Photoluminescence of Hexagonal Boron Nitride (h-BN) Film

Moon-Seog Jin* and Nam-Oh Kim†

Abstract – Hexagonal boron nitride (BN) films were prepared. The process involved, spraying BN powder-dispersed $\text{H}_3\text{BO}_4\text{-BCl}_3$ -ethyl alcohol solution on quartz plates, and the drying off quartz plates before, and annealing at 1070 °C in a nitrogen atmosphere. The optical energy band gap of the BN films was 5.28 eV. Photoluminescence peaks with energies of 3.44, 3.16, 2.97, and 2.35 eV at 10 K were observed and analyzed. Accordingly, these have resulted from donor-acceptor pair recombinations.

Keywords: BN (boron-nitride), Energy gap, Photoluminescence, Recombinations

1. Introduction

Boron nitride (BN) semiconductors with ultra-wide-energy band gaps are of two types: namely, cubic BN (c-BN) and hexagonal BN (h-BN), which are structurally similar to diamond and graphite, respectively [1]-[3]. The h-BN film type has received much attention because of similarities to carbon and its promising properties such as good chemical and mechanical stability. Optical properties [1]-[4] and deep levels [5], [6] of h-BN prepared by various methods have been explored because the relatively easier in preparation of h-BN compared with c-BN. In contrast, few studies on the photoluminescence (PL) spectra of h-BN have been reported. Meanwhile, the PL transition mechanism of h-BN has not yet been reported to date. Based on the discussion above, we coated a BN film into the inner part of a quartz tube. Thereafter, the quartz tube was used to grow single-crystal semiconductors without impurities. Next, we coated BN film into quartz plates. This process allowed us to obtain well-grown h-BN films. Then, we explored the PL mechanism of h-BN films by investigating the crystal structures and optical energy band gaps. Finally, PL spectra measurement was conducted. The PL transition mechanism of h-BN was also identified.

2. Experimental

We dispersed BN powder (purity 99.99%, nano-crystalline) with a hexagonal structure into a $\text{H}_3\text{BO}_4\text{-BCl}_3$ -ethyl alcohol solution. The solution was sprayed on quartz plates and then dried off. This process was repeated several times with sprayed thickness of about 1 μm . The sprayed area was $1.5 \times 1.5 \text{ cm}^2$. The dried quartz plates were placed in a tubular electric furnace, heated slowly to 1070 °C with

nitrogen gas blowing, and annealed for 96 min. The grown BN films on the quartz plates were translucent.

The crystal structure of the grown BN films was investigated by analyzing their X-ray diffraction patterns. Optical absorption spectra were measured by using a uv-vis-nir spectrophotometer (Hitachi, U-3501) equipped with 60-mm integrating sphere. Optical absorption spectra were measured with nitrogen gas blowing into a sample chamber at the wavelength range of 187 - 385 nm. Photoluminescence spectra were measured by a conventional PL measurement system consisting of a double monochromator (Spex1403, $f = 0.85 \text{ m}$), a photomultiplier tube (RCA C31034), and a cryogenic system (APD, SH-4). The 1064-nm line of the Nd-YAG laser (Spectra Physics, T10-85) and the 266-nm line by redoubling the 1064-nm line were used as sources of excitation.

3. Results and Discussion

3.1 Crystal Structure and Defect Levels of the Hexagonal BN Film

Fig. 1 shows the X-ray diffraction pattern of the grown BN film. The BN film crystallized into an h-BN structure from the intensive diffraction peaks of (002), (100), (102), (110), and (112). Based on analysis of the diffraction pattern, the lattice constants of the h-BN film were $a = 2.5044 \pm 0.0025 \text{ \AA}$ and $c = 6.6562 \pm 0.0054 \text{ \AA}$.

Thermally stimulated current (TSC) method [7] was used obtain the defect levels in the h-BN film. Three donor levels and three acceptor levels were obtained. The activation energies of the donor levels were 0.63, 1.10, and 1.51 eV, while the activation energies of the acceptor levels were 1.02, 1.21, and 1.42 eV. A comparison of these results with those by Lopatin and Konusov [6], is indicative of the reasonable values for the donor and acceptor levels.

