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Pressure-induced superconducting state in crystalline boron nanowires

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We report high-pressure induced superconductivity in boron nanowires (BNWs) with rhombohedral crystal structure. Obviously different from bulk rhombohedral boron (β-r-B), these BNWs show a semiconductor-metal transition at much lower pressure than bulk β-r-B. Also, we found that these BNWs become superconductors with $T_c=1.5$ K at 84 GPa, at the pressure of which bulk β-r-B is still a semiconductor, via *in situ* resistance measurements in a diamond-anvil cell. With increasing pressure, T_c of the BNWs increases. The occurrence of superconductivity in the BNWs at a pressure as low as 84 GPa probably arises from the size effect.

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It is well known that bulk solid boron is a semiconductor with a band gap of ~2 eV at ambient pressure. Theoretical calculations predicted that at sufficient high pressure, band overlap occurs, which drives the bulk boron to a poor metal.[1,2] Recently, two striking resistance measurements under high pressure found that the semiconductor-metal transition occurs at room temperature in bulk β boron at 130 GPa (Ref. 3) and in bulk α boron at 160 GPa.[4] At low temperature, they both showed a superconducting transition at ~4 K and 160 GPa. Nanomaterials with the same crystal structure as the corresponding bulk solid are expected to have interesting physical properties in comparison with their bulk counterparts. For example, when the size of the solid is small enough, solid-solid phase transition pressures vary with size change.[5,6] Superconducting properties are also altered when the effective size of a superconductor is reduced.[7–16] Progress in preparation of boron nanomaterials[18,19] motivated this investigation of solid-solid phase transition and physical properties at ambient and at high pressures. In this study, we report observations of semiconductor-metal-superconductor transitions in crystalline boron nanowires (BNWs) under high pressure. In addition, the pressure dependence of the superconducting critical temperature (T_c) was studied up to 240 GPa. The correlation between the measured value of T_c and pressure in BNWs is compared with the data of bulk solid boron.

Bulk solid boron has a variety of phases, including α-rhombohedral B_{12} (α-B_{12}), α-tetragonal B_{50} (α-B_{50}), and β-rhombohedral B_{105} (β-r-B).[17,20] All forms mentioned above have the common structural component of boron icosahedrons B_{12} in the unit cell.[21] To determine the structural properties, the BNW samples fabricated by chemical vapor deposition[19] were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS). and x-ray diffraction (XRD) measurement. Figure 1(a) shows the SEM image of BNWs stripped off the Si substrate. The diameter of the wires varies from 200 to 500 nm and the length from 20 to 50 μm. High-resolution TEM observations on the nanosamples reveal the presence of complex structural features, as typically illustrated in Fig. 1(b). From a partial enlargement of Fig. 1(b), the notable contrast anomalies in association with structural distortion, indicated by arrows, exclude the possibility of stacking faults, as shown in Fig. 1(c). Actually alterations of crystallographic orientation can

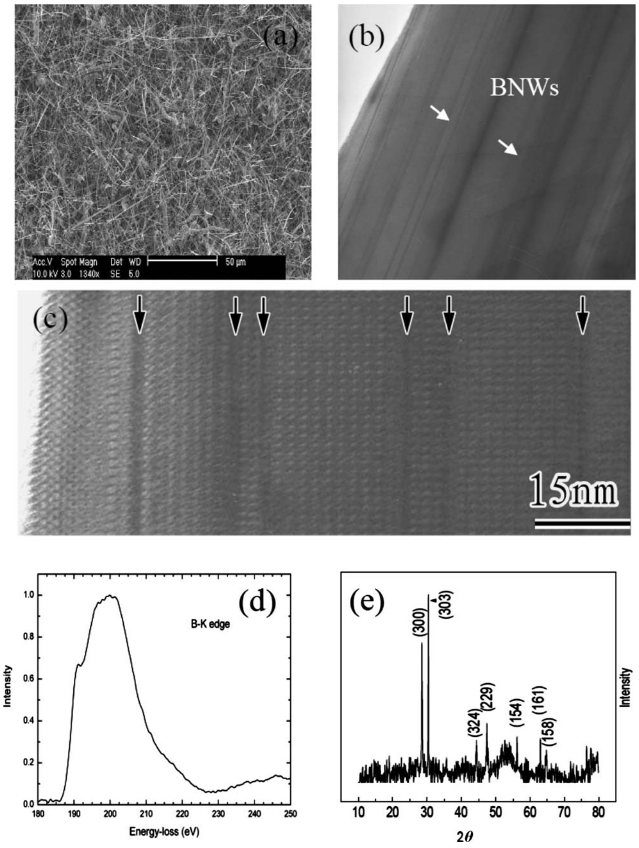

FIG. 1. (a) SEM image of the BNWs stripped off the silicon substrate, (b) TEM image of one of wire samples used in this study, (c) partial enlargement of Fig. 1(b), (d) EELS of the BNWs at K shell ionization edge (~190 eV), and (e) x-ray diffraction spectrum of the BNWs.

