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Raman study of color-zoning cubic boron nitride single crystals

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ABSTRACT

Unintentionally doped cubic boron nitride (cBN) single crystals with color zoning were investigated by Raman spectroscopy. Besides the TO mode at 1053 cm^{-1} and the LO mode at 1304 cm^{-1}, some little vibrational bands at 925 cm^{-1}, 955 cm^{-1} and 1247 cm^{-1} corresponding to the amber regions in the $\{\bar{1}\,\bar{1}\,\bar{1}\}$N sectors of cBN crystals were observed. These vibrational bands probably result from the disorder-activated Raman scattering (DARS) due to the high defect densities. It is shown that these defects and impurities are nonuniform, easily formed and incorporated in $\{\bar{1}\,\bar{1}\,\bar{1}\}$N growth sectors during the growth process of cBN crystals. These defects and impurities are color centers in cBN, therefore, the cBN crystal exhibits symmetrical color zoning relative to the {111} growth sectors.

1. Introduction

Cubic boron nitride has the widest bandgap (~6.4 eV) in III–V compounds [1]. It can be transformed into *n*- and *p*-type semiconductor by doping with Si and Be, respectively, and UV light emission from a cBN *p*-*n* junction has been observed [2,3]. By virtue of its excellent heat conductivity (~13 W/cm·K) [4], and exceptional chemical and thermal stability, the cBN crystal attracts much attention in high temperature microelectronic as well as optoelectronic devices [3,5].

However, it is very difficult to synthesize large-scale cBN single crystals with high quality, which greatly inhibits the studies of electrical and optical properties of cBN, as well as the applications of cBN in electronics and optoelectronics. O. Mishima et al. synthesized large cBN single crystals (~3 mm in size) using $LiCaBN_2$ as a solvent under high pressure and high temperature (HPHT) conditions [6]. The cBN crystals exhibit nearly colorless, amber and black due to different growth conditions [7,8]. Some researchers supposed that impurities, defects, and boron excess were probably the origin of color centers [8,9]. Generally, growth habit and surface morphology of cBN crystals depend on the individual growth condition and the crystallographic polarity. However, most of cBN crystals usually have irregular surface morphologies under HPHT conditions [7,10], which hinders cBN crystals from being substrates of electronic or optoelectronic devices.

It should be noticeable that there is sometimes inhomogeneity of the color in doped cBN crystals [8,11,12]. Similar phenomena were also observed in doped diamonds. It was reported that the inhomogeneity of blue color in B-doped diamonds

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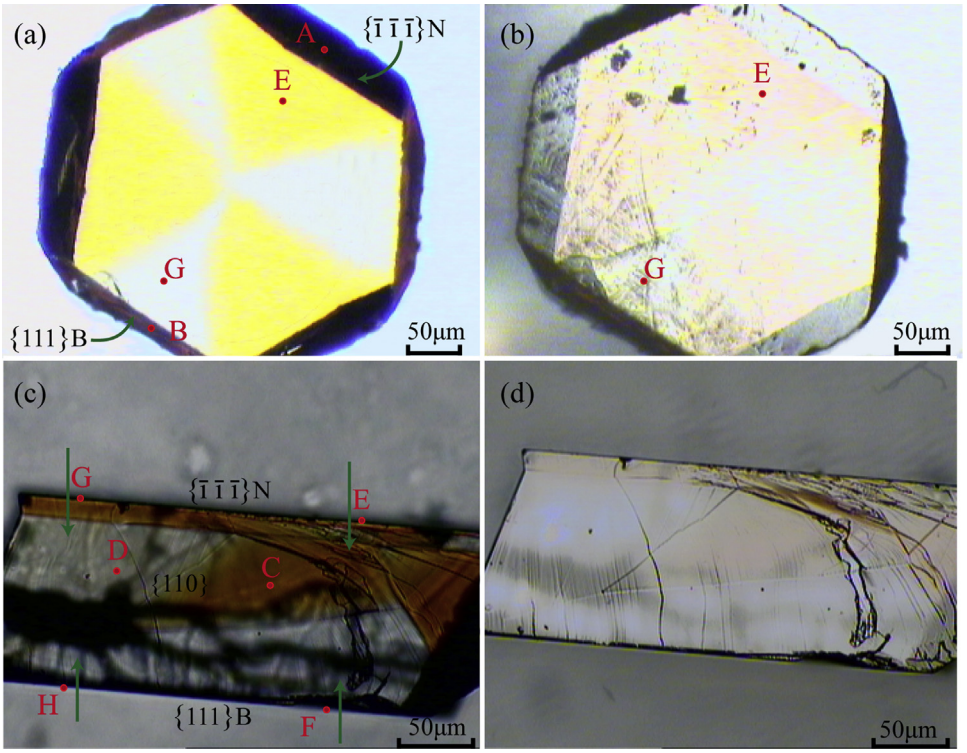

