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Morphology and diameter controllable synthesis of boron nanowires

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Different morphology and diameter boron nanowires were synthesized by means of chemical vapor deposition on silicon substrates through controlling the growth temperature and the thickness of catalyst Au films. Smooth boron nanowires were fabricated at the temperature ranged from 800 to 900°C. The diameter of boron nanowires increased slightly with the growth temperature increasing. Boron nanochains with the periodic modulated diameter could be fabricated at the temperature of 950°C. As the thickness of Au films increases, the diameter and length of boron nanowires increase dramatically. The growth process of boron nanowires and nanochains was also discussed. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Among one-dimensional nanomaterials, boron nanowires (BNWs) and nanotubes are very attractive due to the special properties of boron. Boron has a high melting temperature, low density, as well as hardness close to that of diamond. It is a promising material for high-temperature devices, low-weight protective armor and some products used in the nuclear industry. The recent discovery of superconductivity at 39 K in MgB_2 has triggered an intensive interest in boron and boride compounds [1]. Boron nanotubes, contrary to carbon nanotubes are predicted to be metallic and not to be susceptible to electromagnetron [2], which provide possibility for potential applications. More than ten years ago, β-rhombohedral boron whiskers and platelets have been prepared by S. Komatsu [3] in plasma enhanced chemical vapor deposition (PECVD), they also studied the transition from amorphous to crystal growth of boron films in PECVD [4]. During the past few years, amorphous boron nanowires have been synthesized by radio frequency (RF) magnetron sputtering [5, 6], laser ablation [7] and physical vapor transport deposition method [8]. Crystalline boron nanowires have been synthesized by laser ablation [9] and chemical vapor deposition (CVD) [10, 11]. Boron nanowire Y-junction and nanowire joints have also been synthesized by thermal vapor transport process [12]. The temperature ramping rate in the cooling process after the high-temperature growth of the BNWs was found to be good for controlling the alignment of BNWs [13]. And the experiments showed that crystalline boron nanowires are semiconductor and their electrical properties are consistent with those of elemental boron [10]. Pure boron single-wall nanotubes have been synthesized by reaction of BCl_3 with H_2 over an Mg-MCM-41 catalyst with parallel, uniform diameter cylindrical pores [14]. Among the various methods used for nanowire fabrication, CVD method using metals as catalysts, allowing controlled and selective growth of nanowires

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by patterning metal on the substrate, is an effective and promising method for the growth of nanowires.

Recently, several new morphologies of nanowires such as tadpole-like Si nanowires [15], chain-like Si nanowires [16], helical self-assemble SiO_2 nanowires [17], Y-junction AlN nanowires [18] have been reported. And it was also found that the diameter and morphology of Si nanowires mainly depended on the growth temperature [19]. However, the diameter and morphology controllable synthesis of boron nanowires is still a challenge so far.

Aligned boron nanowires [11] and MgB_2 nanowires [20] have been synthesized by our group by means of CVD and subsequent process using nanochannel-Al_2O_3 as the substrates. In this paper, we report our recent study of the morphology and diameter controllable synthesis of boron nanowires on silicon substrates by CVD using Au as the catalyst.

2. Experimental

The experimental apparatus consists of a horizontal tube furnace (75 cm in length), a reacting chamber made of quartz tube (Φ5.5 × 150 cm), a rotary pump system, and a gas supply and control system. The ultimate vacuum for this configuration is ~20 Pa. Several silicon (100) substrates coated with Au films as the catalysts were placed in the center of the furnace for collecting growth products. Au films with the thickness of about 5 nm as the catalysts were deposited on silicon (100) substrates for 30s by RF magnetron sputtering system. The thickness of Au could be controlled through varying the time of sputtering. The reacting chamber was pumped down to 20 Pa and heated under N_2 flow. Before growing boron nanowires, the Au coated substrate was annealed at 800°C in N_2 flow for 1 h to break the Au film into catalyst islands. As the temperature reached to the scheduled temperature, the mixture gas of nitrogen, hydrogen and diborane with a flow ratio of 10:50:1 was allowed into the chamber. The holding temperature varied from 750 to 1000°C. The pressure in the chamber was kept at 5×10^4 Pa. After deposition for 5 h, the furnace was cooled down, and the products were removed out and characterized by field emission scanning electron microscopy (FESEM, Siron, FEI) equipped with energy dispersive X-ray spectrometer (EDX, GENESIS4000, Philips). Then the nanowires were ultrasonically separated from the silicon substrates and characterized by transmission electron microscopy (TEM, CM200, Philips) and selected area electron diffraction (SAED).

