

Free exciton emission from hexagonal boron nitride films grown on sapphire substrates by low pressure chemical vapor deposition

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Abstract

The hexagonal boron nitride films were grown on c-plane sapphire substrates by low pressure chemical vapor deposition using BCl_3 and NH_3 as sources at 1200 °C. By reducing the growth pressure to 10 kPa, the films showing free exciton emission in cathodoluminescence were grown for the first time on sapphire substrates. The peak wavelength of the emission was about 214 nm. The luminescence property of the films were discussed in terms of the influences of growth conditions and substrates.

1. Introduction

Hexagonal boron nitride (h-BN) has a graphite-like crystal structure consisting of sp^2 -hybridized atomic sheets of boron and nitrogen. In addition to high thermal and chemical stability, h-BN shows the characteristic luminescence in the ultraviolet spectral region including the free exciton emission at 215 nm and the impurity related emissions such as that around 320 nm owing to its wide bandgap energy of about 6.0 eV [1, 2]. From such features, h-BN has been expected to be applied for deep ultraviolet light emitters, substrates for graphene devices, releasing layers for nitride semiconductors and so on [3-5]. Thus far, high quality h-BN bulk crystals have been grown by the high pressure and high temperature technique [1]. At present, however, their size is limited to several mm in diameter. Therefore, high-quality single-crystal h-BN thin films on a large-area substrate are required for such electronics applications.

h-BN thin films have been grown by several techniques such as metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy [6-10]. However, the quality of these films is still insufficient for device fabrication in terms of the efficiency of band edge luminescence and the surface flatness. From such a technological background, our study has intended to develop the manufacturing method of high quality h-BN thin films. To achieve this aim, we have been paid attention to the CVD with BCl_3 and NH_3 gases for precursors, which is currently used for the production of commercially-available pyrolytic BN. We have reported that the low pressure growth at 20 kPa leads to the significant improvement of crystalline quality compared to those grown at an atmospheric pressure. However, the grown films did not show the band edge luminescence [11]. In this study, we have achieved the growth of h-BN films showing the free exciton emission around 214 nm at room temperature by reducing growth pressure to 10 kPa and investigated the influence of growth conditions on the luminescence property.

2. Experimental procedures

The CVD apparatus used in this study consists of a BN ceramics reactor tube (i.d. = 40 mm) and a high temperature tubular furnace. The source gases were BCl_3 diluted to 0.03 % in N_2 and 99.9997 % - pure NH_3 . BCl_3 gas was supplied through a coaxial gas nozzle with a sheath flow of N_2 outside the BCl_3 flow. A c-plane sapphire substrate was placed 30 mm away from the nozzle. Prior to growth, the substrate was subject to a heat-treatment in a flow including NH_3 at growth temperature (T_g) for 10 min. The growth was carried out for 2 h under 10 kPa. The supply rates of BCl_3 was 0.2 sccm, whereas those of NH_3 was varied from 100 to 600 sccm. T_g and the total gas flow was kept at 1200 °C and 5 slm, respectively, for all the growths. The growth rate of the samples was about 0.65 $\mu\text{m}/\text{h}$.

The structural and luminescence properties of the samples were evaluated by X-ray diffraction (XRD) and cathodoluminescence (CL) measurements, respectively. The CL spectra were taken at room temperature and 20 K. Surface morphology was observed using a scanning electron microscope (SEM).

3. Results and discussion

Figures 1 and 2 shows the XRD patterns and CL spectra of the sample grown at different NH_3 supply rates from 100 to 600 sccm. The CL spectra were measured at room temperature by an electron beam with an accelerating voltage of 10 kV. As seen in Fig.1, the diffraction only from h-BN (002) was observed except for that from a sapphire substrate, indicating that the grown h-BN films are strongly oriented towards the c-axis. The CL spectra were dominated by the

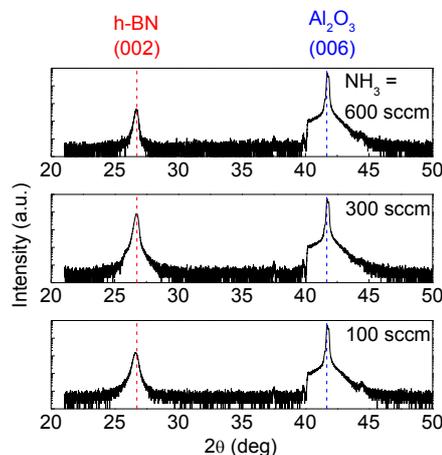


Fig. 1 XRD patterns of the samples grown at different NH_3 supply rates.

