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Characteristics of plate-like and color-zoning cubic boron nitride crystals

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ABSTRACT

The polarities of a kind of plate-like and color-zoning cubic boron nitride (cBN) crystal were extensively investigated by microscopy, chemical etching, XPS, Raman scattering, and current–voltage measurements. The {1 1 1}B faces and {$\bar{1}\,\bar{1}\,\bar{1}$}N faces of the cBN samples can be easily distinguished by optical microscope as there are a lot of defects incorporate in {$\bar{1}\,\bar{1}\,\bar{1}$}N sectors serving as the color centers, while the {1 1 1}B sectors have less defects and are nearly colorless. Both XPS and Raman spectra also revealed the uneven distributions of N vacancies and substitutional impurities in cBN crystals. The determination of {1 1 1}B faces and {$\bar{1}\,\bar{1}\,\bar{1}$}N faces can also be verified by the results of the chemical etching because the {$\bar{1}\,\bar{1}\,\bar{1}$}N faces have much faster etch rates than the {1 1 1}B faces. According to XPS, the {1 1 1}B faces have more C and O contaminations than the {$\bar{1}\,\bar{1}\,\bar{1}$}N faces, however the {$\bar{1}\,\bar{1}\,\bar{1}$}N faces have larger atomic ratio of B:N after surface cleaning by Ar^+ sputtering. In the Raman spectra of the {$\bar{1}\,\bar{1}\,\bar{1}$}N sectors of cBN, several small broad infrared-active phonon bands emerge nearby TO and LO modes because of the disorder-activated Raman scattering. As for the {1 1 1}B sectors, this phenomenon disappears. In addition, the {1 1 1}B faces have much smaller leakage current than the {$\bar{1}\,\bar{1}\,\bar{1}$}N faces, which indicates that the {1 1 1}B sectors have higher crystalline quality.

1. Introduction

The cubic boron nitride (cBN) crystal with a zinc blende structure is well-known as an excellent abrasive because of its ultrahigh hardness next to that of diamond. By virtue of its wide bandgap (~6.4 eV) [1], its excellent heat conductivity (~13 W/cm K) [2], and exceptional chemical and thermal stability, the cBN crystal also attracts much attention for its potential applications to optical and electrical devices [3–6]. In addition, the cBN crystal can be used as an ideal substrate for the growth of diamond films because of proper lattice match with each other [7,8].

However, it is very difficult to synthesize the high-quality and large-scale cBN single crystal, which greatly inhibits the studies of electrical and optical properties of cBN, as well as the application of cBN in electronics and optoelectronics. At present, the common way of synthesizing cBN single crystals is to transform hexagonal boron nitride (hBN) directly into cubic phase at high pressure and high temperature (HPHT) [9–11]. An effective approach for transforming hBN sheets into high-quality cBN nanofilms based upon fluorination was also theoretically demonstrated recently [12,13]. Although intrinsic cBN should be colorless, amber crystals are typically obtained by using alkali earth metals and BN compound solvents under HPHT conditions [10]. Some researchers supposed that N vacancies (V_N) and oxygen impurities were possibly the origin of amber color [14]. In principle, growth habit and surface morphology of cBN crystals depend on individual growth conditions and the crystallographic polarity. However, most cBN crystals synthesized under HPHT usually have irregular surface morphologies [10,15], which hinders cBN crystals from being substrates of electronic or optoelectronic devices.

