CUBIC BORON NITRIDE PN JUNCTION DIODE MADE AT HIGH PRESSURE AS A HIGH TEMPERATURE DIODE AND AN ULTRAVIOLET LED

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The temperature difference method was applied to grow a large crystal of cubic boron nitride (cBN) under ~55 kbar and ~1700°C using LiCaBN₃ as a solvent. cBN crystals of ~3 mm in size were obtained. A pn junction diode of cBN was then fabricated by growing a silicon-doped n-type crystal epitaxially on a beryllium-doped p-type seed crystal. Formation of the pn junction was clearly confirmed by rectification characteristics and by the existence of a space charge layer of the junction as observed by electron beam induced current (EBIC) measurement. The rectification characteristics were observed from room temperature to 650°C. Injection luminescence was observed at the cBN pn junction. Microscopic observation showed that the whitish blue light was emitted only in the forward-bias condition. Spectroscopic studies revealed that the spectra had a peak in the ultraviolet and the shortest observed wavelength was ~215 nm.

1. Introduction

Cubic boron nitride may be useful as an electronic material. It can be made into both p- and n-type semiconductors as reported by Wentorf and its energy gap (>6.4 eV) is the widest among the known semiconductors. This paper briefly reviews our recent work on the growth of cBN, and fabrication and properties of cBN pn junction diodes.

2. Crystal growth of cBN

For the growth of large crystals of cBN, a temperature difference solvent method was used under pressure. A nutrient (hexagonal or cubic boron nitride) was melted into a solvent (LiCaBN₃) at the high-temperature end of a growth cell and large cBN crystals precipitated at the low temperature end of the cell. The cell was made of molybdenum and located in a belt-type high-pressure and high-temperature apparatus (~55 kbar, ~1700°C). The temperature difference in the cell was not measured because of the difficulty of measurement. However, the temperature difference could be changed by changing the shape and location of the cell in a heater. The observed differences of the shapes of the grown cBN, which varied from a small polyhedral lump to a large hollow crystal, were qualitatively explained by the present understanding of crystal morphology in relation to supersaturation, which provided technical guidance for growing desirable crystals of good quality. Growth conditions for large crystals could be found by changing the temperature and temperature difference in the cell. cBN crystals of ~3 mm in size were obtained as shown in Fig. 1.

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Fig. 1. The cBN crystal grown at the low-temperature end in the solvent. Width of the crystal is ~3 mm.

3. Semiconducting cBN

Using the temperature difference method, we could obtain large semiconducting crystals (2~3 mm in size) by adding suitable impurities to the solvent\(^5\). Following the work of Wentorf\(^4\), beryllium and silicon were doped to make p- and n-type crystals, respectively.

Electrical measurement on the semiconducting cBN crystals was made by a four-point probe method to eliminate contact resistance (10^4~10^6 ohms at room temperature)\(^3\). Silver-painted electrodes were used and a direct current was flowed. The measured electric resistance of the semiconducting crystals (1~2 mm in size) from room temperature to ~600°C is shown in Fig. 2. Resistivities of the p- and the n-type crystals at room temperature were roughly estimated to be 1~10^2 and 10~10^3 ohm-cm, respectively. Activation energies of the conductivity of the p- and n-type crystals were ~0.23 and ~0.24 eV, respectively. The origin of the activation energy of 1.1 eV observed in ref. 5 has been found to be not of cBN but of the ZrO\(_2\)-base sample holder, which had low resistivity at high temperatures\(^6\).

4. cBN pn junction diode

4.1 Fabrication of the pn junction

We have further fabricated pn junction diodes of cBN by growing a silicon-doped n-type crystal epitaxially on a beryllium-doped p-type seed crystal by using the temperature difference method\(^5\). The fact that flat cleavage over the pn boundary was obtainable indicated the epitaxial growth on the seed. These composite crystals were shaped by grinding with a diamond wheel to expose both the p- and n-type regions so that the diode could be tested (Fig. 3(a)).

Figure 3(b) shows an electron beam induced current (EBIC) image. The bright continuous line

![Fig. 2. Temperature dependence of resistance of cBN semiconducting crystals.](image)

![Fig. 3. The cBN pn junction. (a) Microscopic picture. The right- and left-hand sides correspond to the p- and n-type regions, respectively. (b) EBIC image. (c) Luminescence in a forward-bias condition.](image)
in the figure shows the existence of a space charge layer at the junction. The EBIC flowed from the n-type to the p-type region and the intensity of the EBIC varied along the junction line, showing the lack of uniformity of the crystal. The width of the junction was less than \( \sim 200 \) nm. This EBIC image, without a doubt, confirmed the formation of the pn junction.

4.2 High temperature diode

The usual rectification characteristics were observed by the four-point probe method from room temperature to \( 650^\circ C \)\(^6\) which is comparable to the highest operation temperature of a SiC transistor\(^7\) and a diamond diode\(^8\) (Fig. 4).

4.3 Ultraviolet LED

The cBN pn junction diode was found to be functional as a light-emitting diode (LED)\(^9\). Figure 3(c) shows the luminescence from the pn junction in a forward-bias condition. A whitish-blue emission was observed along the entire pn interface region. The intensity of the emission varied along the junction, seemingly corresponding to the intensity of the EBIC. This whitish-blue emission was easily recognized under room light by the naked eye when \( 2 \sim 3 \) mA was supplied. When a substantial reverse current flowed, the whitish-blue emission was not found, but there was a faint orange emission distributed in the n-type crystal. The intensity of the orange emission was much less than that of the blue emission.

The spectrum of the light from the cBN LED was measured by using a Spex 1402 double-monochromator and an EMI-6256S photomultiplier. The spectral pattern differed after the electrodes were repaired and the diode was reset to the instrument, which probably reflects the lack of uniformity of the crystal and a lack of reproducibility of forming the electrode (Fig. 5). The shortest observed light wavelength from the present cBN LED was \( \sim 215 \) nm (\( \sim 5.8 \) eV). This value of \( \sim 215 \) nm was the shortest among those of known n-type diodes and was comparable to that of the ms-type AlN diode\(^10\).

In the reverse-bias condition, there was a weak emission in the long-wavelength region.

![Fig. 5. The typical spectra of the cBN LED. The spectra were corrected by using the preliminarily calibrated spectral sensitivity of the instrument. A and B correspond to two different electrode conditions.](image)

5. Discussion

The principal results of this cBN work may be summarized as follows;

1. It was found that the large cBN crystals could be obtained by the temperature difference solvent method under high pressure,
2. The existence of semiconducting cBN was reconfirmed,
3. A functional electronic device (diode) and an optoelectronic device (LED) were made of cBN for the first time,
(4) A high-temperature semiconductor device (diode) operating at the highest temperature region was obtained,

(5) A pn-type LED emitting the shortest wavelength-light was obtained,

(6) It is probably the first time that complicated electronic and optoelectronic devices have been made under very high pressure.

Although the purity and perfection of the sample were not optical in the present experiment, the cBN pn diode demonstrated extraordinary characteristics, due of course to the remarkable electronic properties of this simplest III-V compound; namely, the existence of both p- and n-type semiconductors and the widest energy gap among known semiconductor materials.

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REFERENCES