impurity related emission band around 350 nm, which probably originates from O or C impurities in h-BN. On the other hands, a pronounced emission was also observed around 214 nm although its intensity was low. This emission can be ascribed to the recombination of free exciton of h-BN if it is compared with 215 nm observed for the h-BN bulk crystal [12]. It is noteworthy that the free exciton emission was observed for the first time from the h-BN film grown on a c-plane sapphire substrate. At present, the origin of the difference in the peak wavelength is not clear. One of the possibilities is a strain induced by the difference in the thermal expansion coefficients of h-BN and sapphire. From Fig. 2, the improvement of luminescence properties was achieved for

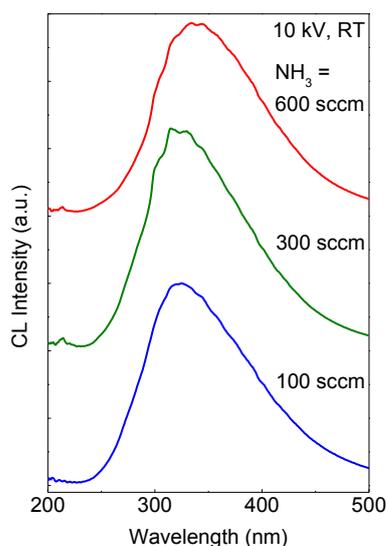


Fig. 2 Room temperature CL spectra of the samples shown in Fig. 1. The measurements were carried out with an accelerating voltage of 10 kV.

the film grown at $\text{NH}_3 = 300$ sccm, which was evidenced by the most intense free exciton emission. The observed improvement in the luminescence property by reducing the growth pressure from 20 to 10 kPa indicates that the reaction of BCl_3 and NH_3 in the vapor phase was not sufficiently suppressed at 20 kPa.

Figure 3 shows the CL spectrum measured at room temperature by an electron beam with an acceleration voltage of 2 kV for the sample grown at a NH_3 supply rate of 300 sccm.

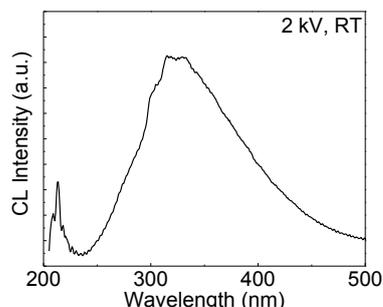


Fig. 3 CL spectrum of the sample grown at a NH_3 supply rate of 300 sccm measured at an accelerating voltage of 2 kV.

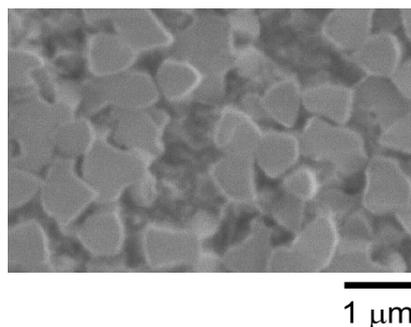


Fig. 4 Surface morphology of the sample shown in Fig. 3.

In comparison with CL spectrum measured at 10 kV, the intensity ratio of the free exciton emission to the impurity related emission significantly increased. This result indicates that the film quality of the region near the surface was better than that near the substrate. Fig. 4 shows the SEM image of surface morphology of the same sample as shown in Fig. 3, which reveals that the film consisted of columnar crystal grains with a flat top face. Therefore, it is essential to control the interface between films and substrates to further improve the film properties.

4. Summary

The h-BN films were grown by low pressure CVD using BCl_3 and NH_3 as sources on c-plane sapphire substrates at 1200 °C. We have found that reducing the growth pressure to 10 kPa improves the luminescence property, resulting in the first observation of the free exciton emission at room temperature from the h-BN films grown on sapphire substrates. The peak appeared at about 214 nm, which is slightly shorter than that observed for the bulk crystal. The dependence of CL spectra on the accelerating voltage of an electron beam indicates the improvement of film quality with the increase of its thickness.

Acknowledgments

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