O U R N A L O F

Ceramic Processing Research

Growth of crystalline boron nanowires by pulsed laser ablation

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Crystalline boron nanowires were grown on Pt coated sapphire substrates using pulsed laser ablation at different temperatures under a pressure of 50 Pa. High-resolution TEM and transmission electron diffraction (TED) analyses were performed to determine the crystal structure of these nanowires. These nanowires had diameters ~100 nm and lengths in the micrometer range. Systematic analyses showed that a vapour-liquid-solid (VLS) mechanism plays an important role in the growth of boron nanowires. The role of the Pt catalyst in the synthesis of boron nanowires is also discussed.

Key words: Boron, Nanowire, Pulsed Laser ablation, HR-TEM, VLS growth.

Introduction

Boron and its related nanostructures have attracted increasing interest for their potential applications in nanotechnology owing to their extraordinary properties, such as high melting point (~2300 °C), low density (d=2.35 g/cm⁻¹), good resistance to corrosion, and hardness (Hv = 3000 kg) [1]. Moreover, boron and boron-rich compounds are semiconductors with unique electronic properties that are controlled by their icosahedral structure.

Recently, nanoclusters of quasicrystalline boron, with convex, spherical, quasi planar and tubular geometries, were calculated from an *ab initio* study, in which the basic unit cells of these quasicrystalline boron nanoclusters are composed of two different rhombohedral cells containing B_{12} icosahedra [2]. These boron nanotubular clusters are predicted to be metallic conductors independent of the structural chirality with stronger covalent intertubular bonds than CNTs via van der Waals bonding. Owing to these potential properties, boron is a good candidate for use in high-temperature devices, fusion reactor wall components, thermoelectric energy converters and elemental semiconductors [1].

Recently, some experimental research has been carried out on boron nanostructures. Single-wall boron nanotubes (BNTs) were reported by Ciuparu *et al.* [3] but they had high sensitivity to electron beam damage leading to difficulty in the detailed characterization of the tubular structures. Several groups synthesized amorphous or crystalline boron nanowires (BNWs) by RF magnetron sputtering [4], laser ablation [5, 7] and chemical vapor deposition [8]. BNW growth by a vapor-liquid-solid (VLS)

*Corresponding author: Tel : +82-41-550-3536 Fax: +82-41-550-3536 mechanism had been proposed [5] but no tip attachment of the catalyst particles was found at the end. In addition, this mechanism cannot be applied to BNWs formed without a catalyst on various substrates [4, 8]. Another suggestion of a vapor-solid (VS) growth mechanism [6, 7] was proposed in that the solidification of boron or boron oxide vapour could be the key to explaining BNW growth. However, it is unclear if factors, such as the supersaturation level of the B precursors in the vapour phase and the complex structure of boron clusters, play a role in the anisotropic growth of boron wires.

In this study, crystalline boron nanowires were fabricated on Pt coated sapphire substrates using pulsed laser ablation. The effects of the preheating-temperature on the production of catalyst dots were investigated. The role of the Pt catalyst in the synthesis was also demonstrated.

Experimental

A third harmonic Nd : YAG laser (wavelength = 355 nm, pulse width = 5 to 7 ns, repetition rate = 1 Hz) was used for ablation. Fig. 1 shows a schematic diagram of the experimental apparatus. The chamber for nanowire preparation was a quartz glass tube placed in an electric



Fig. 1. Experimental set up for the boron nanowires preparation by laser ablation.

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furnace. The laser was introduced through a quartz glass window at the end of the tube and a target was irradiated with a pulsed laser with an energy of 250 mJ/ and a spot size of 3.2 mm².

A hot-pressed boron pellet (99.5%) purchased from Kojundo Chemical Laboratory was mounted as the target on a rotating holder placed at the center of the furnace. For catalyst dots, a sapphire substrate (C-plane) was coated with Pt by electron beam deposition. A substrate was located just below the pure boron target. The flow rate of argon gas was 5.0 sccm (standard cubic centimeters per minute) and the pressure in the chamber during deposition was 50 Pa. The preheating temperature for preparing the Pt dots was varied from 850 °C to 950 °C for 1 hour. During laser ablation, the temperature of the furnace was varied from 850 °C for 1 hour.

X-ray diffraction (XRD, Rigaku, RAD-C) was used to examine the phases of the boron nanowires. The morphology was characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). An energydispersive X-ray (EDX) spectroscopy system attached to the FE-SE microscope was used to analyze the chemical composition of the products.

Results and Discussion

Boron nanowires were synthesized on Pt coated sapphire substrates by laser ablation at various temperatures. Fig. 2 shows the typical XRD patterns of the boron nanowires deposited at 50 Pa with a 250 mJ/pulse at temperatures ranging from 850 °C to 950 °C for 1 hour. Crystalline boron was not observed in the sample deposited at 850 °C. However, crystalline boron with a b-rhombohedral and a-tetragonal phase could be obtained at temperatures > 900 °C. The peak observed at 22.7° 20 was assigned to the (111) peak of a-tetragonal boron. The (111) peak increased with increasing temperature from 900 °C to 950 °C. Hence, the optimal fabrication condition for crystallized a-tetragonal boron nanowires was 950 °C. Crystallized boron films are generally grown above 1200 °C by CVD



Fig. 2. XRD patterns of boron nanowires deposited at 50 Pa with a 250 mJ/pulses at various temperatures.

method [9, 10], and more than 1100 °C is needed for to prepare crystallized nanowires by CVD [11]. In a previous report [7], well-crystallized a-tetragonal boron nanobelts were fabricated at 20 Pa at temperatures ranging from 700 °C-900 °C. However, the growth mechanism was unclear.

