Synthesis of well-aligned boron nanowires and their structural stability under high pressure

2002 J. Phys.: Condens. Matter 14 11017

(http://iopscience.iop.org/0953-8984/14/44/420)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 11017–11021 PII: S0953-8984(02)37311-9

Synthesis of well-aligned boron nanowires and their structural stability under high pressure

Limin Cao[1,5], Jing Liu[2], Cunxiao Gao[3], Yancun Li[2], Xiaodong Li[2], Y Q Wang[4], Z Zhang[4], Qiliang Cui[3], Guangtian Zou[3], Liling Sun[1] and Wenkui Wang[1]

[1] Institute of Physics, Centre for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, China
[2] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China
[3] National Laboratory for Superhard Materials, Jilin University, Changchun 130023, China
[4] Beijing Laboratory of Electron Microscopy, Chinese Academy of Sciences, Bejing 100080, China

E-mail: caolm@aphy.iphy.ac.cn

Received 22 May 2002
Published 25 October 2002
Online at stacks.iop.org/JPhysCM/14/11017

Abstract

Owing to its unusual bonding and vast variety of unique crystal structures, boron is one of the most fascinating elements in the periodic table. Here we report the large-scale synthesis of well-ordered boron nanowires and their structural stability at high pressure. Boron nanowires with uniform diameter and length grown vertically on silicon substrates were synthesized by radio-frequency magnetron sputtering with a target of pure boron using argon as the sputtering atmosphere without involvement of templates and catalysts. Detailed characterization by high-resolution transmission electron microscopy and electron diffraction indicates that the boron nanowires are amorphous. Structural stability of the boron nanowires at room temperature has been investigated by means of *in situ* high-pressure energy-dispersive x-ray powder diffraction using synchrotron radiation in a diamond anvil cell. No crystallization was observed up to a pressure of 103.5 GPa, suggesting that the amorphous structure of boron nanowires is stable under high pressure at ambient temperature.

Boron and its compounds have attracted considerable experimental and theoretical interest because of the complexity of their uncommon structures based on regular B_{12} icosahedra or related icosahedral fragments such as the common structural elements and their unique and useful properties ranging from those of superconducting metals to those of wide-gap

[5] Author to whom any correspondence should be addressed.

insulators [1–5]. The superconductivity at 39 K in magnesium diboride is considered the most important discovery since that of the high-temperature superconductors [6, 7]. In addition, boron possesses a hardness similar to that of diamond, and has interesting and also useful thermoelectric and nuclear properties. Theoretical results on pure boron have indicated previously unknown boron structures, such as quasiplanar, tubular, spherical, and convex boron clusters, which are fundamentally different from the well-known boron crystals consisting mainly of B_{12} icosahedra [8–11]. However, none of the novel boron structures proposed has been fabricated experimentally. Here, we report large-scale synthesis of well-aligned boron nanowires without involvement of templates and catalysts and their structural stability at high pressure. Pressure is a useful tool both for the synthesis of new solid-state phases with advanced properties and for precise tuning of the structures and properties of existing phases of scientific or technological significance [12, 13]. Recently, Mao [14] found superconductivity in elemental β-boron at pressures above 160 GPa. Our experimental work adds the new aspect of one-dimensional nanowires and might introduce a new form of boron structure to investigations of superconductivity and other properties of elemental boron under high pressure.

The aligned boron nanowire array films were synthesized by radio-frequency (rf) magnetron sputtering of pure boron (purity 99.9%) in argon gas on Si substrates [15]. The nanowire samples were characterized using x-ray diffraction (XRD, Macscience M03XHF with Cu Kα radiation), scanning electron microscopy (SEM, S-4200), and a transmission electron microscope (TEM, CM200/FEG) equipped with a Gatan imaging filter (GIF).

Figure 1 shows SEM images of the well-oriented boron nanowire arrays grown perpendicularly on the surface of silicon substrates. The nanowire arrays can be easily stripped off (figure 1(a)) with tweezers, suggesting that the boron nanowires stand freely on the substrate surface. A high-resolution SEM image (figure 1(b)) provides more details of the morphology and alignment of the products. The boron nanowires, which are of uniform length and diameter around 40–50 nm, are parallel to each other and perpendicular to the substrate, forming self-oriented regular arrays. They have smooth surfaces and are straight along their axis. No metal nanoparticles can be found on the tips of the boron nanowires.

TEM observations reveal that the deposit is composed of wire-like structures with remarkably uniform diameters of about 40 nm. The nanowires are clean, smooth, and straight. No metal particles can be found at either end of the nanowires. Figure 2 shows a high-resolution transmission electron microscopy (HRTEM) image of the typical boron nanowire with a solid core. No crystalline fringes can be identified in the HRTEM image at the lattice-resolved scale. This indicates that the boron nanowires are amorphous.

