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Synthesis, analysis and electrical properties of silicon doped BN nanowires

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ABSTRACT

Element doping of one dimension BN nanomaterials enables great improvement of electrical properties and then broaden their application in nanoelectronic and optoelectronic fields. Silicon as a well-informed material widely used in electronics offers a promising direction for doping BN nanomaterials. Si-doped BN nanowires (BNNWs) and BN nanotubes (BNNTs) were synthesized through a ball milling-annealing approach. Interestingly, the Si doping transfers the BNNWs and BNNTs from insulators to semiconductors. And these BN nanomaterials present typical semiconductor characteristic which were studied using an electrical parameter analyser HP4145 and probe station at room temperature. Since the improvement of electrical properties, these nanomaterials will be able to extend their applications in designing and fabricating electronic nanodevices.

1. Introduction

Since one-dimensional (1D) semiconductor nanostructures possess outstanding qualities due to their peculiar morphology, they have been receiving increasing attention and been widely recognized as building blocks in nano-devices and nano-systems [1–4]. Studies showed that the application of semiconductor nanomaterials is beneficial to various existing electronic/optoelectronic devices [7]. 1D carbon nanostructures have been used to fabricate nanodevices, such as light-emitting diodes, laser diodes [5], field-effect transistors [6], and integrated logic gates [2]. As analogues to carbon nanostructures (CNTs), boron nitride nanostructures (BNNTs) have attracted wide research interest, since they have splendid mechanical properties [8], high thermal conductivity [9], excellent thermal and chemical stability [10,11]. However, unlike CNTs, which can present metallic and semiconducting characteristics, BNNTs have wide bandgap of ~5.5 eV [12] and present insulating characteristic. Their bandgap is independent of tube diameter, number of walls, and chirality. Moreover, BNNTs are chemically and thermally more stable compared to CNTs [12,13]. These physical and chemical properties provide BNNTs with excellent foregrounds of more suitable materials than CNTs for various applications, such as fabricating nanodevices applying to harsh environments and cutting edges of nanotechnology. Despite of the positive attributes of BN nanostructures, there is a serious drawback associated with its use: the wide band gap narrowing their application in nanoelectronics. To circumvent the particular limitation, a number of strategies [14] have been proposed to tune the band gap and reduce the electronic bandgap of BN nanostructures, including surface functionalization [15–18], doping of ions [19,20], radial deformation [21], applying transverse electric field s [22–24]. Among these strategies, surface functionalization and doping are considered as the practical methods to tune the electronic bandgap of BN nanostructures [25].

Enhanced electrical properties on doping BN nanostructures have been reported in the past few years. There are numerous theoretical investigations on properties of doped BNNT [26–28]. Atomistic simulations have shown that Si atoms can be strongly stabilized over the vacancy defect of the BNNT and has a strong interaction between these dopant atoms and the tube surface [29]. Bond lengths increase and bond angles decrease after Si doping. And impurity states arise in HOMO–LUMO gap. Si doping of BNNT improves the electronic transport property of the BNNT [28]. In the same way, other studies have proposed that C or transition metals doping might increase the electronic transport property of BNNTs [30,31]. For experimental investigations, previous studies have mainly focused on the carbon or fluorine doping BN

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nanostructures, which resulted in a modification on the electronic or optoelectronic properties of BN nanostructures [32–36]. For instance, the studies of Xiang and his coworkers show that the F-doped BNNTs with high conductivity might be of p-type due to the adsorbed F atoms. And Tang et al. have reported the substantial reduction of the resistivity of F-doped BNNTs, which was found to be three orders of magnitude smaller than that of the undoped BNNTs. Besides, Hua Chen and his coworkers synthesized europium and ytterbium doped BNNT and investigated their cathodoluminescence emission properties [37–39].

To date doping of BN nanostructures with silicon is also an area of interest, in which silicon is supposed to be a substitution dopant and can resulted in reduced bandgap of BNNTs [40–42]. Fan and coworkers synthesized Si (~6%)-doped bamboo like multiwalled BNNTs via catalyst-assisted pyrolysis of a boron-containing polymeric precursor. And they reported that the Si dopants cause significant changes in the structure and phonon characteristics of the nanotubes. Thermal chemical vapor deposition synthesis of Si (~5%)-doped multiwalled BNNTs were reported by Cho et al. they demonstrated that the Si doping decreases the bandgap of BNNTs by about 1.7eV. Nevertheless, Up to date, to the best of our knowledge, the changes of semiconductor parameters of BN nanostructures, especially the carrier concentration and mobility, have not been investigated theoretically or experimentally before and after Si-doping.

In the present work, we present a facile synthesis method to produce Si-doped BN nanostructures. And experimental investigations of the characterization and electrical properties of the resulting nanostructures were investigated. The resistivity, carrier concentration, and carrier mobility of the BN nano-structures before and after doping, were drawn from the experimental current-voltage characteristics.

