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The etching process of boron nitride by alkali and alkaline earth fluorides under high pressure and high temperature

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ABSTRACT

Some new etching processes of hexagonal boron nitride (hBN) and cubic boron nitride (cBN) under high pressure and high temperature in the presence of alkali and alkaline earth fluorides have been discussed. It is found that hBN is etched distinctly by alkali and alkaline earth fluorides and the morphology of hBN is significantly changed from plate-shape to spherical-shape. Based on the "graphitization index" values of hBN, the degree of the crystallization of hBN under high pressure and high temperature decreases in the sequence of LiF > CaF_2 > MgF_2. This facilitates the formation of high-quality cBN single crystals. Different etch steps, pits, and islands are observed on cBN surface, showing the strong etching by alkali and alkaline earth fluorides and the tendency of layer-by-layer growth. A special layer growth mechanism of cBN with a triangular unit has been found. Furthermore, the morphologies of cBN crystals are apparently affected by a preferential surface etching of LiF, CaF_2 and MgF_2. Respectively, the plate-shape and tetrahedral cBN crystals can be obtained in the presence of different alkali and alkaline earth fluorides.

1. Introduction

Boron nitride (BN), a group III–V compound composed of boron and nitride, is well known for its unique physical and chemical properties, such as high temperature stability, high melting point, and high chemical inertness. HBN and cBN are its representative crystal structures, and its properties are highly dependent on the crystalline modification [1–3]. HBN, also known as "white graphite", has key properties such as low density, low thermal expansion, and lubricious, and many different methods have been used to prepare hBN. CBN is a high-pressure form of hBN, as one of the hardest materials like diamond, and it has attracted much attention in the aspects of synthesis and application. Unlike diamond, the growth of cBN is more complicated due to its binary nature. The high-quality of bulk cBN is only obtained under high pressure and high temperature (HPHT) conditions [4–6]. In the past two decades, cBN formation under HPHT has been intensively studied, and fundamental understanding of their phase diagram, synthetic approaches, and physical properties is highly developed [3,5–8].

However, since the growth of cBN happens frequently under extreme conditions, it is difficult to study the characteristics of the growth process directly. As a very important aspect to understand cBN growth mechanism, much attention has been paid to the study of surface properties of cBN [9–12]. Chemical etching is one of the methods frequently used. Extensive theoretical and experimental studies have been performed on surface reactivity of cBN thin films. It is noticed that fluorine is mostly used as a selective etching agent to prevent the formation of sp^2 BN phases and stabilize sp^3 bonds of BN in the chemical process, indicating the crucial role to improve the quality of the cBN materials [13–18]. It is also very important to note that, under HPHT conditions, the etching process of BN is much stronger and some characteristics of surface etching are easily obtained, which do not exist under deposition conditions. The decay mechanism of cBN is resembles the cBN growth, and their etch features can possibly elucidate cBN growth mechanism. But, until now, the etching of BN under HPHT has not been investigated.

As mentioned above, study of etching process of BN under HPHT conditions is obviously necessary and fluorides have played the important role in this process. To the best of our knowledge, the effects of alkali and alkaline earth fluorides on surface etching of BN are still rare. Our previous works indicate that the high-quality cBN crystals have been obtained and the growth conditions have been reduced in the presence of alkali-metal fluoride [19]. However, the etching effects have not been discussed in details.

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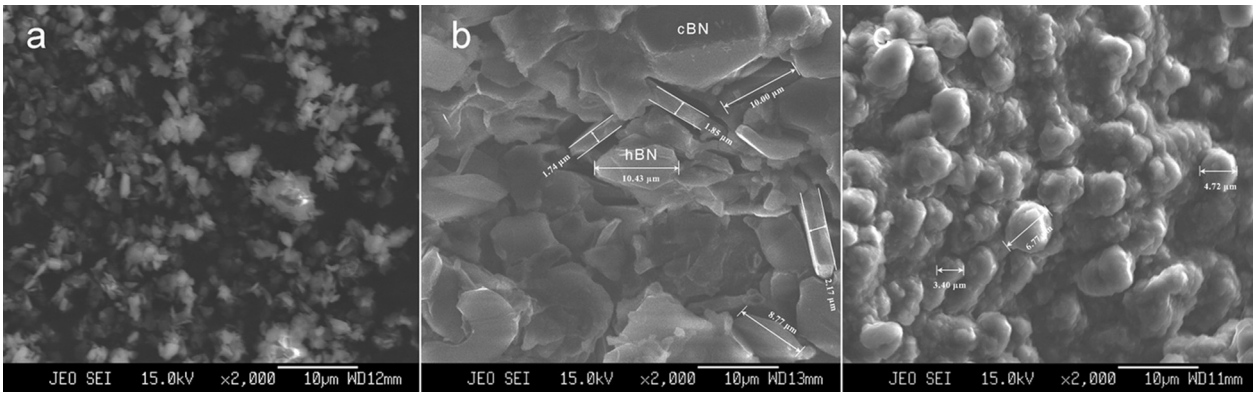

Fig. 1. SEM micrographs of hBN. (a) Starting hBN; (b and c) Li_3N-hBN and Li_3N-CaF_2-hBN system respectively, at 5.0 GPa and 1460 °C for 8 min.

