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LETTERS

Doping and Electrical Transport in Silicon Nanowires

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Single-crystal n-type and p-type silicon nanowires (SiNWs) have been prepared and characterized by electrical transport measurements. Laser catalytic growth was used to introduce controllably either boron or phosphorus dopants during the vapor phase growth of SiNWs. Two-terminal, gate-dependent measurements made on individual boron-doped and phosphorus-doped SiNWs show that these materials behave as p-type and n-type materials, respectively. Estimates of the carrier mobility made from gate-dependent transport measurements are consistent with diffusive transport. In addition, these studies show it is possible to heavily dope SiNWs and approach a metallic regime. Temperature-dependent measurements made on heavily doped SiNWs show no evidence for Coulomb blockade at temperatures down to 4.2 K, and thus testify to the structural and electronic uniformity of the SiNWs. Potential applications of the doped SiNWs are discussed.

Introduction

Currently, there is intense interest in one-dimensional (1D) nanostructures, such as nanowires and nanotubes, due to their potential to test fundamental concepts about how dimensionality and size affect physical properties, and to serve as critical building blocks for emerging nanotechnologies.[1−3] Of particular importance to 1D nanostructures is the electrical transport through these "wires", since predictable and controllable conductance will be critical to many nanoscale electronics applications. To date, most efforts have focused on electrical transport in carbon nanotubes.[4−11] These studies have shown interesting fundamental features, including the existence of coherent states extending over hundreds of nanometers,[4] ballistic conduction at room temperature,[5] and Luttinger liquid behavior,[6] and have demonstrated the potential for devices such as field effect transistors.[7−9] However, there are important limitations of nanotubes. First, the specific growth of metallic or semiconducting tubes, which depends sensitively on diameter and helicity,[12] is not possible. Studies dependent on the specific conducting behavior must thus rely on chance observation. Second, controlled doping of semiconducting nanotubes is not possible, although it is potentially critical for devices applications. Semiconductor nanowires,[13−15] however, can overcome these limitations of carbon nanotubes. These nanowires will remain semiconducting independent of diameter, and moreover, it should be possible to take advantage of the vast knowledge from the semiconductor industry to dope the nanowires.

To this end, we here report the first demonstration of controlled doping of SiNWs and the characterization of the electrical properties of these doped nanowires using transport measurements. Gate-dependent, two-terminal measurements demonstrate that boron-doped (B-doped) and phosphorus-doped (P-doped) SiNWs behave as p-type and n-type materials, respectively, and estimates of the carrier mobilities suggest diffusive transport in these nanowires. In addition, temperature-dependent measurements made on heavily doped SiNWs show no evidence for Coulomb blockade at temperatures down to 4.2 K.

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Experimental Section

SiNWs were synthesized using the laser-assisted catalytic growth (LCG) method we have described previously.[13−15] Briefly, a Nd:YAG laser (532 nm; 8 ns pulse width, 300 mJ/pulse, 10 Hz) was used to ablate a gold target, which produces gold nanocluster catalyst particles within a reactor, and SiNWs were grown in a flow of SiH_4 as the reactant. SiNWs were doped with boron by incorporating B_2H_6 in the reactant flow and were doped with phosphorus using a Au−P target (99.5:0.5 wt %, Alfa Aesar) and additional red phosphorus (99%, Alfa Aesar) at the reactant gas inlet. Transmission electron microscopy (TEM) measurements demonstrate that the doped SiNWs have a single-crystal silicon core that is covered by a dense SiO_x sheath as described previously.[13]

Electrical contacts to individual SiNWs were made using standard electron beam lithography methods using a JEOL 6400 writer. The nanowires were supported on oxidized Si substrate (1−10 Ω cm resistivity, 600 nm SiO_2, Silicon Sense, Inc.) with the underlying conducting Si used as a back gate. The contacts to the SiNWs were made using thermally evaporated Al (50 nm) and Au (150 nm). Electrical transport measurements were made using a home-built system with ≤1 pA noise under computer control. The temperature-dependent measurements were made in a Quantum Design magnetic property measurement system.

Results and Discussion

TEM studies show that the boron- and phosphorus-doped SiNWs are single crystals, although these measurements do not have sufficient sensitivity to quantify the boron or phosphorus doping levels in individual wires. We can, however, demonstrate unambiguously the presence of p-type (boron) or n-type (phosphorus) dopants and the relative doping levels using electrical transport spectroscopy. In these measurements, a gate electrode is used to vary the electrostatic potential of the SiNW while measuring current versus voltage of the nanowire. The change in conductance of SiNWs as a function of gate voltage can be used to distinguish whether a given nanowire is p-type or n-type since the conductance will vary oppositely for increasing positive (negative) gate voltages.

