

Electrical and Mechanical Properties of Boron and Metal-boride Nanowires, and Devices Built from Them

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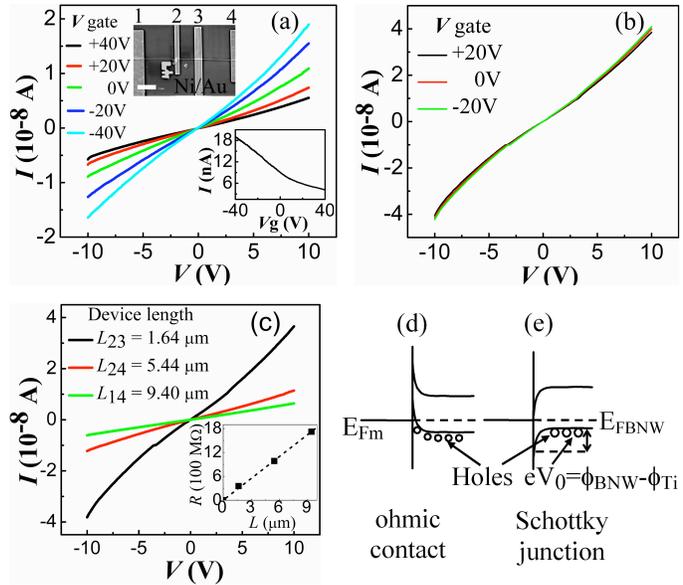
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Much progress has been made in the last few years on nanoelectronic devices constructed from nanotubes, nanowires, or their crossed junctions, including field-effect transistors, single-electron transistors, p-n diodes, and Schottky-barrier rectifiers. Such devices may serve as building blocks for future memory devices and logic circuits, and will require both conducting interconnects and semiconducting components. Nanodevice construction using C nanotubes has received considerable attention, although the electrical properties of C nanotubes depend markedly upon diameter and chirality (wall orientation). Here we investigate the synthesis, electrical-transport behavior and mechanical properties of boron nanowires, which we believe should have mechanical strengths, chemical and thermal stabilities, and electrical conductivities that may surpass those of C nanotubes and other related families of 1D nanostructures. In our studies to date, we find that Ni and Ti electrodes make ohmic and Schottky-barrier contacts to the B nanowires, respectively. Gate-dependent measurements establish them to be *p*-type semiconductors. We have applied the metal-specific contact behavior to fabricate nanowire rectifying devices. We have also measured the bending moduli of boron nanowires in electrically and mechanically induced resonance experiments. Synthetic methods under development include catalyzed CVD and plasma-based techniques. These fundamental studies, which will inform subsequent device construction, are summarized below.

A high resistance gap around 0 V was apparent in boron nanowire devices fabricated with Ti electrodes, as is typical for nanowire devices with Schottky barrier contacts on both sides. However, the *I* – *V* response of boron-nanowire devices with Ni electrodes (top inset of Fig. 1a) did not show such a gap (Fig 1a). The *I* – *V* measurements made on three segments of differing length for the device in Fig 1a (top inset) showed the resistance to be proportional to the length of the nanowire segment (Fig. 1c), which implied that the resistance was dominated by the nanowire itself rather than the contact. These results establish that Ni forms ohmic contact with the B nanowires. The conductivity of the nanowire in this device determined to be $10^{-2} (\Omega \text{ cm})^{-1}$ from the slope of the fitted line in the *R* vs. *L* plot (Fig 1c inset). This value is higher than that of pure bulk boron ($\approx 10^{-6} (\Omega \text{ cm})^{-1}$ for the α -rhombohedral structure).² We tentatively attribute the increased conductivity to impurity doping in the nanowire.

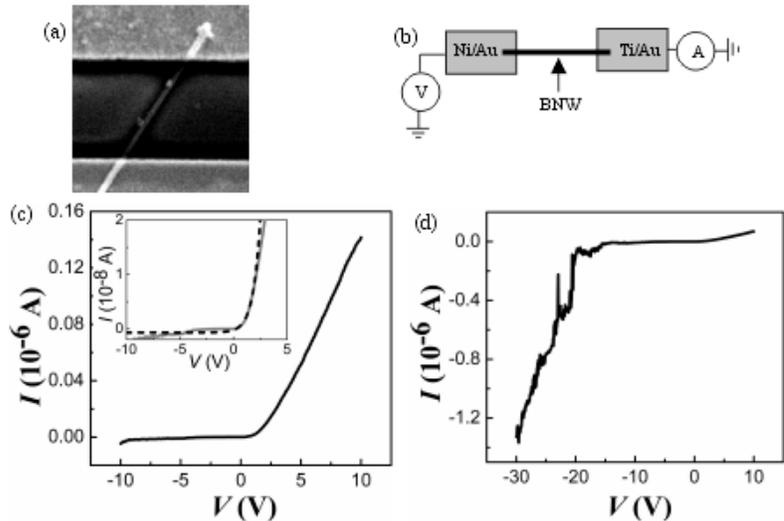
Figure 1a and b also show the *I* – *V* curves of the nanowire device at different gate voltages before and after annealing, respectively. The bottom inset of Fig. 1a contains the current vs. gate-voltage data biased at 10 V. Significantly, higher currents were obtained at negative gate voltages, demonstrating that the nanowire is a *p*-type semiconductor. Bulk α -rhombohedral boron also exhibits *p*-type character,³ which is attributed to a high density of acceptor states at 0.2 eV above the valence-band edge resulting from intrinsic structural defects and Jahn-Teller distortions in the unusual icosahedral-cluster-based crystal structure.³ The carrier mobility estimated from the data in Fig. 1a (bottom inset) is on the order of $10^{-3} \text{ cm}^2/\text{Vs}$. This low mobility is consistent with the values for α -rhombohedral boron ($10^{-2} - 10^{-8} \text{ cm}^2/\text{Vs}$).²