be clearly recognized crossing certain defective regions, as displayed in Fig. 1(b). These facts suggest that each nanowire sample observed from SEM is texturally made up from many slim nanowires with diameter of ~30 nm. To determine the composition, we analyzed the slim nanowires using EELS. Figure 1(d) exhibits the representative EELS of a slim wire sample. The boron absorption features at the *K* shell ionization edge (~190 eV) are clearly seen, which indicates that no other elements or impurities are observed in the BNWs. XRD measurements demonstrate that all peaks of the BNWs can be indexed to β-rhombohedral (B_{105}) structure, as shown in Fig. 1(e). This indicates that the BNWs used in this study have the same crystal structure as bulk β-*r*-B.[3]

High-pressure experiments were performed using a diamond-anvil cell made of Be-Cu alloy. Diamonds were selected carefully for very low birefringence with tips whose diameter is 300 μm for the first experiment and 40 μm for the second. A standard four-lead technique was used for the first experiment below 60 GPa, and a pseudo-four-lead technique was used for the second experiment. The pseudo-four-lead pattern was made by thin-film fabrication and photolithography technology. A layer of titanium (Ti) was deposited onto the diamond surface, followed by a layer of platinum deposited over the Ti layer. Four layered leads were then connected to 5-μm-thick Pt wires. Insulation from the rhenium gasket was achieved by a thin layer of a mixture of diamond powder and epoxy. The size of each wire sample used in this study was measured under a high magnification observation microscope. Seven well-aligned wire samples were placed on the top anvil and then pressed into the insulating gasket with leads. No pressure medium was used. The pressures were determined at room temperature by ruby fluorescence method[22,23] and at low temperature with the diamond Raman shift.[24,25] Superconducting transitions under pressure were measured in a ^{3}He/^{4}He dilution refrigerator.

Figure 2 shows the pressure dependence of resistivity (ρ) of the BNWs for two individual experiments, which were carried out at room temperature. Unlike bulk β-*r*-B,[3] the resistance of the sample is measurable (~83 K Ω) at 300 K and 0.7 GPa. With increasing pressure, the ρ value decreased significantly at 28 GPa and is saturated at this value at higher pressures. The ρ value of the BNWs at 28 GPa is about 2×10^{-3} Ω cm (corresponding conductivity $\sigma=500$ Ω^{-1} cm^{-1}) which is close to that of minimum metallic conductivity.[3,26] The results suggest that the BNWs become a poor metal at this pressure. At 84 GPa the resistance plunges at 1.5 K, as shown in Figure. 3. The abrupt drop in resistance from a finite value at 1.5 K and a pressure of 84 GPa is a sign of superconducting transition. To confirm that the resistance drop at 1.5 K is related to the superconducting transition of the BNWs, the resistance versus temperature is measured at different magnetic fields and at the fixed pressure. The resistance curve of the sample is magnetic field dependent. The resistance drop is suppressed by an applied magnetic filed and disappears at 2.5 T. It is known that the observed resistance (R_o) is composed of three parts, sample resistance (R_s), contact resistance between the sample and leads (R_c), and deformation resistance (R_d); i.e., $R_o=R_s+R_r$ (here R_r is residual resistance, $R_r=R_c+R_d$). As the resistance of the sample was measured with pseudo-four-lead (two-point contact) technique, *T*-independent behavior with $R_o\sim50$ Ohm at $T<0.5$ K (as shown in Fig. 3) indicates zero resistance of the sample. According to our previous experiments, no superconducting was observed from the same leads at temperature down to 20 mK in megabar pressure range. Therefore, the significant resistance drop at 1.5 K is unambiguously assigned to a superconducting transition of the sample.

Figure 4(a) shows the resistance (*R*) of the BNWs versus temperature (*T*) at selected pressures. The shift of the *R*-*T* curve toward high temperature gives evidence that the critical temperature of superconducting transition (T_c) of the BNWs is enhanced with increasing pressure. Meanwhile, we note that the resistance of BNWs in their normal state increases with increasing pressure, the reason for which is that the value of R_d increase is bigger than that of R_c decrease (generally R_c decreases with pressure), as a result, the ob-