High-resolution TEM observations and transmission electron diffraction (TED) analyses were performed to determine the crystal structure of these nanowires. Fig. 3 represents a HR-TEM image of the nanowires obtained at 950 °C and 50 Pa. The nanowires were composed of a well-crystallized phase with a width of approximately 100 nm. TEM revealed the presence of straight nanowires with Pt particles at their tips. When Pt catalyst particles are involved in growth, their sizes determine the diameter of the nanostructures. Owing to the thick Pt film (100 nm in this case), most of the Pt islands had a diameter of approximately 100 nm. The weight of the large catalyst islands prevented them from rising up during growth. The nanostructures were characterized by electron diffraction, which revealed a crystalline boron phase. These results are also consistent with the XRD, shown in Fig. 2.

Fig. 4 shows typical FE-SEM images of boron nanowires with diameters of ~ 100 nm and lengths in the micrometer range. Most of the Pt catalyst particles formed due to surface tension during the heating process were almost the same diameter as the boron nanowires.

The composition of the deposited nanostructures was



Fig. 3. HR-TEM image of a boron nanowires obtained at 950 °C and 50 Pa, and the selected area diffraction patterns (SAED). (a) : SAED pattern from the Pt tip and (b) : SAED pattern from boron nanowires.



Fig. 4. SEM images of boron nanowires obtained at 950 °C and 50 Pa along with an EDAX spectrum.



Fig. 5. Schematic diagram of the proposed growth mechanism for Pt-catalyzed boron nanowires.

determined by the EDX analysis, as shown in Fig 4. The main constituents in the surface deposits were B, Pt, O, and Al, in which Pt was from the catalyst thin film, and Al and O were mainly from the sapphire substrate. The percentage of B was approximately 92.97 at%, and no appreciable amount of N (0.73 at%) was detected. The nitrogen could be attributed to contamination from chemical adsorption after sample preparation.

A VLS growth mechanism clearly plays an important role in the growth of boron nanowires in this study. The droplet composed of a Pt catalyst particle and B were observed in one end of the nanowires (Fig. 3), which is a property of the VLS growth mechanism. Heating the substrate with a very thin Pt film results in the formation of small Pt nuclei due to surface tension. Subsequently, boron particles are produced during the laser ablation of a boron target. The decomposed B might react with the Pt catalyst to form Pt borides (B2Pt3, BPt3) on the surface of the Pt catalyst paricles, which can decrease the melting point of Pt dramatically from 1772 °C to 790-890 °C. On the other hand, the size effect of the nanoscale structures can result in a further decrease in melting point, compared to the bulk material [12]. Both these facts help produce a liquid phase on the Pt droplets. The continuous supply of B from the B target migrates into Pt droplets and reacts with the Pt particles, leaving a coexisting system of Pt and PtB. When the dissolved B reaches its saturation limit, it will precipitate and accumulate on the Pt particles. Since Pt particles cannot grow during the growth of nanowires, there is no likelihood of secondary nucleation occurring, which leads to the BNWs, as shown in Fig. 5.

Conclusions

Crystallized B nanowires with a diameter of ~100 nm and length in the micrometer range were grown on Pt coated sapphire substrates by a laser ablation method in a furnace at a temperatures ranging from 900 to 950 °C in 50 Pa of argon. TEM revealed the presence of straight nanowires with Pt particles at their tips. The size of the Pt catalyst particles determines the diameter of the resulting B nanostructures. A VLS growth mechanism was suggested for the growth of straighter and size-dependent B nanowires.

Acknowledgements

This study was conducted by the research fund of Dankook University in 2010.

References

- 1. Y. Kumashiro, "Electric Refractory Materials," (Marcel Dekker, NewYork, NY,USA, 2000)
- I. Boustani, A. Quandt and A. Rubio, J. Solid State Chem. 154 (2000) 269-274.
- 3. D. Ciuparu, R.F. Klie, Y. Zhu and L. Pfefferle, J. Phys. Chem B 108 (2004) 3967-3969.
- L. Cao, Z. Zhang, L. Sun, *et al.*, Advanced Materials 13 (2001) 1701-1704.
- 5. Y. Zhang, H. Ago, M. Yumura, *et al.*, Chem. Comm. 23 (2002) 2806-2807.
- X.M. Meng, J.Q. Hu, Y. Jiang, C.S. Lee and S.T. Lee, Chem. Phys. Letts. 370 (2003) 825-828.
- Z. Wang, Y. Shimizu, T. Sasaki, K. Kawaguchi, K. Kimura and N. Koshizaki, Chem. Phys. Letts, 368 (2003) 663-667.
- C.J. Otten, O.R. Lourie, M.-F. Yu, *et al.*, J. Amer. Chem. Soc. 124 (2002) 4564-4565.
- Y. Kumashiro, T. Yokoyama, A. Sato and Y. Ando, J. Solid State Chem. 133 (1997) 341-321.
- N.A. Sezgi, T. Dogu, H.O. Ozbelge, Chem. Eng. Process 40 (2001) 525-530.
- C.J. Otten, O.R. Lourie, M.F. Yu, J.M. Cowley, M.J. Dyer, R.S. Ruoff and W.E. Buhro, J. Amer. Chem. Soc. 124 (2002) 4564-4565.
- N.A. Sezgi, T. Dogu and H.O. Ozbelge, Chem. Eng. Sci. 54 (1999) 3297-3304.