The objectives of the present investigations are to describe in detail the role of alkali and alkaline earth fluorides (LiF, CaF_2 and MgF_2) in BN etching process under HPHT and especially the etching characteristics of surface morphologies of hBN and cBN, to establish the etching mechanism and to change the cBN morphology, which is of interest in improving the quality of cBN single crystals and broadening its application fields.

2. Experimental

The experiments were carried out in a China type SPD 6 × 600 cubic-anvil high-pressure apparatus (CHPA). The pressure was calibrated by the pressure induced phase transition of bismuth, thallium and barium. The temperature was measured by the Pt6%–Pt30%Rh thermocouple. Li_3N (99.4%), hBN (99.5%), LiF (99.9%), CaF_2 (99.9%) and MgF_2 (99.9%) powders were used as raw materials in our experiments. A mixture consisting of Li_3N-hBN (1:9 wt%) and AF_χ (A = Li, Ca, Mg; χ = 1 or 2; 1–5 wt%) was mechanically mixed in a sealed container for 3 h and then the mixture was pre-pressed into a cylindrical shape under dry and clean conditions. Then, the experiments were carried out under the conditions of 4.5–5.5 GPa and 1200–1600 °C for 8 min to investigate etching effect of alkali and alkaline earth fluorides on BN phases. The temperature was quenched by shutting off the heat power, and the pressure was gradually decreased to atmosphere.

After experiments, hBN was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Then, the products were cracked and treated by hydrochloric, molten hydroxides and sulfuric acid in order to remove the remaining hBN and other components. The surface morphology of cBN obtained was characterized by SEM.

3. Results and discussion

3.1. The etching process of hBN

Many studies of grown cBN films have shown that fluorine had the preferential etching of sp^2 BN and suppressing hBN, so high-quality cBN films could be obtained. CBN grown under HPHT conditions is different from that by vapor deposition, since crystalline hBN is usually used as starting material in this process and single crystals could be obtained. After experiments, the morphologies of hBN were observed carefully by SEM.

The morphology of hBN used as starting material is like rice grains, whose average length is 2 μm, and some is grumous (Fig. 1a); usually, crystallized hBN of a plate-like shape with well faceted and smooth surface would be appeared during cBN grown under HPHT without alkali and alkaline earth fluorides (Fig. 1b). The average particle size can be estimated in the following ranges, 1–3 μm in thickness, and 8–11 μm in diameter; however, the morphology of hBN has a significant change by introducing alkali and alkaline earth fluorides. HBN of a spherical shape is observed, and average particle size can be estimated as 3–8 μm in diameter (Fig. 1c). It clearly indicates that the distinct etching effect of alkali and alkaline earth fluorides on decreasing the crystallinity of hBN is due to the dissolution of B and N atoms in alkali and alkaline earth fluorides. The reaction between alkali or alkaline earth fluorides and hBN, just like the reaction of alkaline nitrides and BN, may be: $AF_\chi + \chi hBN \leftrightarrow A(FBN)_\chi$ (A = Li, Ca, Mg, χ = 1 or 2). During this reaction, dissolution and mobility of hBN is enhanced, and the crystallization of hBN is suppressed by alkali and alkaline earth fluorides under the HPHT conditions, as it creates a possibility to form high-quality c-BN crystals.

To obtain the effects of three kinds of alkali and alkaline earth fluorides on hBN crystallization, the three-dimensional ordering of hBN was studied by the method proposed by Thomas and Wetson using powder XRD [20]. As a measure of three-dimensional ordering, "the graphitization index" (GI), is applied according to the usual definition: $GI = [I(1\,0\,0) + I(1\,0\,1)]/I(1\,0\,2)$. According to this definition, a higher value of GI would means less three-dimensional ordering in hBN and vice versa. In order to avoid the influence of Li_3N, hBN was mixed with LiF, CaF_2 and MgF_2, respectively, and treated at 4.8 GPa, and 1200 °C for 8 min. The X-ray data of hBN in different systems after experiments was shown in Fig. 2 and the calculated GI values listed in Table 1. The GI values of hBN undergone HPHT are dramatically decreased (from 4.98 to

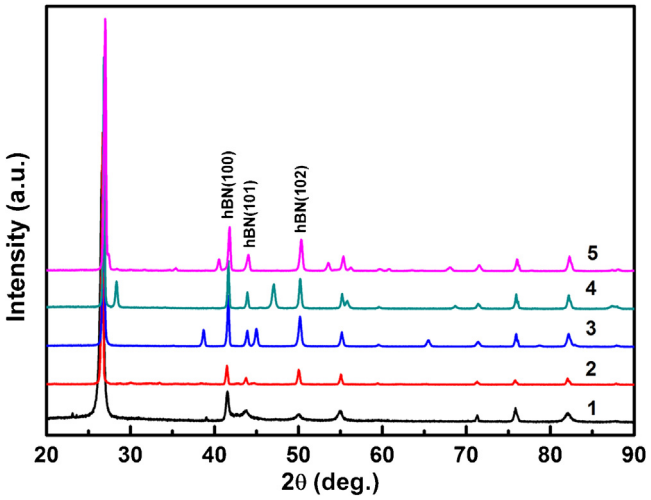

Fig. 2. The X-ray patterns of hBN treated under different conditions. (1) Starting hBN; (2) hBN; (3) hBN-LiF; (4) hBN-CaF_2; (5) hBN-MgF_2; (2)–(5) were treated at 4.8 GPa and 1200 °C for 8 min.