The fact that there were no diffraction spots but some diffusive rings, as shown in the selected-area electron diffraction (SAED) pattern (figure 2, inset) of the boron nanowire, confirm the amorphous nature of the boron wires. Composition analysis using the electron energy-loss spectroscope (EELS) inside the TEM (CM200/FEG) and the energy-dispersive x-ray (EDX) spectroscope attached to the SEM (S-4200) revealed that the boron nanowires are composed of pure boron.

Prior to high-pressure experiments, the boron nanowire arrays were characterized using XRD. Figure 3 shows the XRD pattern of boron nanowire arrays grown vertically on a Si substrate. No diffraction peaks can be observed, further confirming the amorphous nature of the boron nanowires as demonstrated by TEM and SAED analysis.

We carried out *in situ* high-pressure energy-dispersive x-ray powder diffraction (EDXD) measurements at Beijing Synchrotron Radiation Facility (BSRF) using synchrotron radiation and a diamond anvil cell. Pressure was generated using diamond anvils with a 360 μm diameter flat culet which was combined with pressure determination equipment using gold as the x-ray diffraction reference. A mixture of methanol, ethanol, and H_2O (16:4:1) served as

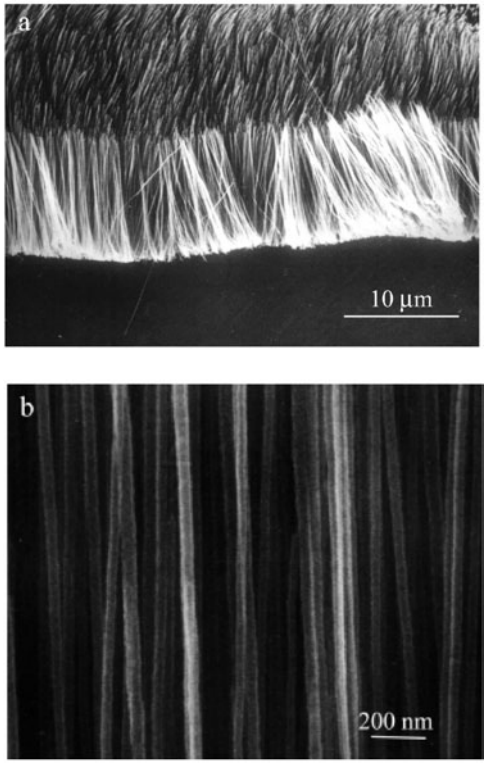

Figure 1. (a) A low-magnification SEM image of the vertically aligned boron nanowire arrays that grew uniformly on the substrate over large areas. (b) A high-magnification SEM image of the aligned boron nanowires with uniform sizes and distribution that grew perpendicular to the substrate surface.

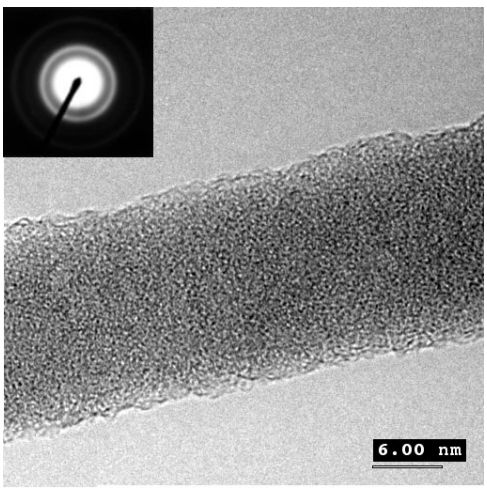

Figure 2. A HRTEM image of a typical boron nanowire. Inset: the SAED pattern taken from the nanowire showing some halo rings, which further confirms the amorphous nature.

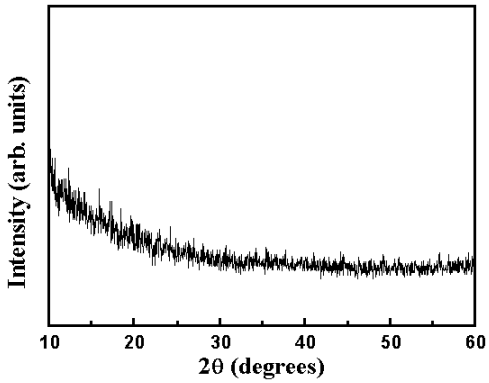

Figure 3. The XRD pattern of the aligned boron nanowire arrays.

