

## Full Length Article

# Auger electron spectroscopy analysis for growth interface of cubic boron nitride single crystals synthesized under high pressure and high temperature

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## ABSTRACT

After rapid cooling, cubic boron nitride (c-BN) single crystals synthesized under high pressure and high temperature (HPHT) are wrapped in the white film powders which are defined as growth interface. In order to make clear that the transition mechanism of c-BN single crystals, the variation of B and N atomic hybrid states in the growth interface is analyzed with the help of auger electron spectroscopy in the Li-based system. It is found that the  $sp^2$  fractions of B and N atoms decreases, and their  $sp^3$  fractions increases from the outer to the inner in the growth interface. In addition, Lithium nitride ( $Li_3N$ ) are not found in the growth interface by X-ray diffraction (XRD) experiment. It is suggested that lithium boron nitride ( $Li_3BN_2$ ) is produced by the reaction of hexagonal boron nitride (h-BN) and  $Li_3N$  at the first step, and then B and N atoms transform from  $sp^2$  into  $sp^3$  state with the catalysis of  $Li_3BN_2$  in c-BN single crystals synthesis process.

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## 1. Introduction

Cubic boron nitride (c-BN) single crystals are of considerable current interest as an abrasive material and potentially for electronic applications owing to its high hardness, high thermal stability, oxidation stability, chemical stability and doping ability for both p- and n-type conductivity [1–3]. The static high temperature and high pressure (HPHT) catalytic method is the most common method to synthesize c-BN single crystals with hexagonal boron nitride (h-BN) as raw materials and lithium nitride ( $Li_3N$ ) as catalysts. However, the quality of c-BN single crystals synthesized under HPHT in recent years cannot meet the demand of development of further promising products [4]. The unclear transition mechanism is the main factor to limit the development and application of high quality c-BN single crystals production. Therefore, it is desirable to study the transition mechanism to guide the high quality c-BN single crystals synthesis in industry. Previous studies [5,6] show c-BN single crystals are wrapped by white film powders. Since these powders are in direct contact with the c-BN single crystals, their composition and elemental contents may be of great significance to explain c-BN single crystals transition mechanism [7]. However, few investigations on the film powders of c-BN single

crystals are reported due to the difficulty for in-suit study and sample preparation. A narrow V-shaped area of temperature and pressure is observed in the synthesis process of c-BN single crystals under HPHT, which possesses the short-range ordered or medium-range ordered structure (a solid microstructure) in the growth interface [8]. Thus, the information of c-BN single crystals transition in the interface under HPHT can be retained as much as possible at ambient temperature and atmospheric pressure when the synthetic cell assembly was cooled rapidly [9].

Auger electron spectroscopy is an effective tool to obtain compositions, concentrations, and chemical states of the solid surface as well as other information directly or indirectly by measuring the characteristics energy, intensity, peak shift, line shape and width of AES [10]. In this work, the growth interfaces of c-BN single crystals after rapid cooling were examined by AES. The research would provide direct information to make clear the transition mechanism of c-BN single crystals, and be helpful to synthesize the c-BN single crystals with high quality.

## 2. Experimental method

The c-BN single crystals were synthesized by static HPHT catalytic method with high-purity ( $\geq 98\%$ ) h-BN as raw materials and  $Li_3N$  as catalysts, and the weight ratio is 9:1. The HPHT experiments were performed using the cubic anvil apparatus HTDS-

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034HM ( $6 \times 25$ MM). In these experiments, the range of synthetic pressure is 4.5–5.3GPa, and the range of synthetic temperature of 1350–1500 °C. The c-BN synthetic block was removed from the cubic anvil and prepared for further examination.