Typical gate-dependent current versus bias voltage ($I-V$) curves recorded on intrinsic and B-doped SiNWs are shown in Figure 1. The two B-doped wires shown in parts b and c were synthesized using SiH_4:B_2H_6 ratios of 1000:1 and 2:1, respectively. In general, the two-terminal $I-V$ curves are linear and thus suggest that the metal electrodes make ohmic contacts to the SiNWs. The small nonlinearity observed in the intrinsic nanowire indicates that this contact is slightly nonohmic. Analysis of $I-V$ data, recorded at zero gate voltage ($V_g = 0$), which accounts for contributions from the contact resistance and oxide coating on the SiNW, yield a resistivity of 3.9×10^2 Ω cm. Significantly, when V_g is made increasingly negative (positive), the conductance increases (decreases). This gate dependence shows that the SiNW is a p-doped semiconductor (discussion below). Similar $I-V$ versus V_g curves were recorded for the lightly B-doped SiNW and show that it is also p-type. Moreover, the $V_g = 0$ resistivity of this B-doped SiNW (1 Ω cm) is more than 2 orders of magnitude smaller than the intrinsic SiNW and demonstrates clearly our ability to control conductivity chemically. This latter point is further supported by $I-V$ measurements on the heavily B-doped SiNWs shown in Figure 1c. This wire has a very low resistivity of 6.9×10^{-3} Ω cm and shows no dependence on V_g; that is, $I-V$ data recorded with V_g of 0 and 20 V are overlapping. These results are consistent with a high carrier concentration that is near the metallic limit.

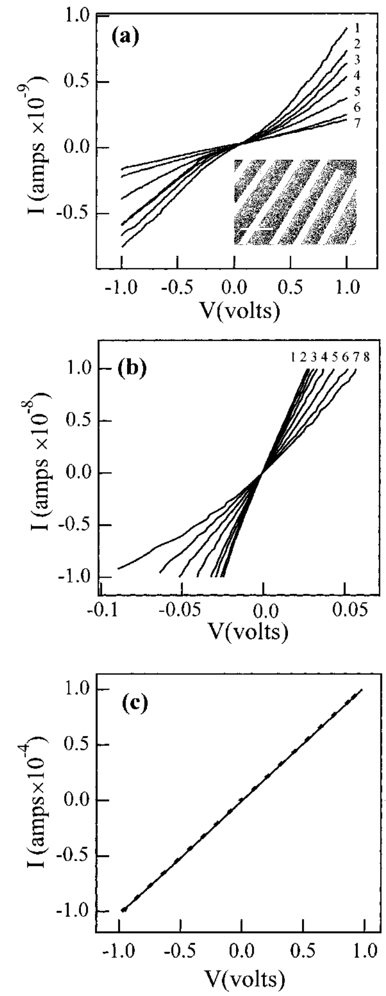

Figure 1. (a) Current (I) vs bias voltage (V) curves recorded on a 70 nm diameter intrinsic SiNW at different gate voltages (V_g). Curves 1, 2, 3, 4, 5, 6, and 7 correspond to $V_g = -30, -20, -10, 0, 10, 20,$ and 30 V, respectively. The inset is a typical scanning electron micrograph of the SiNW with metal contacts (scale bar = 10 μm). (b) $I-V$ data recorded on a 150 nm diameter B-doped SiNW; curves 1−8 correspond to $V_g = -20, -10, -5, 0, 5, 10, 15,$ and 20 V, respectively. (c) $I-V$ curves recorded on a 150 nm diameter heavily B-doped SiNW; $V_g =$ 20 V (solid line) and 0 V (heavy dashed line).

We have also measured V_g-dependent transport in lightly and heavily P-doped SiNWs. The $I-V$ recorded on the lightly doped nanowire (Figure 2a) is somewhat nonlinear, which indicates nonideal contact between the electrodes and nanowire, and the V_g dependence is opposite of that observed for the B-doped SiNWs. Significantly, this observed gate dependence is consistent with n-type material as expected for P-doping. The estimated resistivity of this wire at $V_g = 0$ is 2.6×10^2 Ω cm. This relatively high resistivity is suggestive of a low doping level and/or low mobility. In addition, heavily P-doped SiNWs have also been made and studied. The $I-V$ data recorded on a typical heavily P-doped wire are linear, have a resistivity of 2.3×10^{-2} Ω cm, and show no dependence on V_g. The low resistivity (4 orders of magnitude smaller than the lightly P-doped sample) and V_g independence demonstrate that high carrier concentrations can also be created via P-doping of the SiNWs.

