

Chemical vapor deposition of hexagonal boron nitride films on c-plane sapphire substrates

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Abstract

The hexagonal BN films were grown on c-plane sapphire substrates by chemical vapor deposition using BCl_3 and NH_3 as sources at substrate temperatures from 1200 to 1700 °C under 100 or 20 kPa. The grown films were oriented preferably toward the c-direction. It has been found that the structural and luminescent properties, which are dependent on the growth temperature and pressure, are strongly correlated with each other. The low pressure growth successfully yielded the film with a unique in-plane orientation, $\{100\}_{\text{h-BN}} // \{110\}_{\text{sapphire}}$. The lateral growth was also enhanced under the reduced pressure.

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 physical and chemical stability, it has been reported that h-BN shows the characteristic luminescence in the ultraviolet spectral region including the band edge 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 single crystals have been grown by a high temperature solution method [1]. On the other hand, thin films are necessary for such novel electronics applications. h-BN thin films have been grown by several techniques such as chemical vapor deposition (CVD) and molecular beam epitaxy [6-10]. However, the quality of these films is still insufficient for device fabrication in terms of the efficiency of bandedge luminescence and the surface flatness. From such a technological background, our study has intended to establish 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. In this study, we investigated the influence of growth conditions systematically on structural and luminescence properties of the h-BN films.

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 tube 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 100 or 20 kPa. The supply rates of BCl_3 was 0.03 and 0.05 sccm for these growth pressures, respectively, whereas that of NH_3 was kept at 240 sccm. The total gas flow was 5 slm for all the growths. T_g was varied from 1200 to 1700 °C. Under these conditions, the growth rates were about 0.5 and 0.4 $\mu\text{m}/\text{h}$, respectively. The structural and luminescence properties of the samples were evaluated by X-ray diffraction (XRD) and cathodoluminescence (CL) measurements, respectively. Surface morphology was observed using a scanning electron microscope (SEM).

3. Results and discussion

3-1 Growth under the atmospheric pressure

Figure 1 (a) shows the out-of-plane XRD patterns measured for the samples grown at T_g from 1300 to 1700 °C under the atmospheric pressure. It can be seen that the crystallization of h-BN thin films is dramatically promoted with increasing T_g from 1300 to 1500 °C, resulting in the growth of films strongly oriented towards c-axis at 1500 °C. However, the further increase of T_g deteriorated the crystalline quality. It should be noted that the diffraction peak from AlN started to appear in the same T_g region, which suggests that the excessive nitridation of the substrate surface had a negative influence on the film formation. The crystalline quality recovered for the growth at 1700 °C although the formation of turbostratic (disordered) phase was observed.

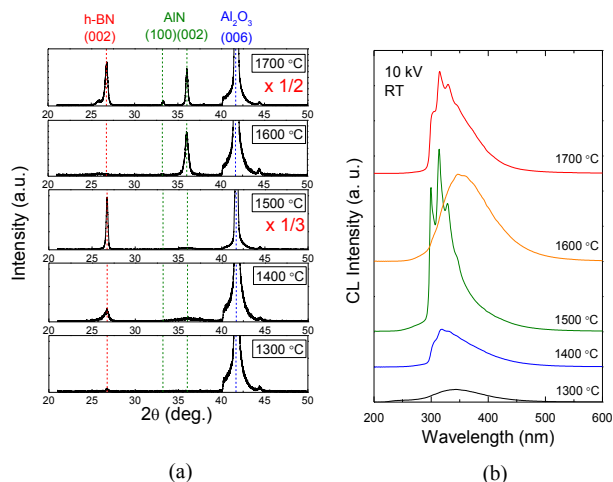


Fig. 1 Out-of-plane XRD patterns (a) and room temperature CL spectra (b) of the samples grown at different T_g under the atmospheric pressure.

Figure 1 (b) shows the CL spectra of the same samples shown in Fig. 1 (a). The film grown at 1300 °C showed a broad emission of unknown origin around 350 nm. With increasing T_g , the impurity related emission band from h-BN, which is associated with a characteristic phonon-related fine structure, appeared around 320 nm and became dominant at 1500 °C. However, this emission band disappeared at $T_g = 1600$ °C. Instead, that of unknown origin became dominant. The both emission bands were observed for the film grown at 1700 °C. The above-mentioned T_g dependences of the XRD and CL results were very similar, which leads us to conclude that the luminescence property of the grown films is strongly correlated with the crystalline quality.

