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Full Length Article

Growth and characterization of porous sp^2-BN films with hollow spheres under hydrogen etching effect via borazane thermal CVD

Yuanpeng Chen, Hongwei Liang *, Qasim Abbas, Jun Liu, Jianjun Shi, Xiaochuan Xia, Heqiu Zhang, Guotong Du

School of Physics & School of microelectronics, Dalian University of Technology, Dalian 116024, PR China

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ABSTRACT

Porous sp^2-boron nitride (sp^2-BN) films were directly grown on c-plane Al_2O_3 substrates by low pressure thermal chemical vapor deposition (CVD) using borazane (NH_3-BH_3) as a single precursor and without any catalyst. It was found that the BN films grown under 20 mbar are porous and consist of nano-scaled hollow BN spheres of various sizes, with outer radius (r_o) ranging from 7.20 nm to 13.32 nm. The B-N bonding was confirmed to be sp^2-bonded by the Raman scattering whereas, the crystal structure was determined by TEM and XRD to be turbostratic BN (t-BN) having a lattice constant 'c' larger than the hexagonal BN (h-BN) bulk crystal. Homogenous nucleation played a vital role in the porous sp^2-BN formation that is contrary to normal CVD growth under such low pressure i.e. 2 mbar for denser BN films. Additionally, because of the H_2 chemical etching effect, the H_2/N_2 ratio shows a strong influence on the film growth. All of the as-grown films have shown good ultraviolet (UV) absorption edge near 210 nm, hence providing a feasible route towards the synthesis of porous sp^2-BN with higher surface-volume ratio for high performance photo sensors and smart energy storage devices.

1. Introduction

Sp^2-bonded boron nitride (sp^2-BN) is a layered material having structure similar to graphite with strong in-plane B-N bonding and weak out-of-plane Van der Waals bonding. The basal plane is constructed of sp^2-bonding from B to N forming a hexagonal lattice with lattice constant of 0.2504 nm, the individual layers of sp^2-BN are atomically thin, smooth and can be easily isolated due to the weak Van der Waals interaction. Unlike the graphene, the sp^2 B–N bonds are partially ionic, making sp^2-BN a wide bandgap material with excellent physical and chemical properties including good insulating and dielectric property [1], strong mechanical strength [2], high thermal conductivity [3], high chemical stability [4], high band-edge optical absorption coefficient [5], high p-type doping performance than AlN [6] and a large indirect band gap of 6.58 eV [7]. These properties make sp^2-BN a promising wide-band semiconductor posing huge potential application in the deep ultraviolet field [8,9] also an excellent substrate and gate material for two-dimensional (2D) electronics [10,11]. In addition, the smooth and multifunctional surface of sp^2-BN brings numerous special applications [12]. Particularly, nano and micro sized sp^2-BN materials with large surface-volume ratio are believed to be the most promising materials for hydrogen storage due to the excellent hydrogen storage performance [13]. Four possible sites on the surface of sp^2-BN nanoparticles including the top site of the boron, the top site of the nitrogen, the bridge site over BN bond and the hollow site of the hexagon BN ring can be used to adsorb the approached hydrogen [14]. For gas-sensing and detection, BN films also exhibit exceptional moisture-sensing properties. The influence of humidity on the current–voltage characteristics of BN films have been reported by Soltani et al. [15], makes it possible for moisture detection.

Recently, nano and micro sized sp^2-BN materials have been extensively studied to improve the surface dependent applications [16,17]. Until now, considerable investigations have been devoted to the controllable growth and properties of various nano-sized sp^2-BN, such as nanotubes [18], hollow spheres [14], micro-belts [19], nanoparticles [13] and so on. Among all the nano structures, hollow spheres have attracted extensive interest in various fields since past few decades owing to their well-defined morphology and wide range of potential applications such as; a catalyst promoter and carrier, organic pollutant adsorption, drug delivery, gas purification, hydrogen storage and so on [12,16,20]. For example, hollow spheres can be used to increase the catalysis activity and adsorption due to their low density and high specific surface

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* Corresponding author.
E-mail address: hwliang@dlut.edu.cn (H. Liang).

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area [14,20,21]. The large fraction of void space within hollow spheres can also be used for loading and controllable releasing of some specific materials, such as drugs, peptides, iodine and other biomedical molecules [12,22,23]. Especially for hydrogen storage, porous sp^2-BN material containing hollow spheres is more attractive nowadays because of its high porosity, large surface area, high durability and high hydrogen adsorption/desorption ability at room temperature as compared to other nanostructured BN materials, including BN porous micro-belts, multi-walled BNNT, flower-type BN nanostructures and BN whiskers [12–14,19].

At present, chemical vapor deposition (CVD) is employed mostly to synthesize BN materials [24]. For the repeated and controlled growth of 2D sp^2-BN materials, borazane assisted thermal CVD is the most widely used. The extensive use of this CVD is beneficial due to non-toxicity and stable chemical behavior of precursor in dry air. And more importantly, the relatively lower equilibrium vapor pressure compared with the liquid ($N_3B_3H_6$, liquid @ 300 K) and gas (BH_3, gas @ 300 K) precursors, makes it the utmost appropriate choice to realize the highly controlled growth of high quality nano and micro sized 2D sp^2-BN materials on catalyzing transition metal substrates like Cu and Ni [25–27]. However a major attention has been paid to the growth and properties of 2D layers on transition metal substrates and device assembling with graphene as well [28–30]. Research on growth of sp^2-BN porous film consisting of hollow spheres using borazane assisted thermal CVD method has been rarely reported. Based on the above grounds, further detailed research on the growth mechanism and properties of porous sp^2-BN film via non-catalytic CVD method using NH_3-BH_3 precursor is needed.

