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# Micromorphology and structure of pyrolytic boron nitride synthesized by chemical vapor deposition from borazine

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## ABSTRACT

Pyrolytic boron nitride (PBN) plates were synthesized by chemical vapor deposition (CVD) with temperatures of 900–1900 °C and total pressures of 50–1000 Pa on graphite by using borazine as the precursor. The effects of temperature and pressure on the micromorphology and crystal structure of the PBN were investigated. The as-deposited PBN possessed three typical types of micromorphologies depending on the deposition condition. PBN with dense and laminated structure (Type A) were deposited at temperatures of 1150–1900 °C with relative low pressures of 50–200 Pa, and PBN with porous and isotropic structure (Type C) was deposited at temperatures above 1100 °C with higher pressures above 250 Pa. PBN with dense and glass-like fracture structure (Type B) was obtained at the other range of the deposition condition. The interlayer spacing ( $d_{(002)}$ ) and the preferred orientation ( $PO$ ) of the crystallite were calculated by using XRD data of the PBN plates. The degree of the preferred orientation tended to be higher with the increase of temperature and decrease of pressure, and higher temperature led to smaller value of  $d_{(002)}$ . The crystal growth mechanism of the three types of PBN was discussed.

## 1. Introduction

Pyrolytic boron nitride (PBN) possesses plenty of remarkable performances such as extreme chemical inertness, high dielectric strength, excellent thermal shock resistance, non-wetting, non-toxic, oxidation resistance and negligible outgassing [1,2]. It has highly ordered planar texture analogous to pyrolytic graphite (PG) which exhibits evident anisotropic properties such as lower dielectric constant vertical to the crystal plane and higher bending strength along the crystal plane [3,4]. Therefore, PBN material has been widely manufactured as crucibles of compound semiconductor crystals, output windows and dielectric rods of traveling-wave tubes, high-temperature jigs and insulators [5–7]. Furthermore, in the incoming space exploration of Solar Probe Plus (SPP, NASA), PBN has been tested as the candidate material for the protective coating of the heat shield on the solar probe, not only for its excellent thermal and chemical stability in vacuum, but also for its high emissivity and reflectivity in the solar spectrum which would reduce the surface temperature of the spacecraft [8].

The synthesis of PBN has been carried out by a number of researchers using various reaction systems by chemical vapor deposition (CVD) [9–11]. The commercial production of PBN is based on the pyrolysis of  $BCl_3$  and  $NH_3$  at temperatures of 1900–2100 °C and pressures below 1 Torr in a hot-wall thermally insulated furnace [12,13]. In order to obtain stoichiometric PBN, the flow rate and relative ratio of

the reactants must be controlled precisely. Moreover, complicated simulation and verification of the gas flow field are need in order to realize the intensive mixing of the reactants gases and the obtaining of homogeneous products. Therefore, this process had a high production cost and several disadvantages such as low yield, long deposition duration, and high deposition temperature and energy consumption. There are also problems of the corrosive and toxic substances both in the precursors and by-products which may corrode the device and pollute the environment [14].

Borazine ( $B_3N_3H_6$ ), which possesses the same stoichiometric proportion of B/N with hexagonal boron nitride (h-BN), provides a potential alternative to the conventional CVD precursors [15]. It is isostructural and isoelectronic with benzene and has no impurity element except hydrogen [16,17]. Moreover, borazine is liquid at room temperature and has a relatively high vapor pressure [18]. Lots of investigations have been reported on the CVD of h-BN monolayer and nanosheet by using borazine as precursor in the last decade [19–21]. Borazine is also reported to prepare thin films about hundreds of nanometers thick by plasma enhanced (PE)CVD [22,23]. However, there has been little study on the preparation of PBN with the thickness of millimeter scale using borazine as the precursor. There must be several issues generated when extending the two-dimensional h-BN monolayer or film to the three-dimensional PBN [18]. In this work, we report the CVD of PBN using borazine as the precursor in temperatures of

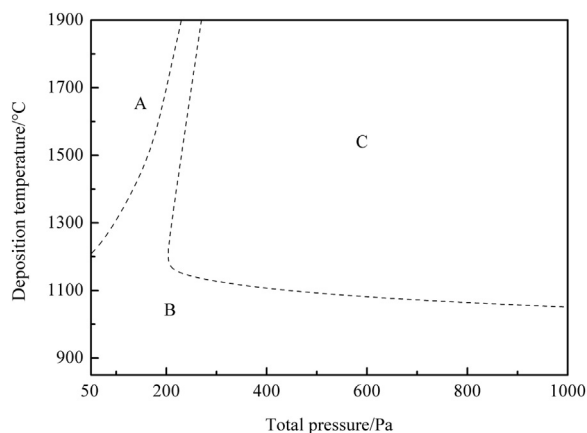
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**Fig. 1.** Effect of deposition temperature and pressure on the morphology of the PBN. Type A: product with dense and obviously laminated structure; Type B: product with dense and glass-like structure; Type C: product with porous and isotropic structure.

900–1900 °C and total pressures of 50–1000 Pa. The micro-morphological and crystal structural characterizations of the PBN are presented.