The synthetic block was broken into suitable pieces, and the one in which one part of c-BN single crystal was bare and the other parts were wrapped by the white film powders were selected to perform AES experiments. The AES experiments were performed by a PHI-700 Nano Scanning Auger system using a CMA energy analyzer and a coaxial electron gun of which energy resolution was 1‰ and incident angle was 30° with a diameter of beam  $\leq 40$  nm. The vacuum degree of analysis chamber was better than  $3.9 \times 10^{-9}$  Torr. Ion beam sputtering with Ar<sup>+</sup> at 5 kV kinetic energy was applied to sputtering the influence of surface pollution elements, and the sputtering rate was about 100 nm/min. By conducting fracture surface, the interface of c-BN single crystal was coated by a white film powders which was likely to dissolve into c-BN single crystal (Fig. 1). Several groups of homogeneous point-by-point scanning were performed in this work. For the distances between two points were about 10  $\mu$ m, the different layers in the growth interface were defined by the distances from the c-BN single crystal. One group of spectra data including three points in three different layers (Fig. 1) were selected to analyze in details the transition of c-BN single crystals. The film powders of c-BN single crystals were carefully collected under the view of an optic microscope, and their phases structures were determined by means of EQUINOX 4000 X-ray diffraction (XRD).

### 3. Results and discuss

#### 3.1. Chemical states in the interface layer

The compositions of growth interface are examined by the AES technology as shown in Fig. 2. It is found that the elements in the growth interface are mainly B, N, Li, C, O (B > N > O > Li > C), which contents are 32.9%, 22.1%, 17.7%, 5.8%, 21.5%, respectively. The Li atoms exist mostly in the form of Li<sub>3</sub>BN<sub>2</sub> [11,12], and the C, O elements may be the constituent of contamination (B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub> etc) in the interface. Because of the impurity in raw materials, the oxygen in working cells and the oxidation process occurred in the growth interface, a certain amount of C, O contamination exists in the interface. The presence of oxygen at HPHT could cause the generation of defects and effect the quality of c-BN crystals in synthesis process of c-BN crystals. The formation of c-BN crystals depends heavily on the the c-BN stability region in *p*-*T* conditions of experiment. The reduction in amount of oxygen in working cells

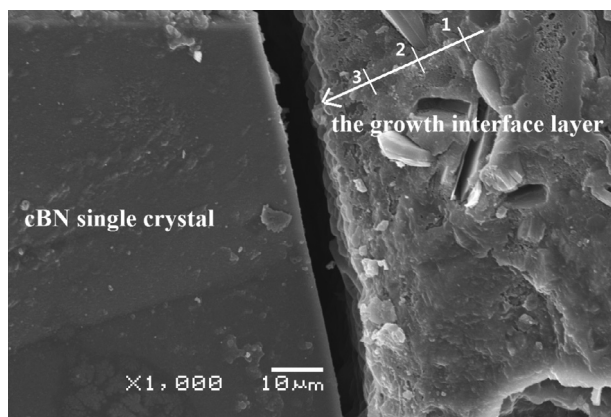


Fig. 1. Fracture SEM image of c-BN synthetic block and AES image of c-BN synthetic block.

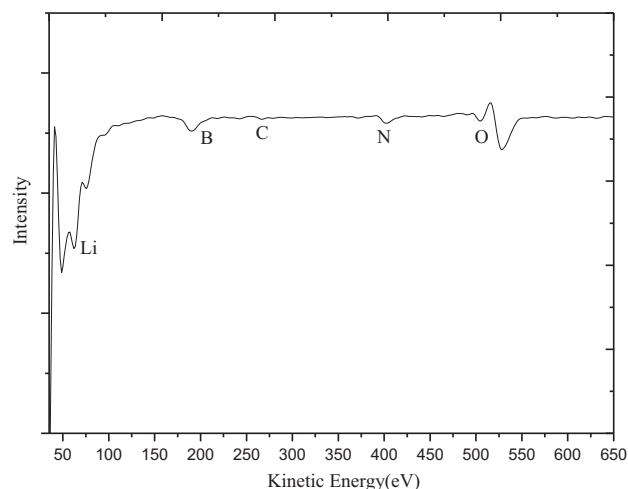


Fig. 2. Auger whole spectrum of c-BN growth interface after Ar<sup>+</sup> sputtering treatment.

of high pressure apparatus and raw materials should cause a decrease in the pressure of c-BN synthesis due to the increase in the h-BN  $\rightarrow$  c-BN equilibrium temperature [13].

