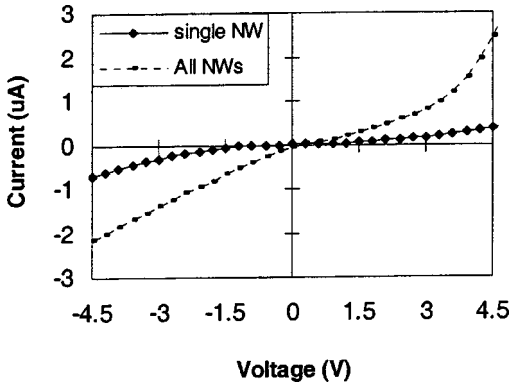

FIG. 3. $I-V$ profile of seven NSNWs and a single NW at room temperature.

temperature producing narrower diameter NWs. Several phases of nickel silicide were observed, depending on the growth conditions. It has been demonstrated that directed growth of SNWs can be achieved with the aid of an electric field.

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