3. Results and discussion

FESEM images of the boron nanowires grown at 750, 800, 900, and 950°C are shown in Fig. 1a–d, respectively. It can be seen that the nanowires grown at 750°C are rough in surface and connected with each other (Fig. 1a). They look like a crazed film. Actually, only amorphous boron films but no boron nanowires could form as the reaction temperature was lower than 750°C. The smooth boron nanowires were fabricated at the temperatures ranged from 800 to 900°C. And the boron nanochains could be prepared at 950°C. The nanochains have a wire-like structure; however, their diameters are periodically modulated. The mean diameter and spacing of the nanospheres

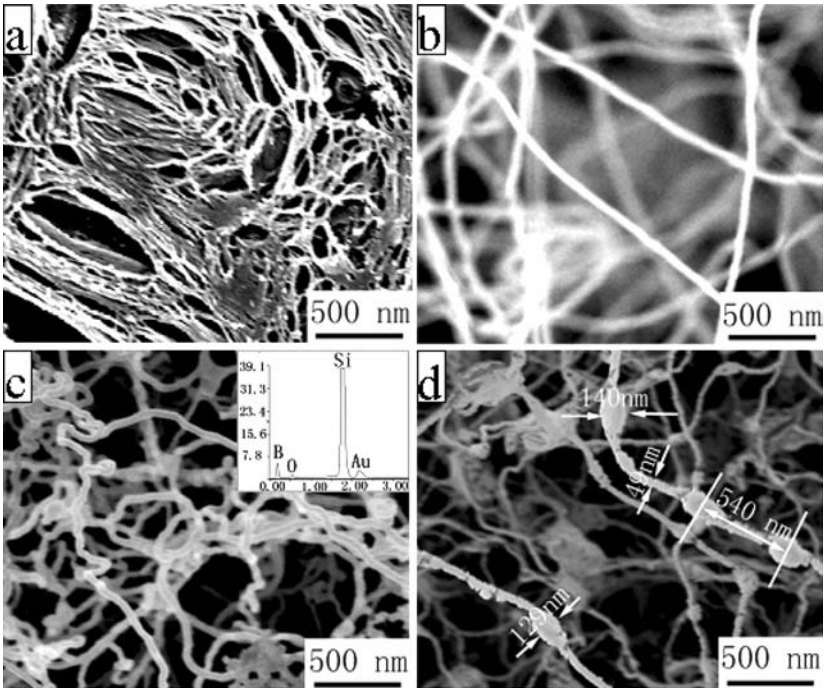

Figure 1 FESEM images of the boron nanowires synthesized by CVD on the silicon substrates at 750°C (a), 800°C (b), 900°C (c) and 950°C (d), respectively, when the the thickness of catalyst Au film was 5 nm. The inset in Fig. 1c is EDX spectrum of the boron nanowires synthesized at 900°C.