In this effort, growth of porous sp^2-BN films, having hollow spheres through nucleation controlled theory via CVD is demonstrated. Two different nucleation processes have been confirmed by the characterization of the sp^2-BN films grown with different H_2 flow rate. The H_2 etching effect on the growth rate, morphology, stress states and optical properties of the grown porous sp^2-BN films have also been investigated in detail. With a suitable growth pressure and H_2/N_2 ratio, the prepared porous sp^2-BN films have shown good ultraviolet optical property and it is desirable to promote the application of porous sp^2-BN materials in hydrogen storage and detection field.

2. Experimental details

The BN films were grown on 2 inch c-plane Al_2O_3 substrates in a high-temperature tubular furnace using LPCVD method. Borazane (97% purity, Sigma Aldrich 682098) was used as a single precursor. A continuous source supply in 60 min growth process was provided by 100 mg borazane which was heated separately using a heating belt (maintained at 105 °C). With the corundum substrate holder heated to the optimized growth temperature (1370 °C), the c-plane Al_2O_3 substrate was annealed for 30 min in a nitrogen/hydrogen (N_2/H_2, 1:2) flow of 150 sccm. The film homogeneity was improved by keeping the Al_2O_3 substrate at an angle of 30 degree parallel to the gas flow direction in a horizontally configured CVD system. After surface treatment of the substrate, the film growth was initiated by opening the borazane valve. The growth pressure was set to 20 mbar. In the growth, high purity N_2 was used with a flow rate of 30 sccm to carry source into the high temperature growth region and keeping the total gas flow at 150 sccm. The hydrogen etching effect on the growth was studied using different H_2/N_2 ratios A (0:150), B (50:100), C (100:50) and D (150:0) and after 60 min growth, the samples were fast cooled to 700 °C in N_2 flow of 200 sccm within 60 min.

The surface morphology and the thickness of the sp^2-BN films were measured with scanning electron microscope (SEM, Hitachi S-4800). A High resolution transmission electron microscopy (HRTEM, FEI tecnai F20 G2 S-TWIN 200 kV) was conducted to reveal the microstructure of sp^2-BN films. Also the elemental composition was determined by elemental mapping in TEM measurement equipped with Energy Dispersive X-ray Detector (EDX). Raman spectra using Thermo Scientific DXR Raman spectroscopy with laser excitation wavelength and power of 532 nm and 10 mW were collected to determine the crystalline phase and quality of the BN films. In addition, the crystallinity and crystal structures of the BN films were analyzed by XRD-6100 (SHIMADZU). The optical characteristics of the BN film were investigated by a UV-Vis spectrometer (Shimadzu UV3600).

3. Results and discussion

In our earlier efforts, the growth temperature effect on the BN film grown by borazane assisted thermal CVD has been studied [31]. With a growth temperature higher than 1350 °C, borazane will undergo three steps of dehydrogenation which lead to the formation of BN [32,33]. At first, it is initially broken down into amino-borane (BH_2NH_2) and subsequently into borazine ($B_3H_6N_3$) when heated beyond 60 °C. The decomposed products are then transported towards the substrate surface where they bear further dehydrogenation beyond 1000 °C, here it is directly converted into active molecules consisting of $(BNH_y)_x$ ($1.2 < y < 2.4$). As the growth continues, active molecules will pass through the third dehydrogenation step and finally will be converted into BN. Consequently, dense sp^2-BN films with smooth surface can be grown at 2 mbar pressure. The growth is confirmed to be hetero epitaxial initiated by heterogeneous nucleation. As seen from Fig. 1(a–d), a comparison of sp^2-BN films grown at 2 mbar with films grown at higher pressures, latter are porous with clusters on surface and also are different from the samples grown at 2 mbar and low growth temperature (1200 °C) having BNH_x clusters on surface [31]. Therefore, the formation of porous sp^2-BN materials is speculated to originate from homogenous nucleation. In conventional CVD growth, growth pressure is a critical controlling parameter. Even two nucleation processes (heterogeneous and homogeneous nucleation) can be achieved via an adequate pressure control. As in nucleation, the chemical free-energy change per unit volume drives the condensation reaction [34], which is given by

$$\Delta G_V = -\frac{k_B T}{\Omega}\ln(1+S)$$

where, S is the vapor super saturation defined by $(P_V - P_S)/P_S$; P_s and P_V are the vapor pressure above solid and the pressure of the supersaturated vapor, respectively, Ω is the atomic volume, k_B is the Boltzmann's constant and T is the growth temperature.

In homogeneous nucleation, the total free-energy change in nucleus formation is thus

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

where, γ is the solid-vapor interfacial energy per unit area and r is the radius of the nucleus. Then minimization of ΔG with respect to r yields the nucleus of equilibrium with size r_c equals to $r_c = -\frac{2\gamma}{\Delta G_V}$. Substitution in above relation between ΔG and r gives

$$\Delta G^*_{homo} = \frac{16\pi\gamma^3}{3(\Delta G_V)^2}$$

In heterogeneous nucleation, due to the interaction between substrate and nucleus, the contact or wetting angle between heterogeneous nucleation and substrate is Θ. The energy barrier to the heterogeneous nucleation process is given by