



Full Length Article

Morphological transformations of BNCO nanomaterials: Role of intermediates

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ARTICLE INFO

Article history:

Received 11 December 2017

Accepted 19 February 2018

Available online 22 February 2018

Keywords:

Boron and nitrogen co-doped tube-like carbon nanorods
 Carbon and oxygen co-doped boron nitride nanosheets
 Chemical vapor deposition
 Behaviors of intermediate product B₂O₃
 Photoluminescence

ABSTRACT

Highly controllable structural transformation of various doped carbon and boron nitride nanomaterials have been achieved with the perspective of their application in microelectronics, optoelectronics, energy devices and catalytic reactions. Specifically, the syntheses of one-dimensional (1D) boron and nitrogen co-doped tube-like carbon nanorods and 2D vertical carbon and oxygen co-doped boron nitride nanosheets on silicon coated with gold films in N₂-H₂ plasma was demonstrated. During the synthesis of nanomaterials, boron carbide was used as carbon and boron sources. The results of characterizations by scanning and transmission electron microscopes, as well as micro-Raman and X-ray photoelectron spectroscopes indicate that the formation of different nanomaterials relates to the growth temperature and quantity of boron carbide. Specifically, 1D tube-like carbon nanorods doped with boron and nitrogen are formed at ~910 °C using a small quantity of boron carbide, while 2D vertical boron nitride nanosheets doped with carbon and oxygen are grown at ~870 °C using a large quantity of boron carbide. These studies indicate that the behaviors of a reactive intermediate product B₂O₃ on surfaces of Au nanoparticles play an important role in the formation of different nanomaterials, i.e., whether the B₂O₃ molecules deposited on Au nanoparticles are desorbed mainly determines the formation of different nanomaterials. The formation of 2D vertical carbon and oxygen co-doped boron nitride nanosheets is related to the high growth rate of edges of nanosheets. Furthermore, the photoluminescence (PL) properties of 1D boron and nitrogen co-doped tube-like carbon nanorods and 2D vertical carbon and oxygen co-doped boron nitride nanosheets were studied at room temperature. The PL results show that all the nanomaterials generate the ultraviolet, blue, green and red PL bands, but the 2D vertical carbon and oxygen co-doped boron nitride nanosheets emit more and stronger PL bands than the 1D boron and nitrogen co-doped tube-like carbon nanorods. The significant differences in the PL properties can be attributed to different carbon structures in these nanomaterials. These achievements can be used to synthesize and control the structures of nanomaterials and contribute to the development of the next generation optoelectronic nanodevices based on 1D and 2D nanomaterials.

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1. Introduction

Low dimensional carbon nanomaterials exhibit many properties different from those of bulk carbon materials. In particular, the heteroatom (e.g., B and N atoms) doped low dimensional

carbon materials show excellent physical and chemical properties such as high capacitance, superior oxygen reduction reaction, near room temperature ferromagnetism and so on [1]. Due to these features, the heteroatom doped carbon nanomaterials have extensive applications in the areas of energy sources, microelectronics and optoelectronics [1–6], and they are the possible reasons that the heteroatom doped carbon nanomaterials have been extensively studied in last years.

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Hexagonal boron nitride (h-BN) is 2 dimensional (2D) structure, which is isostructural and isoelectronic to graphene [7]. However, the van der Waals force between BN layers is weaker than that in graphene, and the electronic structure of intrinsic h-BN makes it an electrical insulator due to its wide bandgap of 4–6 eV [8]. As a result, it is difficult to apply h-BN in microelectronics and optoelectronics. However, it was found that h-BN can be easily doped with heteroatoms such as carbon and oxygen atoms, which can tune the electronic structure of h-BN. As a result, the bandgap of h-BN could be reduced through carbon and oxygen doping so that the carbon and oxygen co-doped h-BN exhibits outstanding optical properties [9,10], and the carbon and oxygen co-doped h-BN has wide applications in microelectronics, optoelectronics and other applications such as biology and water cleaning [9,11]. Thus, the doped h-BN nanoflakes have attracted much attention in recent years.

The 1D and 2D nanomaterials including carbon nanotubes, nanorods, nanocones and graphene nanoflakes were successfully and effectively synthesized by plasma-enhanced chemical vapor deposition [12–16]. Furthermore, we have successfully used a plasma-enhanced hot filament chemical vapor deposition (PEHFCVD) system to synthesize the C and O co-doped h-BN nanosheets and other nanomaterials in N_2 - H_2 plasma using B_4C as the boron and carbon sources [17,18].

However, control of nanomaterial morphology and controllable transformation between different morphologies still remain a problem. In the early works, Pakdel et al. synthesized differently structured BN nanomaterials by CVD, such as BN nanotubes, BN nanosheets and oriented BN nanosheets through altering the growth temperature and the composition of source materials [19–21]. These motivated us to synthesize the differently doped BN nanomaterials by PEHFCVD through changing the growth conditions. Moreover, while complex C and O co-doped BN nanomaterials (i.e., quaternary BNCO nanomaterials) have already been synthesized [9,10,17,18], the ability to control elemental composition, chemical structure and morphological features by simple means in a single process is quite limited. In particular, the control of reaction parameters such as the quantity of precursors (e.g., boron and carbon) and growth temperature remains limited. Since the BNCO nanomaterials are synthesized by multi-precursors [9,10,17,18], some intermediate products produced by the reactions of multi-precursors take important roles in the formation of different BNCO nanostructures, but the role of intermediate products in predetermining the structural and morphological features of BNCO nanostructures remains largely unexplored. Thus, we aim here to study the roles of intermediate products in the synthesis of different BNCO nanomaterials.