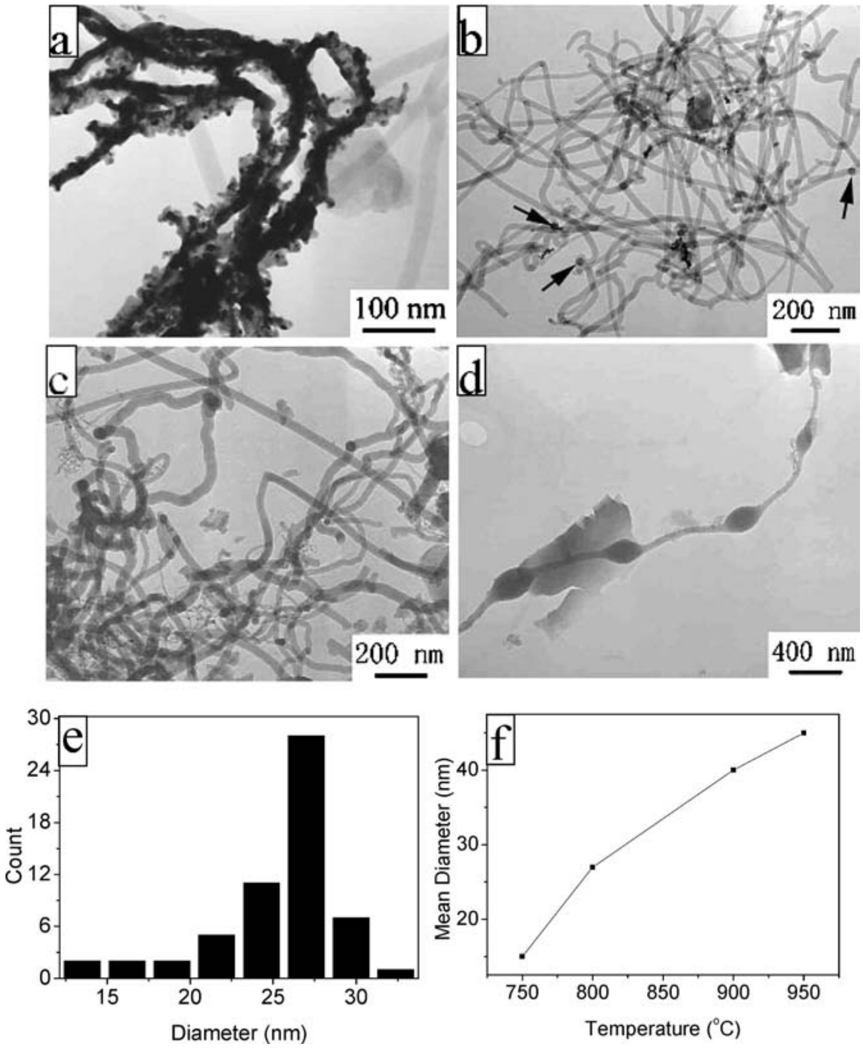

Figure 2 TEM images of the boron nanowires synthesized at 750°C (a), 800°C (b), 900°C (c), and 950°C (d), respectively, while the thickness of catalyst Au film was 5 nm. (e) A typical size histogram for the boron naowires prepared at 800°C. (f) Mean diameter of the boron nanowires as a function of temperature.

in the nanochains are about 140 and 550 nm, respectively. The diameter of the necks is about 45 nm. The ratio of spacing to diameter of a knot is about 4.0 in an array of nanospheres. The EDX spectrum of the boron nanowires synthesized at 900°C is shown in the inset of Fig. 1c. Only boron, traces of oxygen, silicon and gold were detected. The gold originated from both the Au catalyst and the gold film sputtered on the nanowires for SEM investigation and the silicon originated from the silicon substrate. The atomic ratio of B:O:Si is 91.39:3.10:5.50, indicating that the as-synthesized nanowires are boron nanowires. The nanowires synthesized at the other temperatures were also analyzed by EDX, and the spectra are similar to that shown in the inset of Fig. 1c. But the amount of oxygen increases a little with the temperature increasing. The amount of oxygen on the necks is larger than that on the nanospheres.

TEM images of the nanowires are depicted in Fig. 2, and the results are consistent with the results measured by the FESEM. SAED pattern of the nanowires shows that most of the nanowires are amorphous. The size distribution and mean diameter of the boron nanowires grown at different temperature were calculated from the TEM and FESEM images. A typical size distribution of the boron nanowires grown at 800°C is depicted in Fig. 2e, which indicates that the distribution of the wire diameter is narrow around 27 nm. The mean diameter of the boron nanowires as a function of the growth temperature is shown in Fig. 2f, which shows that the diameter increases with the temperature increasing. Additionally, we can see that the nanowires terminate at one end in a nanoparticle (marked by dark arrows in Fig. 2b) that is composed of Au, Si and boron analyzed by EDX. The presence of this alloy droplet suggests the well-known vapor-liquid-solid (VLS) process [21–23] as the growth mechanism.

The diameter of the boron nanowires could be controlled through controlling the thickness of the gold films. Nanowires with diameter of about 1 um formed when the RF sputtering time was 4 min and the thickness of