The SEM surfaces micrograph in Fig. 2 shows the formation of the h-BN film in the layer structure. The film surface is rough with grainy layer morphology. The grain size of the film was with an average grain size of about 3 μm .

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Fig. 1. Powdered X-ray diffraction pattern of the h-BN film.

Fig. 2. SEM surface photographs of the h-BN film.

3.2 Photoluminescence Characteristics of Hexagonal BN Film

Fig. 3 shows the optical absorption spectrum of the h-BN film at 293 K, presenting a peak at the ultraviolet wavelength range and an optical absorption edge at 234.8 nm (5.28 eV). The optical absorption edge corresponds to the optical energy band gap of the h-BN film. The optical energy band gap of 5.28 eV agrees well with 5.2 eV reported by Hoffman et al. [2] and 5.14 eV by Stenzel et al. [3]. In Fig. 2 shows an absorption peak located at 263 nm (4.71 eV), which is believed to be a result of a defect level in the h-BN film. The peak energy of this absorption peak corresponds to the difference between the optical energy band gap (5.28 eV) and the activation energy of the donor level (0.63 eV) as mentioned in the previous paragraph. Accordingly, the absorption peak at 263 nm was influenced by the donor level 0.63 eV, as observed by the TSC method.

Fig. 4 shows the PL spectra of the h-BN film at 300 and 10 K. The PL spectrum at 300 K presented two broad PL peaks at the wavelength ranges of 400 - 430 nm and 500 - 550 nm. To investigate the PL peaks in detail, we measured the PL spectrum at 10 K. The PL spectrum at 10 K exhibited three peaks at the wavelength range of 345 - 450 nm and another peak at the range of 460 - 600 nm, their corresponding values 360.4 nm (3.44 eV, P1), 392.4 nm (3.16 eV, P2), and 417.5 nm (2.97 eV, P3), and the other peak at 527.6 nm (2.35 eV, P4).

Fig. 3. Optical absorption spectrum of the h-BN film at 293 K.

Fig. 4. Photoluminescence spectra of the h-BN film at 10 and 300 K.

P2), and 417.5 nm (2.97 eV, P3), and the other peak at 527.6 nm (2.35 eV, P4).

In accordance with the donor and acceptor levels and the optical energy band gap of the h-BN film, the PL peaks (P1, P2, P3, and P4) might have resulted from donor-acceptor pair recombinations. Fig. 5 shows the PL transition mechanism in the h-BN film. The PL peak at 360.4 nm (3.44 eV,

Fig. 5. Proposed energy band scheme for the radiative mechanism of the h-BN film at 10 K.

P1) might have been a consequence of the radiative transition from the donor level at 0.63 eV below the conduction band to the acceptor level at 1.21 eV above the valence band of the h-BN film. Similar explanations can be extended for the PL peaks at 392.4 nm (3.16 eV, P2), 417.5 nm (2.97 eV, P3), and 527.6 nm (2.35 eV, P4).

4. Conclusion

The h-BN films were grown on quartz plates by spaying a BN powder dispersed- $\text{H}_3\text{BO}_4\text{-BCl}_3$ -ethyl alcohol solution. Subsequently, they were dried off, and heated to 1070 °C. Next, they were crystallized into a hexagonal structure with the lattice constants of $a = 2.5044 \pm 0.0025 \text{ \AA}$ and $c = 6.6562 \pm 0.0054 \text{ \AA}$. The optical energy band gap of the h-BN film was 5.28 eV. There were three donor levels at activation energies of 0.63, 1.10, and 1.51 eV, and three acceptor levels with activation energies of 1.02, 1.21, and 1.42 eV. The four PL peaks at 10 K were at 360.4 nm (3.44 eV), 392.4 nm (3.16 eV), 417.5 nm (2.97 eV), and 527.6 nm (2.35 eV). Based on analysis, these PL peaks were the results of donor-acceptor pair recombinations.

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