In this paper, a kind of plate-like and color-zoning octahedral cBN samples synthesized by phase transition from hBN under HPHT conditions (4.9–5.3 GPa, 1300–1700 °C) is extensively studied. All faces of the cBN samples are {1 1 1} crystallographic planes, and the typical sizes are about 400 μm × 400 μm × 100 μm. The upper and lower faces are parallel, very smooth and flat, and bigger than other facets. Such cBN samples are very suitable for substrates of semiconductor devices. Moreover, the plate-like cBN crystals is prone to be cleaved along {1 1 0} planes and fabricated into appropriate shapes [16]. The cBN samples are amber at a glance, just like other

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cBN crystals synthesized under HTHP. However, through the careful observation under the microscope, the plate-like cBN crystals exhibit an interesting color zoning from the top view: alternate triangular amber zones and colorless zones. As far as we know, there are no reports on such color-zoning cBN single crystals. How does the color zoning come into being? What effects will the color zoning have on the cBN properties? What different characteristics are there between the colorless zones and the amber zones? With these questions, we intensively investigate the plate-like color-zoning cBN sample by chemical etching, X-ray Photoelectron Spectroscopy (XPS), Raman spectroscopy and current–voltage (I–V) characteristic.

2. Experiments and results

2.1. Microscopy of cBN samples

The micrographs of the typical plate-like color-zoning cBN crystal are shown in Fig. 1. Fig. 1(a) is the perspective micrograph of the cBN sample, note that the triangular amber zones and the triangular colorless zones are easily distinguished. It seems that all triangular zones have a common vertex locating at the center of the cBN sample. Fig. 1(b) is the reflective micrograph of the same cBN sample shown in Fig. 1(a). Note that among the six side facets of the cBN sample, three side facets (Λ facets) which are the end of the amber zones make acute angles with the top face of the cBN sample, while the angles of other three side facets (Σ facets) which are the end of the colorless zones with respect to the top face are obtuse. The opposite side facets are parallel and have approximately equal areas, and correspond to different color zones. According to the crystallography and the orientation of crystal by XRD, it has been demonstrated that all faces of the cBN sample are $\{1\,1\,1\}$ crystallographic planes. In general, the zinc blende structure has crystallographic polarity along $\langle 1\,1\,1\rangle$ axes by nature, so cBN crystals should include $\{1\,1\,1\}$B and $\{\bar{1}\,\bar{1}\,\bar{1}\}$N surfaces. The relative orientations of B and N surfaces are shown in Fig. 1(c). Namely, the ideal cBN crystal should grow into a regular octahedron, whereas the actual cBN single crystals possess undergrown plate-like structures probably because of the unideal growth condition. Based on the crystallography theory, the angle between the adjacent same kind of $\{1\,1\,1\}$ faces (such as two adjoining $\{1\,1\,1\}$B faces) is about 70.5°, while the angle between the adjacent $\{1\,1\,1\}$B face and $\{\bar{1}\,\bar{1}\,\bar{1}\}$N face should be an obtuse angle of 109.5°. Therefore, Λ facets and the top face should have the same polarity, and the polarity of Σ facets should be the same as that of the bottom face in Fig. 1. Since many studies indicate that the amber color of cBN crystal is because of the color centers resulting from V_N and some impurities [14,17], we suppose that Λ side facets and the top face of cBN sample should be $\{\bar{1}\,\bar{1}\,\bar{1}\}$N faces, and Σ side facets and the bottom face ought to be $\{1\,1\,1\}$B faces in Fig. 1. This conclusion can also be further verified by the following experiments of etching, XPS, Raman, etc.

2.2. Wet etching and mechanical cleavage of cBN samples

We researched the wet etching properties of cBN crystals by using the molten NaOH, and observed the corrosion morphology of cBN samples. In general, different crystal planes of III–V compounds can exhibit different chemical characteristics due to the differences of surface polarities [18]. Early studies indicate that the polarity of the $\{1\,1\,1\}$ surfaces strongly affected the chemical etching behavior of sphalerite-structure III–V compounds [19,20]. The $\{1\,1\,1\}$ surfaces terminating with group III atoms are less reactive than the $\{\bar{1}\,\bar{1}\,\bar{1}\}$ surfaces terminating with group V atoms. Thus, the reactive $\{\bar{1}\,\bar{1}\,\bar{1}\}$ faces of III–V compounds tend to etch faster in oxidizing