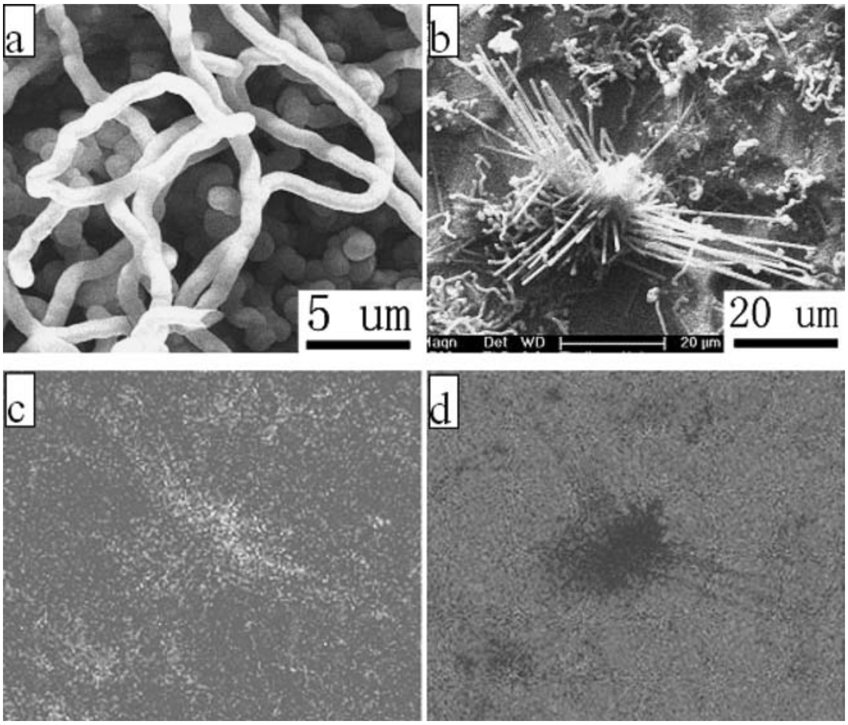

Figure 3 FESEM images of the boron nanowires synthesized at 900°C when the thickness of catalyst Au film was 200 nm. (a) FESEM image of the curved boron nanowires. (b) FESEM image of a straight boron nanowire-flower. (c, d) Elemental mapping of the boron and silicon for the boron nanowire-flower, respectively.

the gold was about 200 nm (Fig. 3a). And the length of the nanowires also increased as the diameter of the nanowires increased. Some ultra-long boron nanowires as long as several millimeters were observed in the products. And the morphology of the nanowires became uneven when the thickness of Au films increased. Besides curved nanowires, some straight boron nanowire-flowers can also be observed (Fig. 3b). Elemental mapping of boron (Fig. 3c) and silicon (Fig. 3d) is achieved from a boron nanowire-flower. The density of white spots represents the elemental distribution. It can be seen that the distribution of boron and silicon is opposite. And the elemental mapping of oxygen shows that oxygen locates evenly on the substrate and the amount of oxygen is small (not shown). The atomic ratio of B:O:Si in a single nanowire is 97.07:2.17:0.76. The result unambiguously shows that the nanowires are made up of boron naowires. The study of the VLS growth kinetics of Si whiskers indicated that thick whiskers tended to grow faster than thin ones [22]. This trend seems also true for boron nanowires growth.

In order to understand the detail growth process of the boron nanowires, some other substrates were introduced to grow the nanowires, including bare silicon substrates without Au films and quartz plates coated with Au films. Boron nanowires couldn't form on both of the substrates, only particles were observed. Of course, if the temperature is high enough and the vacuum system is good enough, we think boron nanowires can also be fabricated on other substrates in a proper condition.

As we can see, VLS growth mechanism works for the growth of the boron nanowires in the present work. And we believe that the coexistence of Au and Si is critical for the easy formation of liquid alloy droplets and the initiation of VLS nanowire growth. In fact, the eutectic temperature in B/Au binary phase diagram is as high as 1056°C at 1 atm while it's only 363°C for Si/Au system. Considering the low eutectic temperature of Si/Au, it is suggested that Si/Au eutectic alloy droplets should form first before the growth of boron nanowires. So the growth process might be as that shown in Fig. 4. First, the Au film became Au/Si liquid droplets when the substrates coated with Au film are annealed at high temperature (Fig. 4a and b). Then boron clusters originated from the decomposition of diborane diffuse into the Au/Si liquid droplets to form Au/Si/B liquid droplets. As boron concentration is supersaturated, boron nanowires will protrude (Fig. 4c). Smooth surface boron nanowires formed when the reaction temperature is from 800 to 900°C (Fig. 4d). This method, adding third substance or use proper substrates to form low eutectic temperature droplets with the traditional metal catalyst such as Au and using this droplets induce the growth of nanowires, may be used to grow other nanowires in relative low temperature.