Figure 1. $I - V$ response of a B-nanowire device having Ni electrodes, (a) gate dependent $I - V$ measurement results, before annealing. Top inset: SEM image; scale bar is 2 μm . The diameter of the nanowire is 75nm. Bottom inset: $I - V_g$ curve, $V_{bias} = 10 \text{ V}$; (b) gate dependent $I - V$ measurements, after annealing (400 $^\circ\text{C}$); (c) $I - V$ response of 3 segments with different lengths on the same nanowire device, $V_g = 0 \text{ V}$, inset: resistance vs. nanowire length L ; (d) band diagram for ohmic contact. (e) band diagram for barrier contact; eV_0 is the built-in potential of the Schottky junction.



Band diagrams to illustrate the ohmic (Ni) and Schottky-barrier (Ti) contacts are shown in Fig. 1d and e, respectively. Intrinsic α -rhombohedral boron has work function around 4.3 eV and band gap of 1.56 eV.² We surmise that the work function in the B nanowires is greater than 4.3 eV on the basis of the contact types we observed to form with the Ti and Ni electrodes. The work functions of Ti (ϕ_{Ti}) and Ni (ϕ_{Ni}) are 4.33 eV and 5.15 eV, respectively.⁴ The results indicate that the work function of the B nanowire falls between those of Ti and Ni, which produces an ohmic contact for Ni and a Schottky barrier for Ti. Thus, the contact type in B-nanowire devices is determined by the identity of the electrode metal.

Figure 2. (a) SEM image of a boron-nanowire device with one Ti and one Ni electrode attached. (b) Schematic of the measurement circuit. (c) $I - V$ curve of the device. Inset: exponential fitting, displayed after zooming in. (d) Breakdown at reverse bias of about -20 V.



Therefore, we expected to observe rectifying behavior in a device with a Ti electrode at one end, and a Ni electrode at the other. Fig. 2a is an SEM image of such a boron-nanowire device. The rectifying effect is clearly seen from the $I - V$ curve in Fig. 2c (inset). At $V < 0.65 \text{ V}$, the current increased exponentially with the bias voltage. Breakdown at reverse bias occurred near -20 V

(Fig. 2d). Thus, a single-nanowire rectifier can be constructed by fabricating a Schottky-barrier contact at one end of the nanowire and an ohmic contact at the other.

Mechanical resonance can be induced in a nanowire when the frequency of the applied force (the forcing frequency) approaches the resonance frequency of the nanowire. For a uniform nanowire with one clamped and one free end, the first mode resonance frequency f_1 is:

$$f_1 = \frac{1.875^2}{8\pi} \frac{D}{L^2} \sqrt{\frac{E_b}{\rho}},$$

where E is the bending modulus, D and L are the nanowire diameter and length, and ρ is the density. Thus the bending modulus of a nanowire of known dimensions can be obtained if its natural frequency can be determined.

Nanowire resonance was achieved using either mechanical or electrical excitation (Figure 3). To date tens of boron nanowires have been tested, with the measured bending moduli ranging between 200 and 300 GPa. The quality factor Q of the resonance is typically over 400, with values as large as 14000 obtained in some cases. For those nanowires that were excited both electrically and mechanically, the two resonance frequencies were very close. In addition, for a few relatively long nanowires we found that the second-mode resonance could be excited, which can be used to verify the first-mode resonance since the ratio between these two frequencies is fixed. An additional benefit of studying the second mode of resonance is that it is less sensitive to nanowire defects than is the first-mode-resonance response.

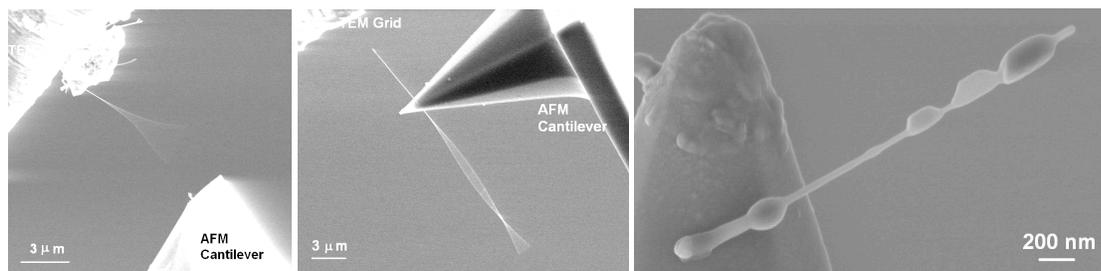


Figure 3. Left: first-mode resonance of a boron nanowire attached to an AFM grid; Center: second-mode resonance of a nanowire attached to an AFM tip; Right: A nanowire melted by dc current.

Our preparative efforts have focused on catalyzed, thermal CVD and plasma-based syntheses. In addition to the boron nanowires discussed above, single-crystalline _ tetragonal boron nanowires and _ aluminum boron (AlB₁₂) nanowires have been synthesized (800-850 °C). Boron nanoribbons have also been obtained. Current work is aimed at the synthesis of highly conductive, doped boron nanowires and metal-boride nanowires.

References

- [1] For further information about this project contact the PIs at email addresses buhro@wustl.edu, r-chang@northwestern.edu, jglu@uci.edu, or r-ruoff@northwestern.edu
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