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Synthesis of crystalline boron nanowires by laser ablation

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Crystalline boron nanowires with tetragonal structure have been synthesized based on laser ablation of a B/NiCo target; the nanowires are sometimes single crystals and have a droplet at one end of the nanowire; the droplet contains B, Ni and Co elements, which indicates that the vapor–liquid–solid (VLS) mechanism may play a key role in the growth of the boron nanowires.

After the discovery of carbon nanotubes,[1] one-dimensional nanomaterials have been attracting increased interest. Among many one-dimensional nanomaterials, boron nanowires or nanotubes are very attractive due to the special properties of boron and its one-dimensional nanomaterials. Boron has a high melting temperature, low density, as well as hardness close to that of diamond. It is also well known that boron is a promising material for high-temperature devices, light-weight protective armor and some products used in the nuclear industry.[2–4] Although boron nanotubes have not been fabricated so far, theoretical calculation shows that the boron nanotubes have higher electrical conductivity than carbon nanotubes.[5,6] On the other hand, experiment shows that crystalline boron nanowires are semi-conducting and exhibit electrical properties consistent with those of elemental boron.[7] In addition, boron nanowires can be used as templates to synthesize MgB_2 nanowires.[8] However, the synthesis of boron nanowires, especially crystalline boron nanowires, is still a challenging issue. Last year, only amorphous boron nanowires were synthesized by two groups respectively.[8,9] Very recently, crystalline boron nanowires have been synthesized by a chemical vapor deposition (CVD) reaction of diborane (B_2H_6) in Ar gas. However, the reported nanowires have twinned structure and the crystal structure does not belong to any of the known boron structures.[7] In this communication, the synthesis of single crystalline boron nanowires based on a laser ablation method is reported.

Samples were prepared by laser ablation[10] of a boron rod doped with 10 wt% of a 50 : 50 mixture of Ni and Co powders. A Nd/YAG laser was used with 532 nm wavelength, 10 Hz frequency, 3.5 W power. The B/NiCo target was placed in a furnace kept at 1250 °C in a vacuum (5–7$\times$10^4 Pa) 80 sccm flowing Ar gas and evaporated by the laser beam for 30 min.[11]

In our work, although there is deposition at the downstream end, this deposition is of particles other than nanowires. Scanning electron microscopy (SEM) study shows that the nanowires are grown at the surface of the target and the morphologies of the products depend on the positions of the products. On the surface of the pore made by the laser beam, no nanowires are seen. At the periphery of the pore, needle-shaped rods as well as nanowires are found as shown in Fig. 1a. The diameter of the rods is about 1 micron and the aspect ratio is less than 10. At one end of these rods, there is a droplet whose diameter is larger than that of the related rod. The nanowires are also observed in this area and the diameters of these nanowires are less than 100 nm. In between the edge of the target and the pore made by the laser beam, a number of nanowires are observed. These nanowires have diameters less than 100 nm and the aspect ratio is lager than 10 (Fig. 1b). In Fig. 1c, the corresponding transmission electron microscopy (TEM) image is given. Some nanowires are found to have a droplet at one end, similar to needle-shaped rods.

These nanowires are crystalline and are likely to be single crystals. Selected area electron diffraction (SAED) of an individual nanowire and diffraction rings of a cluster of nanowires are shown in Fig. 2a and Fig. 2b, respectively. Comparison of inter-plane spacing and their corresponding intensities with an X-ray diffraction card (74-0945) suggests that these nanowires have tetragonal structure with lattice parameters a = 0.875 nm, c = 0.506 nm. Because some rings

