# Growth of Boron Nitride on 6H-SiC Substrate by Flow-rate Modulation Epitaxy

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# 1. Introduction

Hexagonal boron nitride (h-BN) is one of the promising material systems for optical device applications in the ultraviolet spectral region because of the wide bandgap and large exciton binding energies of 5.97 eV and 149 meV, respectively [1]. The growth of a thin high-quality h-BN epitaxial layer by metalorganic vapor phase epitaxy (MOVPE) or vapor phase epitaxy is indispensable for fabricating optical devices with a p-n junction and quantum well structures. However, there has been no report for a high-quality h-BN epitaxial layer on an appropriate substrate so far. Only a few papers have described the growth of BN by conventional MOVPE [2], and there are many unsolved fundamental problems. In this work, we grew BN layers on 6H-SiC substrate by MOVPE using triethylboron (TEB) and ammonia (NH<sub>3</sub>) and found that the growth rate of BN decreases as the NH<sub>3</sub> flow rate increases, indicating that a strong parasitic reaction occurs between TEB and NH<sub>3</sub>. Flow-rate modulation epitaxy (FME) [3] was applied to the BN growth for the first time and it was found that the parasitic reactions could be effectively reduced by using FME. The structure properties of BN grown by FME were also investigated by X-ray diffraction and transmission electron microscopy.

## 2. Experiment

BN layers were grown on (0001) 6H-SiC substrate by low-pressure (300 Torr) MOVPE or FME. The growth temperature of the BN was 1050 °C. The lattice-mismatch between the 6H-SiC substrate and h-BN films is about 19%. TEB and NH<sub>3</sub> were used as the precursors. The molar flux of TEB for BN growth was 20 µmol/min. For BN growth by FME, 1-s-long pulses of TEG and NH<sub>3</sub> were alternately introduced into the reactor. No purge time was inserted between the TEG and NH<sub>3</sub> supply. A p-polarized ultraviolet light was irradiated on the growing surface at the incidence angle of 75° and the reflected light was detected using a Si photodiode. The light source was 325-nm light from a He-Cd laser. During BN MOVPE or FME growth, an oscillation due to optical interference was observed, indicating the thickness could be measured in situ [4]. A high-resolution X-ray diffractometer (Philips X'Pert System) was used to evaluate the structural quality and determine c-lattice parameters. The film crystallography and the film-substrate interface were studied using high-resolution cross-sectional transmission electron microscopy (HRTEM) operated at 300 kV.

#### 3. Results and Discussion

Figure 1 shows the growth rate of BN grown by MOVPE and FME as a function of NH<sub>3</sub> flow rate. The NH<sub>3</sub> flow rates were varied from 60 to 700 ccm while keeping the TEB flow rates constant. For BN growth by MOVPE, the growth rate decreased monotonically with increasing NH<sub>3</sub> flow rate from 60 to 300 ccm. For further increase in NH<sub>3</sub> flow, the growth rate went down to virtually zero. The growth rate also decreased with increasing the reactor pressure from 76 to 300 Torr. These results indicate that a strong parasitic reaction occurs between TEB and NH<sub>3</sub> in BN MOVPE growth. To reduce or eliminate the parasitic reactions, FME was applied to the BN growth for the first time. The growth rate of one cycle (1-s-long pulses of TEG and NH<sub>3</sub>) as a function of NH<sub>3</sub> flow rate is also shown in Fig. 1. The growth rate of BN decreased in small steps with increasing NH<sub>3</sub> flow rate. However, the degree of the decrease in FME growth was much smaller than that in MOVPE. In addition, a growth rate larger that 0.5 monolayer/cycle could be obtained even at the NH<sub>3</sub> flow rate of 700 ccm. It should be noted that the BN growth rates in MOVPE under high NH<sub>3</sub> flow rate (>300 ccm) are almost zero. These results indicate that FME can reduce the parasitic reaction between TEB and NH<sub>3</sub> effectively. The decrease of growth rate in FME with increasing NH<sub>3</sub> flow rate was caused by intermixing of TEB and NH3 at switching times, which occurred because there was no purge time between the TEG and NH<sub>3</sub> supply.



Fig. 1. Growth rate of BN films grown by MOVPE and FME as a function of  $NH_3$  flow rate.



Fig. 2.  $2\theta/\omega$  X-ray diffraction patterns of BN films grown by MOVPE and FME.

The structural properties of BN samples grown by MOVPE and FME were investigated with a  $2\theta/\omega$  X-ray diffraction scan (Fig. 2). The thickness of the BN layers was 1.5 µm. No diffraction peak related to BN was observed for the BN samples grown by MOVPE, indicating that the structure of the film was an amorphous film structure. In contrast, a broad diffraction peak at the diffraction angle of 2 $\theta$  about 25° was observed for BN samples grown by FME. This peak is ascribed to turbostratic BN (t-BN) with the c axis elongated [5]. No other diffraction peak was observed, meaning that the BN films have a structure that has a weakly preferred orientation to the c axis. In general, the transformation of amorphous BN (a-BN) to t-BN occurs with increasing growth temperature. In this study, the growth temperature



Fig. 3 Cross-sectional HRTEM image of the BN films grown by FME. The selected area electron diffraction pattern is also shown.

in MOVPE and FME was the same, 1050°C. We deduce that FME enhances the migration of boron atoms on the growing surface [3], so that t-BN layers could be grown on 6H-SiC substrate in spite of the large lattice mismatch.

To investigate the film crystallography and the film-substrate interface, a HRTEM analysis was performed. The HRTEM image is shown in Fig. 3(a). At the BN/6H-SiC interface, 2-3 nm of a-BN was observed. The t-BN layers were grown on the a-BN intermediate layer. In the t-BN layer, sp<sup>2</sup> layers divided into shorter ones with nanofiber morphology. These nanograins with length of 3-5 nm were significantly buckled. Figure 3(b) shows a selected area electron diffraction pattern (SAEDP) from the BN/6H-SiC interface area. The lattice spacing for the BN layer on the substrate matched that of t-BN. The SAEDP also shows that the structure of the BN layer has a weakly preferred orientation to the c axis, which is consistent with the XRD results. The t-BN structure could be formed by the large lattice mismatch. Therefore, we believe that a well lattice-matched substrate is critical for the growth of high-quality h-BN films.

## 4. Conclusions

We grew BN layers on 6H-SiC substrate by conventional MOVPE using TEB and  $NH_3$  and found that the growth rate of BN decreased as the  $NH_3$  flow rate increased, indicating that a strong parasitic reaction occurred between TEB and  $NH_3$ . In this work, FME was applied to BN growth for the first time and it was found that the parasitic reactions could be effectively reduced by using FME. From XRD, HRTEM and SAEDP analyses, the structure of BN grown by FME was t-BN and has a weakly preferred orientation to the c axis. For further improvement of the quality, a well lattice-matched substrate is critical for the growth of h-BN films.

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