It should be noted that the lattice of Li<sub>3</sub>BN<sub>2</sub> is composed of Li (1), Li (2), and linear (NBN)<sup>3-</sup> ions [14,15]. The B-N type bonds connecting two parallel ring in hBN are weak  $\pi$  bonds, which do not exist in cBN and Li<sub>3</sub>BN<sub>2</sub>. The outer structures of B, N atoms in h-BN and c-BN are *sp*<sup>2</sup> and *sp*<sup>3</sup> chemical states respectively. The chemical states variation of B and N atoms in the interface layer contributes to make clear the phase transition path at the synthesis process of c-BN crystals, and further analysis of their chemical states is desirable to reveal the transition mechanism of c-BN crystals. In this work, all auger peaks are defined as the average of maximum and minimum values in differential curve offset. Auger spectra of B and N atoms in *sp*<sup>2</sup> and *sp*<sup>3</sup> chemical states are obtained in Ref. [11–13]. The B spectrum in *sp*<sup>3</sup> hybridization states have three peaks, A<sub>1</sub> (171 eV), A<sub>2</sub> (157 eV) and A<sub>3</sub> (148 eV); similarly, three peaks in N spectrum are A<sub>1</sub> (380.5 eV), A<sub>2</sub> (360.5 eV) and A<sub>3</sub> (348 eV). The B spectral lines in *sp*<sup>2</sup> hybridization states has six peaks, main peak A<sub>1</sub> (173 eV), A<sub>2</sub> (160.5 eV), A<sub>3</sub> (151 eV), A<sub>4</sub> (143.5 eV), A<sub>5</sub> (180.5 eV), and A<sub>6</sub> (187 eV). High energy peaks A<sub>5</sub> and A<sub>6</sub> are absent in the spectral lines of c-BN. The N spectral lines in *sp*<sup>2</sup> hybridization states has four peaks, the main peak A<sub>1</sub> (383 eV), shoulder peak A<sub>2</sub> (374 eV), A<sub>3</sub> (366 eV), and A<sub>4</sub> (352.5 eV) [16–18]. The peaks of A<sub>5</sub> and A<sub>6</sub> in B spectral lines *sp*<sup>2</sup> hybridization states do not exist in their *sp*<sup>3</sup> hybridization states. Besides, the  $\pi$  bonds cause shoulder peak from main high energy peak, and the presence of shoulder peak at  $\approx 9$ eV from main peak is also one of characteristic peaks to distinguish between B and N *sp*<sup>2</sup> and *sp*<sup>3</sup> hybridization states [19] by AES spectrum. Fig. 3 shows the contrast spectra for c-BN and h-BN crystals. We note that h-BN has a sharper peak line than that of c-BN, besides, the shoulder peaks, which are pointed in the arrows in Fig. 3, are very obvious in h-BN, and it doesn't exist in the spectrum of c-BN.

The auger kinetic energies of B and N atoms are changed due to the occurrence of charge, and oxygen and impurities in the sample. However, their auger peaks do not change significantly, especially the representative spectra [20]. Therefore, compared with the spectrum of pure c-BN single crystal, the relative information of spectra in different points (Fig. 1) in c-BN single crystal interface can be analyzed. Fig. 4 is an auger spectrum of point by point scanning with 5 kV Ar<sup>+</sup> sputtering treatment. The spectra of three points (Fig. 1, 1–3) in the interface layer and a pure c-BN single crystal are correspondent with Fig. 4a–d respectively. As shown

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