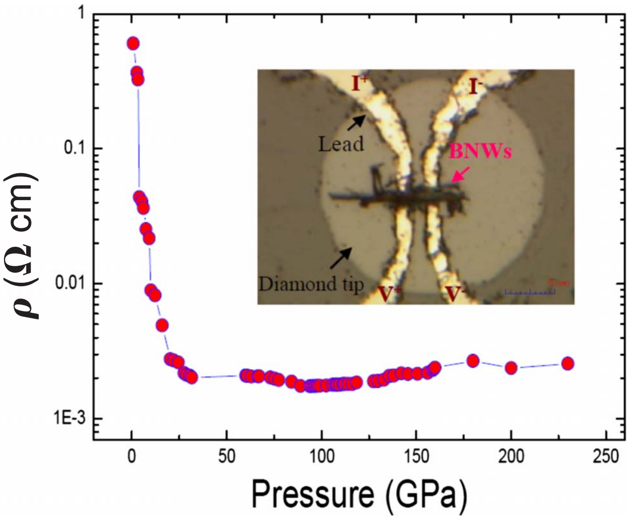

FIG. 2. (Color online) Resistivity (ρ) of the BNWs as a function of pressure at room temperature. The inset of the main figure shows a photograph of pseudo-four-lead and seven well-aligned BNWs on the diamond tip. The diameter of the tip is 40 μm, and the separation between two leads is ~4 μm.

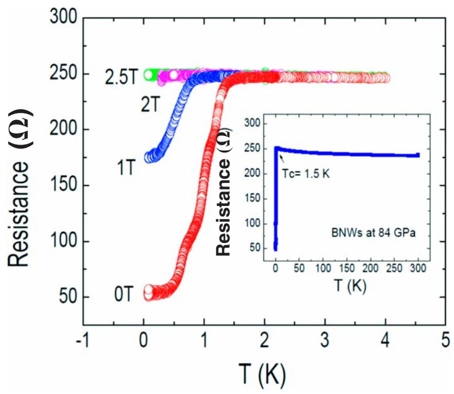

FIG. 3. (Color online) Electrical resistance (*R*) versus temperature (*T*) of superconducting BNWs at 84 GPa measured at different magnetic fields in the low *T* range. The inset is the *R*-*T* curve in the temperature range of 0.08–300 K under zero magnetic field.

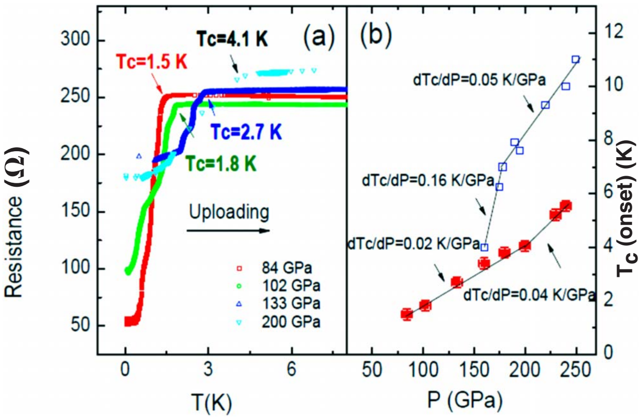

FIG. 4. (Color online) (a) Resistance-temperature curves of the BNWs at selected pressure, (b) Pressure dependence of T_c of BNWs obtained from resistance measurements. Value of T_c is determined from transition onset. Solid square represents data of this study, and open square represents data from Ref. 3.

served resistance R_o elevates. The pressure dependence of T_c is plotted in Fig. 4(b). Here T_c is determined by the onset transition temperature. For comparison, the results from Eremets *et al.*[3] are plotted as open squares in Fig. 4(b). Interestingly, the onset pressure (84 GPa) for the superconducting transition in the BNWs is much lower than that of the bulk boron (160 GPa). The T_c of BNWs increases with increasing pressure. Above 160 GPa, T_c of the BNWs does not increase up to the data of bulk β-*r*-B. Rather, it has a linear behavior up to 200 GPa. Fitting the data of the BNWs from 84 to 200 GPa gives a pressure coefficient $dT_c/dP=0.02$ K/GPa. This value is lower than that (0.16 K/GPa) of bulk β-*r*-B. However, the dT_c/dP of the BNWs was enhanced as pressure further increases. Fitting to data measured from 200 to 240 GPa gives $dT_c/dP=0.04$ K/GPa which approaches the value (0.05 K/GPa) of bulk β-*r*-B achieved at pressure of 178–250 GPa.[3]

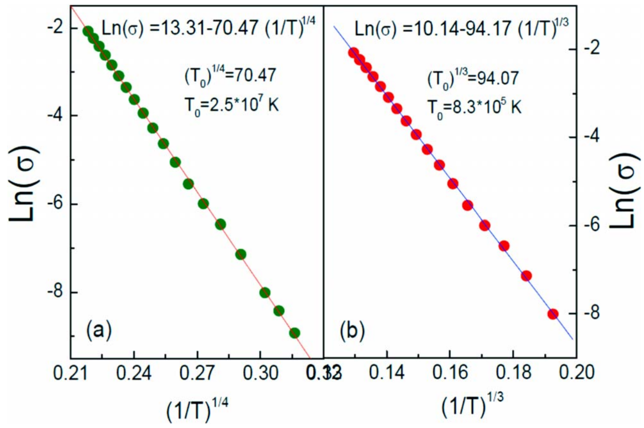

FIG. 5. (Color online) Temperature dependence of conductivity shown as Ln(σ) versus (a) $T^{1/4}$ and (b) $T^{1/3}$ diagram.