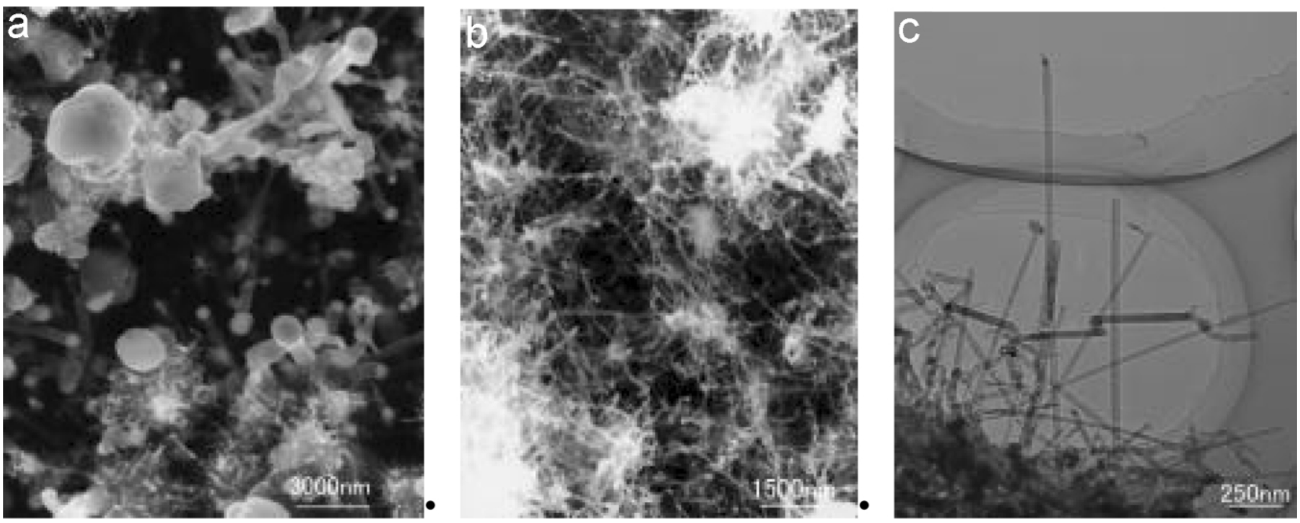

Fig. 1 Images of the boron nanowires obtained at different positions on the surface of B/NiCo target (a) near the pore made by the laser beam, (b) in the middle between the pore and the edge of target, (c) TEM image of B nanowires from (b).

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are so close to each other, we do not mark the lattice indices for these rings. The lattice indices of an individual nanowire has been determined as shown in Fig. 2a. These indices support the nanowire being a single crystal, although there are some polycrystalline B nanowires found in our work.

Electron energy loss spectra (EELS) (Fig. 3) show that the main component of the nanowires is boron while the droplet consists of B, Ni and Co. The last two elements are catalysts used in the present work. We have also tried to synthesize boron nanowires without catalysts, but only few nanowires have been found. This fact suggests the catalysts (Ni, Co) play a key role in the formation of boron nanowires and a VLS mechanism may be the most probable growth mechanism in our work. The diameters of the nanowires grown through VLS mechanism are usually affected by the synthesis temperatures.[12] The spot where the laser beam hits should have very high temperature, which would lead to an increase of the temperature of the target. With increase of distance from the spot, the temperature decreases. In a certain range, the lower synthesis temperature will lead to a smaller diameter of nanowire.[12] Therefore, at the periphery of the pore generated by laser ablation, the boron nanowires have larger diameters while the nanowires grown in the middle between the pore and the edge of the target are usually thinner.

In summary, crystalline boron nanowires with tetragonal structure are synthesized by a laser ablation method. The growth mechanism of the boron nanowires can be attributed to a VLS model. Because few boron nanowires grow in the downstream end, in contrast to the usual nanowires/nanotubes fabricated by laser ablation, further study of the growth mechanism is necessary, which may provide some beneficial results towards the synthesis of other kinds of nanowires. Additionally, the present crystalline boron nanowires may provide more possibilities of finding new applications for this one-dimensional nanomaterial.

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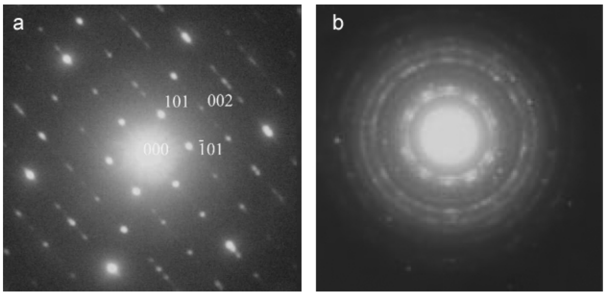

Fig. 2 (a) SAED of an individual B nanowire, (b) diffraction rings of a cluster of nanowires.

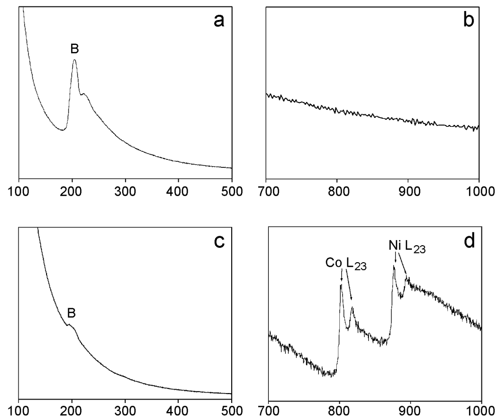

Fig. 3 EELS spectra of the B nanowire (a) and (b) EELS spectrum from the B nanowire, (c) and (d) EELS spectrum from the droplet at one end of the B nanowire.

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