Figure 2 (a) shows the in-plane XRD patterns of the sample grown at 1500 °C, in which diffraction from h-BN{100} and sapphire{110} were detected. The diffraction from h-BN was broad except for very small peaks appearing every 60 deg., which does not indicate well-defined in-plane orientation for the film. The surface morphology reveals that the film consists of randomly oriented grains, as shown in Fig. 2 (b), reflecting the result of in-plane XRD. The grain size tended to become larger with increasing T_g .

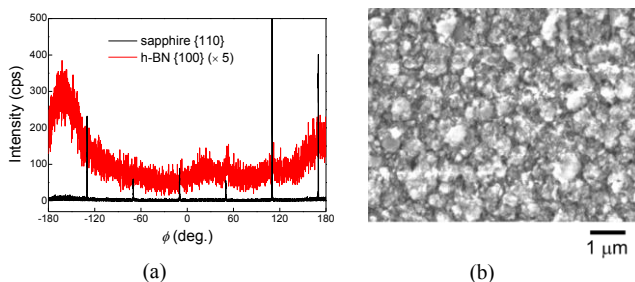


Fig. 2 In-plane XRD pattern (a) and SEM image of the surface (b) of the sample grown at 1500 °C under the atmospheric pressure.

3-2 Growth under the reduced pressure

Figure 3 (a) and (b) show the out-of-plane XRD patterns and CL spectra of the samples grown at T_g from 1200 to 1400 °C under the reduced pressure. As can be seen in these

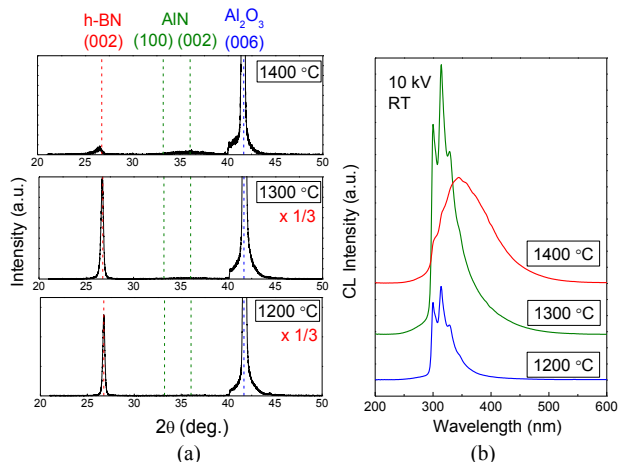


Fig. 3 Out-of-plane XRD patterns (a) and room temperature CL spectra (b) of the samples grown at different T_g under the reduced pressure.

figures, both of the structural and luminescence properties were improved for the films grown at $T_g = 1200$ and 1300 °C. Namely, the films were strongly oriented towards the c-axis and showed CL dominated by the emission band characteristic of h-BN around 320 nm. However, when T_g was raised to 1400 °C, the both properties were deteriorated. From these results, the strong correlation with the crystalline and luminescent properties has also been confirmed for the low pressure growth. On the other hand, we have found that the T_g where the film quality is improved is lower for the low pressure growth.

Figure 4 (a) shows the in-plane XRD patterns of the sample grown at 1200 °C, in which the pronounced diffraction peaks were observed every 60 deg., reflecting the six-fold symmetry of the crystal structure of h-BN. This measurement confirms the unique in-plane orientation of the film, $\{100\}_{\text{h-BN}} // \{110\}_{\text{sapphire}}$. It can be seen in Fig. 4 (b), the lateral growth was enhanced for this film, which leads to the improvement of crystal quality.

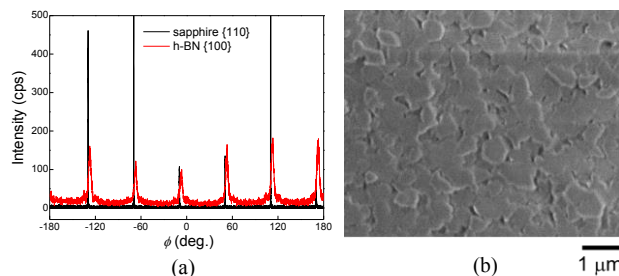


Fig. 4 In-plane XRD pattern (a) and SEM image of the surface (b) of the sample grown at 1200 °C under the reduced pressure.

4. Summary

The growth of h-BN films on c-plane sapphire substrates by CVD using BCl_3 and NH_3 as sources was investigated systematically by changing growth parameters. It has been found that the structural and luminescent properties, which are dependent on the growth temperature and pressure, are strongly correlated with each other. The low pressure growth successfully yielded the film with the unique in-plane orientation, for which the lateral growth was also enhanced.

Acknowledgments

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