The diameter increases with the temperature increase, which can be explained by the change of the contact angle (θ) with temperature between the liquid droplets and the substrates or solid nanowires, according to Young's

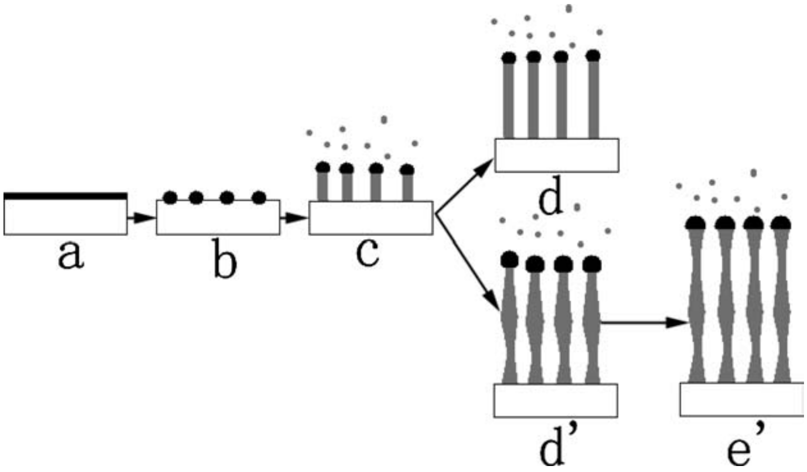

Figure 4 A schematic description for the growth process of boron nanowires and nanochains.

equation expressed as follows:

$$\cos\theta = \frac{\sigma_{S-V} - \sigma_{S-L}}{\sigma_{L-V}} \tag{1}$$

Here, σ_{S-V}, σ_{S-L} and σ_{L-V} represents the surface tension of solid-vapor, solid-liquid and liquid-vapor, respectively. σ_{S-L} and σ_{S-V} are almost unchanged while σ_{L-V} changes with the alteration temperature. Since σ_{L-V} decreases with the temperature increase, accordingly the contact angle between the solid nanowire and the liquid droplet decreases, then the interface area and the diameter of the nanowire increase slightly.

When the temperature was about 950°C, the boron nanochains formed (Fig. 2d), which is due to the periodic instability (self-oscillations) of the catalyst droplets (Fig. 4d′ and e′), as same as the formation of silicon nanochains reported in the previous work [24–26]. In general, the periodic instability of the catalysts can be explained by the positive feedback mechanism and the limitation of avalanche process [24, 26]. The positive mechanism can be assumed as followings: if, as a result of a fluctuation, the curvature of a droplet increases, the solution supersaturation which depends on the curvature decreases, the roughness decreases, and the contact angle that depends on the kinetic roughness increases, then the curvature of the droplet increases further, and so on. In such a sequence of the events, the droplet is constricting. However the sequence will not carry through continuously for the limitation of the avalanche process. There are two interfaces in the VLS growth: the vapor-liquid and the liquid-solid interface. On the first interface where catalytic chemical reactions take place by which the growth material (in our case boron) evolves; this interface can be called the “supplying” interface. On the second interface the material is deposited and the interface can be referred to “consuming” one. The material is transported from the supplying to the consuming interface by diffusion. Hence, the interface supersaturation also depends on the ratio of the supplying and consuming surfaces, $S_{\text{supl}}/S_{\text{cons}}$. When the droplet constricts, the ratio increases, which is equivalent to the decrease of the solution supersaturation. Then a moment will come when the two opposing processes are equalized and a further constriction will stop. In the opposite case, the sequence will be reversed and the droplet is extending, and $S_{\text{supl}}/S_{\text{cons}}$ decreases, the extension will also stop when the two opposing processes are equalized.

Finally, it is noted that the nanowires here are amorphous boron nanowires other than crystalline ones compared with the results in S. Komatsu’s paper [3]. Two main factors may engender the difference. First, the borane-concentration in our experiments is relative higher (1.6% other than about 0.5% in the cited paper). High borane-concentration in the reaction zone is favorable for amorphous growth [3, 4]. Second, the growth temperature needed for crystal growth in pyrolytic CVD is relatively higher than that in PECVD for the absence of plasma [4].

4. Conclusions

Boron nanowires and nanochains were synthesized by means of chemical vapor deposition on silicon substrates. The growth temperature of the nanowires relatively decreased through forming low eutectic droplets of trinary phase. The diameter of the boron nanowires could be controlled through controlling the thickness of the catalyst Au films. The morphology of boron nanowires depends on decomposition temperature. Boron nanochains with the periodic modulated diameter could form when the temperature at 950°C. VLS growth mechanism works for the growth of the as-synthesized boron nanowires. The growth of the boron nanochains could be explained by the positive feedback mechanism and the limitation of avalanche process.

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