In our previous works we have described the carbon and oxygen co-doped h-BN nanosheets synthesized by PEHFCVD using B_4C as the boron and carbon sources, and have found that the intermediate product B_2O_3 is an important precursor for the formation of carbon and oxygen co-doped h-BN nanosheets [17,18]. However, it is not clear how the quantity and states of B_2O_3 influence the structure of BNCO nanomaterials, and how does B_2O_3 affect the formation of different BNCO nanomaterials? In this work, we altered the quantity and states of intermediate product B_2O_3 through adjusting the growth temperature and the quantity of B_4C . Specifically, the B and N co-doped tube-like carbon nanorods and vertical C and O co-doped h-BN nanosheets were synthesized on silicon substrates covered with Au films. The critical evaporation temperature of B_2O_3 was estimated in our experimental conditions by Clausius-Clapeyron equation. The studies indicate that the absorption or desorption of B_2O_3 molecules deposited on the Au NPs mainly determines the formation of different BNCO nanomaterials. Furthermore, the studies also indicate that the C and O co-doped h-BN nanosheets feature high growth rate of edges of nanosheets. Considering the optoelectronic applications, the photolumines-

cence (PL) properties of B and N co-doped tube-like carbon nanorods and vertical C and O co-doped h-BN nanosheets were further studied at room temperature. It is found that all the nanomaterials emit the ultraviolet (UV), blue, green and red PL bands, but there are significant differences in the number and intensity of PL bands. The studies show that the significant differences in the PL properties relate to the existing forms of carbon in these nanomaterials.

2. Experimental details

The synthesis of B and N co-doped tube-like carbon nanorods and vertical C and O co-doped h-BN nanosheets was carried out in PEHFCVD system described in Ref. [17] and shown in Fig. 1. Before synthesis, the silicon substrates were ultrasonically cleaned in the methylbenzene, acetone and alcohol solutions to remove the residual organics, and then the substrates were boiled in the mixed solution of $NH_3 \cdot H_2O$, H_2O_2 and deionized water to remove the inorganics. Au film of about 15 nm was deposited onto the clear silicon substrate by magnetron sputtering.

To synthesize the B and N co-doped tube-like carbon nanorods and vertical C and O co-doped h-BN nanosheets by PEHFCVD, the silicon substrate deposited with Au film was placed on the substrate holder, where the B_4C sheets pressed by B_4C powder were arranged around the silicon substrate. In the CVD chamber, N_2 and H_2 were supplied at the same flow rates of 50 sccm after the CVD chamber was evacuated to a background pressure lower than 2 Pa. Once the pressure in the CVD chamber was stabilized at about 2×10^3 Pa through controlling the vacuum valve, the tungsten filaments in the CVD chamber were heated to ~ 1800 °C. At the same time, the substrate was heated to the growth temperature by the thermal radiation of hot filaments due to the short distance of ~ 8 mm between the filaments and substrate. During the syntheses of nanomaterials, N_2 - H_2 plasma was produced by a DC power supply of which the positive and negative electrodes were connected to the filaments and substrate through a Mo holder, respectively. In this work, four samples A-D were prepared and the growth conditions were shown in Table 1.

The morphology, structure and composition of the synthesized nanomaterials were characterized by S-4800 field scanning electron microscopy (FESEM), Titan G² transmission electron

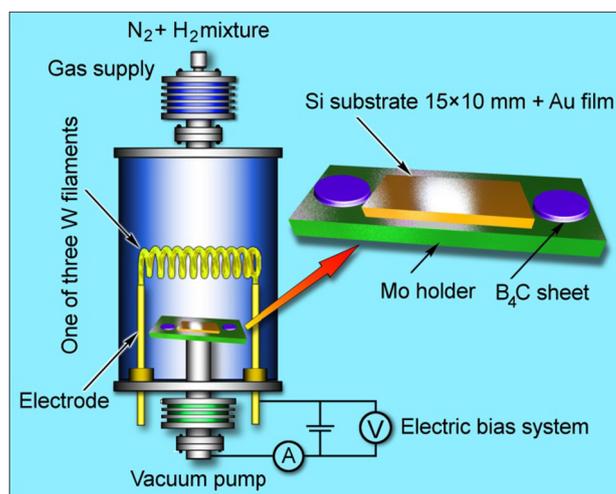


Fig. 1. Schematic of the experimental plasma-enhanced hot filament chemical vapour deposition system used to synthesize graphene nanoflake/BNCO composition using B_4C precursor. N_2 and H_2 were used as reactive gases. The bias current in the electric bias system was gradually increased till a blue glow appeared near the substrate, and then it was set to 160 mA to grow the nanowalls. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reprinted with permission from B. B. Wang et al., J. Mater. Chem. C 4, 9788–9797 (2016)

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