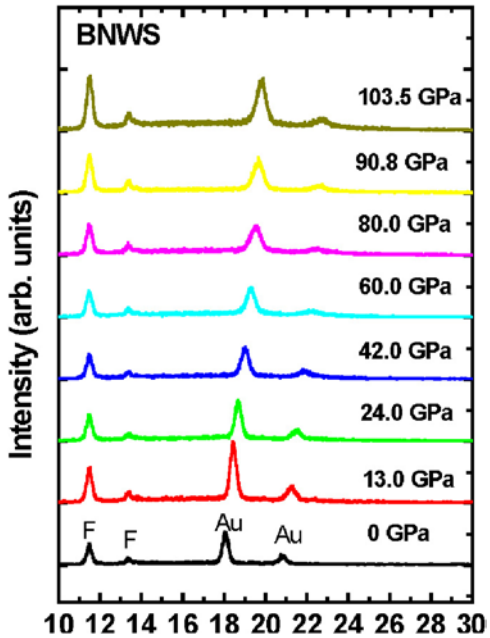

Figure 4. Synchrotron EDXD spectra of the boron nanowires mixed with a Au pressure standard at various pressures.

(This figure is in colour only in the electronic version)

the pressure medium. The boron nanowire samples peeled off from the Si substrate along with the gold powder, and the pressure medium was loaded into a hole of 100 μm diameter in a preindented gasket of 42 μm thickness. A microcollimated x-ray beam of 20 $\times$ 20 μm^2 was employed for the EDXD studies. All of the EDXD spectra were recorded by a Ge detector at $ED = 42.5313$ keV Å. A large number of EDXD spectra (figure 4) were recorded at pressures ranging from 0 to 103.5 GPa at room temperature with increasing pressure. Apart from the fluorescence peaks and the diffraction peaks from the Au marker, no crystalline Bragg reflections from the boron nanowire samples were observed, as shown in figure 4. This suggests that the amorphous structure of boron nanowires is stable up to 103.5 GPa, the highest

pressure achieved in the present study. After decompression to ambient pressure, the samples were taken out from the sample chamber and investigated using TEM. The wire-like structure of the samples disappears, but the dispersive halo rings in the SAED pattern revealed that the samples remained amorphous. Careful examinations showed that the diamond anvils suffered no damage and remained in good condition after decompression.

In summary, we have successfully fabricated large-scale arrays of vertically aligned boron nanowires with excellent uniformity and high density using a simple method of magnetron sputtering. Boron nanowire appears as a new member in the family of one-dimensional nanostructures that are critical building blocks in molecule-based miniature devices. Moreover, large-scale arrays of boron nanostructures provide exciting opportunities to understand more about boron, one of the most important and interesting elements. We have also investigated the structural stability of the boron nanowires under pressures up to 103.5 GPa in a diamond anvil cell by EDXD using synchrotron radiation. Our results suggest that the amorphous structure of boron nanowires is stable under high pressure at ambient temperature. Our results introduce a new form of boron that can be used to probe the unique structures and properties in elemental boron under high pressure. It is reasonable to expect boron nanowires to display some exceptional properties that are different from those of bulk boron at high pressure.

References

[1] Emin D 1987 *Phys. Today* **20** 55
[2] Donohue J 1982 *The Structure of the Elements* ed E Robert (Malabar, FL: Krieger)
[3] Newkirk A E 1964 *Boron, Metallo-Boron Compounds and Boranes* ed R M Adams (New York: Interscience)
[4] Greenwood N N 1973 *Comprehensive Inorganic Chemistry* vol 1, ed J C Bailar, H J Emeléus, R Nyholm and A F Trotman-Dickenson (Oxford: Pergamon) p 665
[5] Matkovich V I (ed) 1977 *Boron and Refractory Borides* (New York: Springer)
[6] Nagamatsu J *et al* 2001 *Nature* **410** 63
[7] Cava R J 2001 *Nature* **410** 23
[8] Boustani I, Rubio A and Alonso J A 1999 *Chem. Phys. Lett.* **311** 21
[9] Gindulyte A, Lipscomb A N and Massa L 1998 *Inorg. Chem.* **37** 6544
[10] Gindulyte A, Krishnamachari N, Lipscomb M N and Massa L 1998 *Inorg. Chem.* **37** 6546
[11] Boustani I, Quandt A, Hernandez E and Rubio A 1999 *J. Chem. Phys.* **110** 3176
[12] Badding J V 1998 *Annu. Rev. Sci.* **28** 631
[13] Holzapfel W B 1996 *Rep. Prog. Phys.* **59** 29
[14] Mao H K 2001 private communication
[15] Cao L M *et al* 2001 *Adv. Mater.* at press