Fig. 1. (a)–(b)Typical geometric shapes of plate-like and color-zoning cBN single crystals. (a) The perspective micrograph; (b) The reflective micrograph. (c)–(d) Cleavage surfaces of cBN crystals (namely {110} planes). (c)The perspective micrograph; (d) The reflective micrograph.

was affected by localization of B atoms, depending on the growth sectors in the diamond crystals [13].The Raman spectra are useful and nondestructive tools for the characterization of cBN crystal in favor of the understanding of the growth mechanism [8,14–17]. In the Raman spectra of B-rich cBN crystals with color zoning, a small vibrational band at 1251.98 cm^{-1} was observed, which was related to excessive B atoms. The excessive B atoms located at the $\{\bar{1}\,\bar{1}\,\bar{1}\}$N growth sectors and led to dark zones in cBN crystals [8].

In the present work, unintentionally doped cBN crystals with color zoning were investigated by Raman spectra. In addition to the TO and LO lines, the small bands at 925 cm^{-1}, 955 cm^{-1} and 1247 cm^{-1} were observed corresponding to amber regions in the $\{\bar{1}\,\bar{1}\,\bar{1}\}$N sectors of cBN crystals. The possible reasons for these small bands in the Raman spectra are analyzed.

2. Experiments

The octahedral cBN samples with color zoning were synthesized by phase transition from hBN under HPHT conditions (4.9–5.3 Gpa, 1500–1700 °C) using Li_3N as a catalyst. The hBN (over 99% purity) and Li_3N had a mass ratio of 10:1, which were uniformly mixed and pressed into cylindrical shape. Carbon tube and pyrophyllite were respectively used as heating vessels and pressure transmission medium in HPHT synthesis. The growth time was varied from 15 to 20 min. The products were treated with HCL so as to remove catalyst, and melted NaOH in order to remove residual hBN. Eight exterior surfaces of cBN samples are all {111} crystal planes, including large top and bottom surfaces and six small side faces, shown in Fig. 1. Judging from the reported morphology of the crystals [12], the $\{\bar{1}\,\bar{1}\,\bar{1}\}$N growth sectors and $\{\bar{1}\,\bar{1}\,\bar{1}\}$N side faces correspond to the amber color regions, and the {111}B growth sectors and side faces correspond to the transparent regions, as shown in Fig. 1(a) and (b). Just like GaAs, since cBN crystals also have zinc blende structures, the cleavage surfaces of cBN should be {110} planes. From the {110} cleavage surfaces, the color zoning can also be observed obviously, as shown in Fig. 1(c) and (d).

The Raman spectra of the cBN samples were measured at room temperature with the 514.5 nm (2.41 eV) line of an argon ion laser. The laser beam was focused onto the sample through a microscope with a spot size of about 2 μm in diameter and a power of about 10 mW. The scattered light was collected in a backscattering geometry and the spectra were detected with a charged couple device (CCD) camera.

The X-ray Photoelectron Spectroscopy (XPS) analyses were performed with an ESCA LAB 250 spectrometer using a focused (the irradiated area was 200 μm in diameter) monochromatic Al Kα ($h\nu$ = 1486.6 eV) X-rays. The background pressure in the analysis chamber at room temperature was in the range of 10^{-8}–10^{-9} Pa.