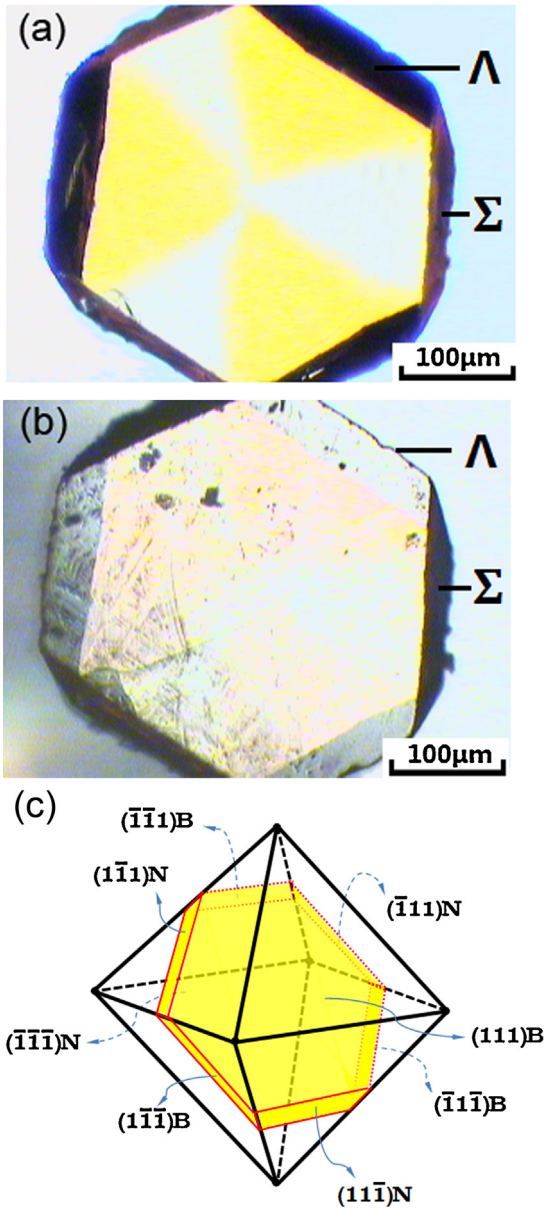

Fig. 1. Typical geometric shapes of cBN single crystals. (a) The perspective micrograph of a plate-like and color-zoning cBN sample; (b) the reflective micrograph of the same cBN sample; (c) the relative orientations of B and N surfaces of cBN crystals.

reagents than the noble $\{1\,1\,1\}$ faces. Therefore, as for cBN samples, the $\{\bar{1}\,\bar{1}\,\bar{1}\}$ N faces should have higher etch rates than the $\{1\,1\,1\}$B faces. Fig. 2 shows the typical corrosion morphologies for $\{\bar{1}\,\bar{1}\,\bar{1}\}$ N faces (the top face in Fig. 1(a)) and $\{1\,1\,1\}$B faces (the bottom face in Fig. 1(a)) of cBN after chemical treatment in melted NaOH at 400 °C for 10 min. Triangular dislocation etch pits are observed on both the $\{\bar{1}\,\bar{1}\,\bar{1}\}$ N and $\{1\,1\,1\}$B faces. Obviously, the etch pits on the $\{\bar{1}\,\bar{1}\,\bar{1}\}$ N faces in Fig. 2(a) are at least four times larger than those on the $\{1\,1\,1\}$B faces in Fig. 2(b). Mishima also observed similar etching results [21]. Meanwhile, the edges of the triangular pits are parallel to the Σ side facets (the $\{1\,1\,1\}$B faces), that means the sides of etch pits should be the $\{1\,1\,1\}$B facets due to the slower etch rates. These etching results and analyses further verify the judgment of the polarities of $\{1\,1\,1\}$ planes of the cBN samples in Section 2.1.

Just like GaAs, since cBN crystals also have zinc blende structures, the cleavage surfaces of cBN should be $\{1\,1\,0\}$ planes. According to the relative orientations of crystal planes, it is easy to determine the cleaving directions of cBN, as shown in Fig. 3(a). The