The above results demonstrate that boron and phosphorus can be used to change the conductivity of SiNWs over many orders of magnitude and that the conductivity of the doped SiNWs

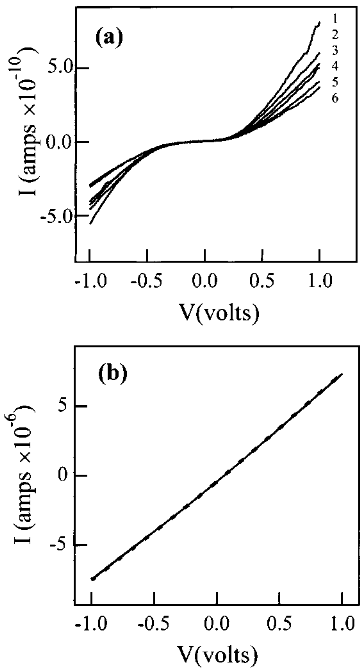

Figure 2. (a) $I-V$ data recorded on a 60 nm diameter P-doped SiNW. Curves 1, 2, 3, 4, 5, and 6 correspond to $V_g = 20$, 5, 1, 0, -20, and -30 V, respectively. (b) $I-V$ curves recorded on a 90 nm diameter heavily P-doped SiNW; $V_g = 0$ V (solid line) and -20 V (heavy dash line).

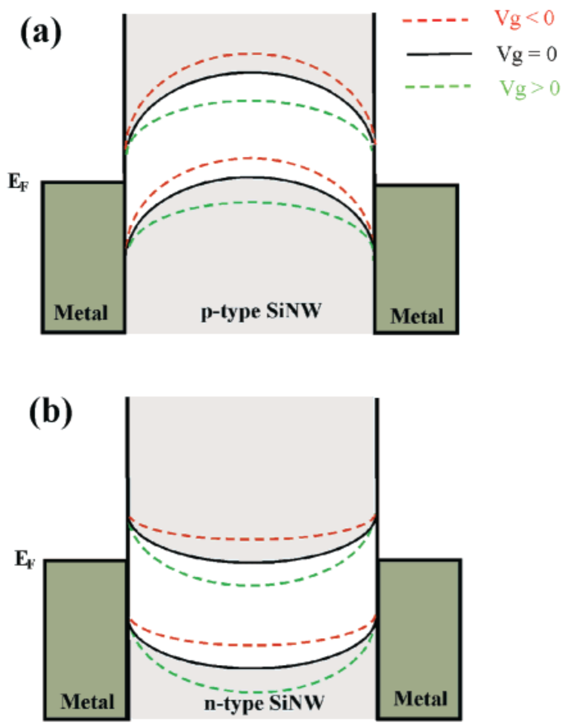

Figure 3. Energy band diagrams for (a) p-type SiNW (b) n-type SiNW devices. The diagrams show schematically the effect of V_g on the electrostatic potential for both types of nanowires.

respond oppositely to positive (negative) V_g for boron and phosphorus dopants. Indeed, the V_g dependence provides strong proof for p-type (holes) doping with boron and n-type (electrons) doping with phosphorus in the SiNWs. The observed gate dependences can be understood by referring to the schematics shown in Figure 3, which show the effect of the electrostatic potential on the SiNW bands. In these diagrams, a p-type nanowire (a) and n-type nanowire (b) are contacted at both ends

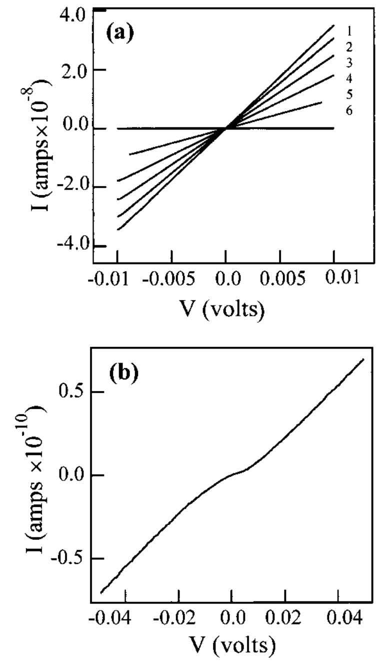

Figure 4. Temperature-dependent $I-V$ curves recorded on a heavily B-doped SiNW: (a) curves 1, 2, 3, 4, 5, and 6 correspond to temperatures of 295, 250, 200, 150, 100, and 50 K, respectively; (b) $I-V$ data recorded on the nanowire at 4.2 K.

to metal electrodes. As for a conventional metal−semiconductor interface,[16] the SiNW bands bend (up for p-type; down for n-type) to bring the nanowire Fermi level in line with that of the metal contacts. When $V_g > 0$, the bands are lowered, which depletes the holes in B-doped SiNWs and suppresses conductivity, but leads to an accumulation of electrons in P-doped SiNWs and enhances the conductivity. Conversely, $V_g < 0$ will raise the bands and increase the conductivity of B-doped (p-type) SiNWs and decrease the conductivity of the P-doped (n-type) nanowires.