## 2. Material and methods

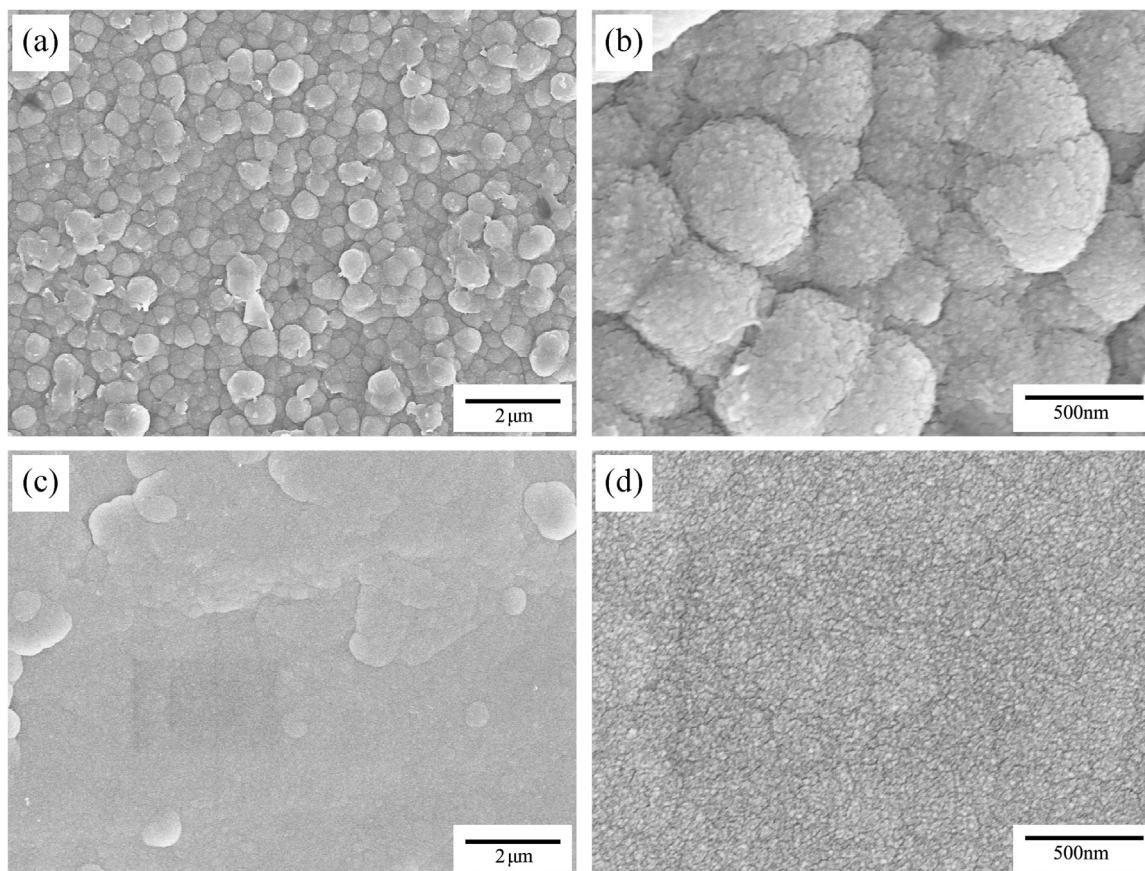
### 2.1. Synthesis of the PBN

The synthesis of PBN was carried out in a vertical hot-wall CVD system. The graphite disc ( $\Phi = 100$  mm) polished as substrate was fixed to the mandrel in the deposition chamber which would revolve on its

own axis during the reaction. The borazine used in this work was produced and purified with trap to trap distillation according to Li's report [24]. Nitrogen was passed into a bubbler which contained the precursor to carry the borazine vapor into the reaction chamber. The temperature of bubbler was kept at 0 °C at which the borazine had a vapor pressure of 11.2kPa during the deposition step. At the same time, the total pressure of the bubbler was conducted at a constant value in order to keep the borazine concentration of the gas mixture controllable. Then the gas mixture was transported into the reaction chamber with 1slm measured by gas mass flowmeter. The total gas pressure of the reactor was maintained at a constant pressure with an automatic pressure controller valve attached to the exhaust side. The deposition pressure was varied in the range of 50–1000 Pa, and the deposition temperature was performed in the range of 900–1900 °C. The as-deposited PBN was peel off from the graphite disc with thickness about 0.2–1 mm.

### 2.2. Characterization of the PBN

The micromorphology of the PBN were observed by field emission scanning electron microscopy (FESEM, Hitachi S4800-II). Due to the insulating property of h-BN, the sample surface was sputtered with a gold film previous to the SEM imaging. The crystallization state of PBN were characterized by X-ray diffraction (XRD, Bruker ADVANCED D8 diffractometer, Germany) at a wavelength of 1.5418 Å (Cu K $\alpha$  radiation). The microstructure of the PBN was examined by transmission electron microscopy (TEM, FEI Tecnai G2 F20) analyses. The samples were prepared according to a simple manner by mechanical grinding and ultrasonic dispersion.



**Fig. 2.** The deposition surfaces of PBN synthesized at 900 °C with different total pressures: (a), (b) 200 Pa; (c), (d) 1000 Pa.

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