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## Crystalline boron nanowires grown on the diamond surface

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#### ARTICLE INFO

#### ABSTRACT

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#### 1. Introduction

Since the discovery of carbon nanotubes (CNTs) in the early of 1990s, one-dimensional nano-materials have attracted intense attention. As the nearest neighbor of carbon, Boron has extraordinary properties of high melting temperature, low density, good resistance to corrosion, as well as hardness closed to that of diamond due to its icosahedra structure [1]. Studies on boron nanostructures have been more and more attractive in the recent years. Theoretical predictions indicate that boron-related nanostructure materials are expected to be candidates for nanoscales inter-connect application [2] and hydrogen storage media [3]. And a systematic study of the stability and electronic and magnetic properties of boron nanowires using the spin-polarized density functional calculations [4] are applied to demonstrate that the considered boron nanowires possess the direction dependence of ferromagnetic and semiconducting behaviors, which seem to open a window toward the applications of boron nanowires in electronics, optoelectronics [5], and spin electronics. In the last several years, a quantity of effort has been performed on synthesis of boron nanowires by means of different methods on various substrates, and a great progress has been obtained up to now [6–10]. Cao et al. reported the growth of amorphous BNWs by radiofrequency (RF) magnetron sputtering on the Si (100) substrate [11–14], where the formation of boron nanowire arrays is independent of the nature of the substrate, Wang and coworkers

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Crystalline boron nanowires (BNWs) have been grown on the entire surface of diamond powders by a solid–solid reaction approach. A series of analysis technique were employed to investigate the as-grown BNWs. The as-grown BNWs are in length of several micron-meters with the diameter ranging from 20–200 nm. And the BNWs crystalline structure is identified to be tetragonal structure. Systematic analyses reveal that the growth models such as classic VLS (vapor–liquid–solid) model are not applicable to explain this kind of BNW's growth mechanism. Hereby, an extended VLS model is proposed which can perfectly interpret the BNW's growth process on diamond surface and match experiment results very well.

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CRYSTAL GROWTH

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produced crystalline BNWs through post-annealing amorphous B nanowires synthesized by radiofrequency magnetron sputtering [15]. Otten et al. [16] and Yang et al. [17] observed that the orthorhombic structure crystalline BNWs fabricated by the chemical vapor deposition (CVD) process on an alumina substrate. Meng et al. [18] prepared amorphous BNWs synthesized by the laser ablation process of B target, using Si wafers as the deposition substrates. Wu et al. [19] and Yun et al. [20] fabricated the amorphous BNWs on the MgO substrate coated with 5 nm Au thin films.

In this study, a simple and effective method for synthesizing crystalline BNWs on the entire surface of diamond particles is presented, which is, for the first time, to combine BNWs and diamond these two kinds of super hard materials together. Covering diamond particles with BNWs is considered to be a very promising way for surface functionalization of diamond, promoting exploitation of superb diamond composites and novel micro/ nano devises, and then an extended VLS model for synthesizing BNWs on diamond particle is also discussed.

#### 2. Experimental

The growth of BNWs on the diamond particle was carried out in a vacuum induction furnace. The mixture of diamond, Cu, and B powders was used as raw material which consists of 200- $\mu$ m diamond particles, oxygen-free Cu powders in size of 5–10  $\mu$ m, and the amorphous B powders. The mass fraction of the mixture was Cu-15 wt% and B-5 wt%. The mixed raw powder materials was first set in a graphite crucible and then placed in the vacuum

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Fig. 1. SEM pictures of nanowires on the diamond particle surface.



Fig. 2. TEM image and EDX spectra of the nanowire.

induction furnace that was pumped to a base pressure of about  $10^{-3}$  Pa. After introducing hydrogen gas into the furnace to prevent the possible oxidation, the powder mixture was heat up to 1273–1373 K and kept for 80 min.

After cooling down, the extra B powers were simply sieved out and the redundant Cu was removed by rinsing in acid. Various analysis technique including SEM, EDS and TEM were employed to investigate the as-grown BNWs on diamond particle surface. For TEM specimen preparation, BNWs/diamond particles were dispersed in ethanol and ultrasonically vibrated for 10 min. As the ultrasonic collision among diamond particles, a few of BNWs broke and suspended in the ethanol, and these suspending BNWs were collected for TEM analysis.

#### 3. Results and discussion

Fig. 1a is a typical SEM image taken from a diamond particle revealing the nanowires densely grow on the diamond surface. The length of these nanowires is up to several micrometers with diameters in the range of 20–200 nm (Fig. 1b). Almost all of the nanowires grow straightly while a very small amount of them show curved sections. It is worth to note that the nanowire growth happens on the whole surface of diamond particles, and an estimated surface coverage of about 80%.

Fig. 2 provides a TEM image of an as-fabricated nanowire, of which a tiny particle in dark contrast is found to embed at the tip. The diameter of the nanowire is about 100 nm, which is consistent with SEM results. The tiny particle at nanowire tip marked by arrow 1 in Fig. 2 was analyzed by EDS, where the intense Cu intrinsic X-ray peak was detected meaning that this tip particle is Cu. A little amount of oxygen detected is considered to come from surface oxygen absorption or slight oxidation during the sample transportation in air. The middle region of nanowire marked by arrow 2 in Fig. 2 was analyzed by EDS as well. In contrast to the EDS spectrum taken at the tip areas, a very intense B peak was recorded, strongly suggesting that this nanowire consists of B. The weak Cu peak originated from the Cu TEM grid that is not the intrinsic signal of this nanowire. The results of EDS tell that the fabricated nanowires are BNWs with Cu particles at the tips.

Electron diffraction (ED) and high-resolution electron microscopy (HREM) were used to identify crystalline structure of BNWs. Fig. 3a was a representive electron diffraction pattern taken from the nanowire. The ED pattern shows that the nanowire is a crystalline rather than amorphous, and the structure of the BNW is identified to be a tetragonal B allotrope whose lattice parameters are a=1.014 nm, c=1.417 nm (X-ray diffraction card 31–0206). It is not difficult to see that a few of diffraction spots divide into two and the parallel streaks run between spots, meaning there are some micro-twins existing in the nanowire. Fig. 3b is a HREM image of the nanowire, it shows that the nanowire is a single crystal but with some stacking faults which is consistent with the ED pattern.

In order to clarify the unique growth mechanism of the BNWs on diamond, the extended experiments were carried out. Using the same experimental parameters, we tried to grow the BNWs on graphite and silicon materials, as graphite is an allotrope of diamond and silicon has the same crystalline structure with diamond. But no nanowires were obtained, indicating in the present process the formation of the nanowires is strongly substrate material dependent, and diamond is an ideal candidate for BNWs planted on. This is guite different with the normal catalyzed CVD or PVD (physical vapor deposition) processes for one-dimensional nanostructure growth. For the latter two, noncatalyst substrate materials majorly serve as the sustaining plates and do not directly involve into the nanostructure growth processes. CVD or PVD nanowire growth could be well understood by the established models such as classic vapor-liquid-solid (VLS) model [21], or oxide-assisted-growth (OAG) model [22] etc.

In the present growth process of BNWs, It seems that boron nucleation and growth is taking place preferentially only on diamond particles. So diamond particles act as a catalyst leading to selective growth. Also, copper was used as catalysts in the growth of these crystalline BNWs. The presence of copper catalysts was found in the EDS analysis of the tip of BNWs, which led the Download English Version:

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