In addition, it is possible to estimate the mobility of carriers from the transconductance,[8] $dI/dV_g = \mu(C/L^2)$ V, where μ is the carrier mobility, C is the capacitance, and L is the length of the SiNW. The SiNW capacitance is given by $C \approx 2\pi\epsilon\epsilon_0 L/\ln(2h/r)$, where ϵ is the dielectric constant, h is the thickness of the silicon oxide layer, and r is the SiNW radius. Plots of dI/dV_g versus V were found to be linear for the intrinsic (Figure 1a) and lightly B-doped (Figure 1b) SiNWs, as expected for this model. The slopes of dI/dV_g for the intrinsic (2.13×10^{-11}) and B-doped (9.54×10^{-9}) SiNW yield mobilities of 5.9×10^{-3} $cm^2/(V\ s)$ and 3.17 $cm^2/(V\ s)$, respectively. The mobility for the B-doped nanowire is comparable to that expected in bulk Si at a doping concentration of 10^{20} cm^{-3}.[16] We also note that the mobility is expected to increase with decreasing dopant concentration, although in our intrinsic (low dopant concentration) SiNW the mobility is extremely low. It is possible that the reduced mobility is due to enhanced scattering in the smaller diameter (intrinsic) SiNW. We believe that future studies of the mobility as a function of diameter (for constant dopant concentration) should illuminate this important point.

Last, we have carried out preliminary temperature-dependent studies of heavily B-doped SiNWs. Temperature-dependent $I-V$ curves show that the conductance decreases with decreasing temperature, as expected for a doped semiconductor (Figure 4). More importantly, we see no evidence for Coulomb blockade down to our lowest accessible temperature (Figure 4b).[17] This indicates strongly that variations in SiNW diameter and defects are sufficiently small that they do not effectively “break up” the SiNW into small islands, which would exhibit Coulomb blockade at these temperatures.[18] These results contrast studies of lithographically patterned SiNWs,[18] which show Coulomb blockade, and testify to the high quality of our free-standing nanowires.

Conclusions

Single crystal n-type and p-type silicon nanowires (SiNWs) have been prepared and characterized by electrical transport measurements. Laser catalytic growth was used to controllably introduce either boron or phosphorus dopants during the vapor phase growth of SiNWs. Two-terminal, gate-dependent measurements made on individual boron-doped and phosphorus-doped SiNWs show that these materials behave as p-type and n-type materials, respectively. Estimates of the carrier mobility made from gate-dependent transport measurements are consistent with diffusive transport and show an indication for reduced mobility in smaller diameter wires. In addition, these studies show it is possible to incorporate high dopant concentrations in the SiNWs and to approach the metallic regime. Temperature-dependent measurements made on heavily doped SiNWs show no evidence for single electron charging at temperatures down to 4.2 K, and thus suggest that the SiNWs possess a high degree of structural and doping uniformity.

We believe that our successful doping of SiNWs to create n-type and p-type materials will open up exciting opportunities in nanoscale science and technology. Doped SiNWs will be candidates for investigating fundamental issues of transport in 1D nanostructures. The structures studies in this paper are also field effect transistors (FETs), and it will be possible using self-assembly techniques to integrate many SiNW FETs into structures, perhaps for nanoelectronics applications. It should also be possible to combine p-type and n-type SiNWs, for example in crossed arrays, to create p−n junctions that could also be considered for devices and sensors in the future.[19]

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(17) The small nonlinearity near $V = 0$ is attributed to a contact effect since high-resolution $I-V$ versus V_g measurements show no signature for coulomb blockade. Coulomb charging effect in this homogeneous wire between the electrodes (a 150 nm thick 2.3 μm long wire) would require a temperature below about 26 mK estimated from $kT = e^2/2C$.

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(19) Crossed SiNW p−n junctions have been formed by directed assembly of p-type (n-type) SiNWs over n-type (p-type) SiNWs. Preliminary transport measurements exhibit rectification in reverse bias and a sharp current onset in forward bias. Simultaneous measurements made on the p-type and n-type SiNWs making up the junction demonstrate that the contacts to these nanowires are ohmic (nonrectifying), and thus that the rectifying behavior is due to the p−n junction between the two SiNWs (Cui, Y.; Lieber, C. M., unpublished results).