The apparent discrepancy between the BNWs and the bulk β-*r*-B in the pressures of the semiconductor-metal-superconductor transitions may probably be attributed to size effect because the BNWs and bulk β-*r*-B are in the same crystal structure, with the difference between them being only size. To prove that the metallization and superconducting transition that occurred at lower pressure are related to the size effect, parallel experiments on transport properties of the BNW have been carried out at ambient pressure. Figure 5 shows experimental measurements of conductivity (σ) of the BNW as a function of temperature (T). According to early studies,[27,28] the boron-rich materials have a Mott's variable-range hopping (VRH) conduction nature:[29,30] $\sigma=\sigma_o \exp[-(T_o/T)^Q]$ $(T_o=\frac{60}{\pi\xi^3 k_B N(E_F)})$ where σ is the conductivity, T is the temperature, ξ is the localization length of the wave function of carriers, k_B is the Boltzmann constant, $N(E_F)$ is the density of state at the Fermi level, and σ_o is a constant. On the basis of Mott's theory we can estimate the $N(E_F)$ from the measured σ. It is noted that the estimation of $N(E_F)$ is completely based on parameters of Q and T_0 of Mott's theory if the localization length remains unchanged. T_0 is determined both by Q value and σ value; the latter is experimental result. Therefore, Q value should be the key factor for the estimation of $N(E_F)$. In Mott's equation, Q value is alterable, $Q=1/4$ for the three-dimensional sample and $Q=1/3$ for the two-dimensional sample. To make the BNW and bulk β-*r*-B comparable, we take value of Q and ξ for the BNW same as that ($Q=1/4$, $\xi=0.1$ nm) of bulk β-*r*-B in the calculations. Using this model, we obtained $T_o=2.5\times10^7$ K and then estimated $N(E_F)$ of the BNW at ambient pressure to be 8.9/eV nm^3. In order to make a precise comparison, we looked up the conductivity data for single crystal of bulk β-*r*-B (the BNW is a single crystal) from Ref. 31, and we found that the $N(E_F)$ of the single crystal of bulk β-*r*-B is about 2.5/eV nm^3. Comparing with the $N(E_F)$ of single crystal of β-*r*-B and the BNW, the $N(E_F)$ of the BNW is still higher than that of bulk β-*r*-B. The same phenomenon also has been found in boron nanobelt.[28] Therefore, the size effect could be the reason that the BNW is easier to be metallized than the bulk β-*r*-B under high pressure at room temperature.

We compared effect of different Q values on the $N(E_F)$. Table I shows the model parameter T_0 of Mott's VRH model and $N(E_F)$ estimated with different Q values. It is seen that the $N(E_F)$ increases with increasing Q value. In this study, the Q value of the BNW should be higher than that of bulk β-*r*-B; therefore, its corresponding $N(E_F)$ is also high. When the BNW is superconducting, its T_c increases gradually with increasing pressure to 160 GPa. With further increase in pressure, T_c of the BNWs continues to increase linearly up to 200 GPa, as seen in Fig. 4(b). In the range from 200 to 240 GPa, the T_c and the value of dT_c/dP of the BNWs approaches that of the bulk β-*r*-B. This means that the size effect is negligible.

TABLE I. Parameter T_0 and $N(E_F)$ value of the BNWs with different Q values. In the estimations, we take $\xi=0.1$ nm.

T_0 (K)	$N(E_F)$ (/eV nm^3)	Q
8.3×10^5	267	1/3
2.5×10^7	8.9	1/4

In conclusion, superconductivity in BNWs with rhombohedral structure was studied under high pressure up to 240 GPa. Resistance measurements in a diamond-anvil cell show that the BNWs exhibit metallization at 28 GPa at room temperature and superconductivity at 1.5 K at 84 GPa where the bulk β-r-B is still a semiconductor. It was found that pressure has a positive effect on the T_c. The pressure coefficient of the BNWs is 0.02 K/GPa over the pressure range of 84–200 GPa, followed by increasing to the value of 0.04 K/GPa from 200 to 240 GPa as that of bulk β-r-B. We proposed that the size effect influences the pressure for metallization and superconducting transition of the BNWs in comparison with bulk β-r-B.

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