2. Experimental

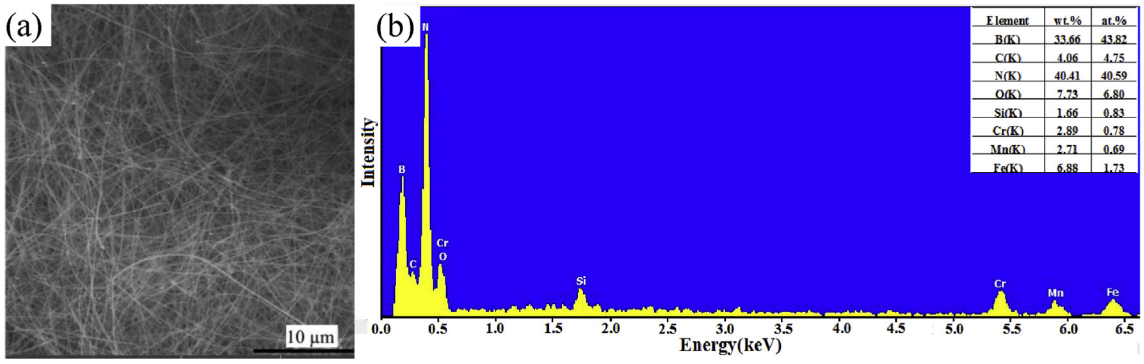
We synthesized the Si-boron nitride nanowires (BNNWs) by using ball milling and annealing method. Si powder was used as the silicon source for doping. Stainless steel wafers were used for the substrates, and 0.08 g $Fe(NO_3)_3$ powders were employed as the catalyst booting nanowire growth during the annealing process. Amorphous boron powders and a mixture of nitrogen and hydrogen gas (N_2/15%H_2) were used as the boron source and the nitrogen source, respectively. The mixture of B, $Fe(NO_3)_3$ and Si powder was milled in a horizontal planetary ball mill within a stainless steel chamber and several steel balls. The milling process was carried out at a rotation speed of 200 rpm for 12 h in N_2 atmosphere. The milled sample was dispersed into ethanol solution to form ink-like solution after 10min ultrasonic treatment. The solution was then uniformly painted onto the upper faces of stainless steel substrates, which were placed on the top of the alumina sintering boat with the upper faces facing up. The alumina sintering boat was pushed into a tube furnace for an annealing treatment to motivate nanowire growth. The annealing process was carried out at 1150 °C under a N_2/15%H_2 atmosphere with a flow of 200sccm for 1 h. After the furnace was cooled to room temperature naturally, white BNNW films can be found on the stainless steels.

Nanowires were investigated using a Tescan VEGA 3 SBH scanning electronic microscope (SEM) to examine the morphology. The chemical composition was confirmed using NORAN system 7 x-ray energy dispersive spectroscopy (EDS) attached to the SEM. Transmission electron microscopy (TEM) investigations were performed using a Tecnai G2 F20 (300 kV) instrument. The X-ray photoelectron spectroscopy analyses were conducted using a Thermo Fisher Scientific Escalab 250Xi X-ray photoelectron spectrometer with Al Kα excitation. Wide survey scans were taken at an analyser pass energy of 100 eV over a 1400–0 eV binding energy with 1.0 eV energy step. The electrical properties of a single doped BNNW were studied using an electrical parameter analyser HP4145 and probe station at room temperature.

3. Results and discussion

SEM image in Fig. 1 shows the stainless steels totally covered by white BNNW films, which indicates as-synthesized BNNWs with a high purity and formation yield. No obvious impurity by-products, such as BN particles and flakes, can be observed under the SEM image. Their diameters are ranging from 60 to 180 nm with an average length of more than 60 μm. The B and N ratio is close to 1:1. The average content of the Si in BNNTs is about 0.83 at% determined by EDS analysis. For comparison, the synthesis method has a little higher doping than other method [40–42].

The as-synthesized doped BNNWs morphology is also analyzed with the aid of TEM and high resolution transmission electron microscope (HR-TEM). The wire-like structures of the doped-BNNWs are shown in Fig. 2(a). The nanowires are straight with uniform diameters from point to point, and the surfaces are clean without impurity adsorption. The diameter ranges from 20 nm to 200 nm, and the length is up to several tens of micros. Under HR-TEM image analysis, a highly well-developed structure of BNNWs is shown in Fig. 2(b). With a careful observation, some bamboo BNNTs can be observed. These BNNTs have thick walls. In general, this procedure gave BNNWs as the majority product rather than BNNTs. And the interlayer spacing is about 0.335 nm, corresponding to the d_{0002} spacing of hexagonal phase BN (h-BN). The electron diffraction (ED) rings of a cluster of nanowires, as shown in the



Element	wt.%	at.%
B(K)	33.66	43.82
C(K)	4.06	4.75
N(K)	40.41	40.59
O(K)	7.73	6.80
Si(K)	1.66	0.83
Cr(K)	2.89	0.78
Mn(K)	2.71	0.69
Fe(K)	6.88	1.73

Fig. 1. (a) SEM micrograph of doped BNNWs, showing a high-density grown on the substrates; (b) its corresponding EDS spectra indicating Si presence.