ABSTRACT

Boron was incorporated into GaN in order to determine its limits of solubility, its ability of reducing the lattice constant mismatch with 6H-SiC, as well as its effects on the structural and optical properties of GaN epilayers. $B_xGa_{1-x}N$ films were deposited on 6H-SiC (0001) substrates at 950 °C by low pressure MOVPE using diborane, trimethylgallium, and ammonia as precursors. A single phase alloy with x=0.015 was successfully produced at a gas reactant B/Ga ratio of 0.005. Phase separation into pure GaN and $B_xGa_{1-x}N$ alloy with x=0.30 was deposited for a B/Ga reactant ratio of 0.01. This is the highest B fraction of the wurtzite structure alloy ever reported. For B/Ga ratio ≥ 0.02, no $B_xGa_{1-x}N$ was formed, and the solid solution contained two phases: wurtzite GaN and BN based on the results of Auger and x-ray diffraction. The band edge emission of $B_xGa_{1-x}N$ varied from 3.451 eV for x=0 with FWHM of 39.2 meV to 3.465 eV for x=0.015 with FWHM of 35.1 meV. The narrower FWHM indicated that the quality of GaN epilayer was improved with small amount of boron incorporation.

INTRODUCTION

One of the most limiting aspects of GaN is its relatively poor crystal quality, due to the necessity of heteroepitaxy. Sapphire (0001) and 6H-SiC (0001) are the most common substrates for GaN epitaxy, but both suffer from large lattice constant mismatches, 16% and 3.5% respectively. It may be possible to reduce or eliminate the lattice constant mismatch by adding boron to GaN, thereby forming a $B_xGa_{1-x}N$ alloy. However, the solubility of boron in GaN under typical growth conditions (by either MOVPE or MBE) may be limited, since hexagonal BN (similar in structure to graphite) is the stable structure at low pressure. The wurtzite structure, the most stable structure for GaN, is only a metastable structure for BN; it is normally produced by shock-compression. This disparity of crystal structures between GaN and BN probably results in a very low mutual solubility.

Several groups attempted to form epitaxial $B_xGa_{1-x}N$ alloys using sapphire as the substrate. A.Y. Polyakov et al reported that the highest solubility of boron in GaN was 1% at 1000 °C by MOVPE [1]. Vezin et al produced a single phase of $B_xGa_{1-x}N$ with x up to 4.56% by MBE [2]. In the present work, 6H-SiC (0001) was used as a substrate, since less boron incorporation (x=0.17) would be necessary to eliminate the lattice constant mismatch. The smaller lattice constant mismatch may be important in enhancing the boron solubility via epitaxial stabilization.
the minimization of the overall free energy by maintaining an epitaxial structure by incorporating an element (boron in this case) at a concentration which exceeds the solubility limit [3].

Another motivation for developing B$_x$Ga$_{1-x}$N alloys is the possibility of fabricating BGaN-based semiconductor devices operating in the UV region. For this application, it is important to know how the energy band gap of B$_x$Ga$_{1-x}$N changes with B content. Honda et al predicted the bandgap energy of B$_x$Ga$_{1-x}$N increased with boron composition based on Harrison’s theory assuming wurtzite BN in GaN [4].

In this paper, B$_x$Ga$_{1-x}$N films were successfully grown on 6H-SiC substrates by MOVPE. The effects of the gas phase B/Ga ratio on the solid film’s growth rate, surface morphology, and structural were studied. Also, the bandgap energy of B$_x$Ga$_{1-x}$N was determined from photoluminescence measurements.

**EXPERIMENT**

B$_x$Ga$_{1-x}$N films were deposited on the Si face of on-axis 6H-SiC (0001) substrates in a vertical reactor by MOVPE at 76 Torr. The 6H-SiC substrates were ultrasonically degreased in sequential baths of trichloroethylene, acetone and methanol, rinsed in deionized water, then dipped into a 10 % HF solution to remove the native oxide layer. Prior to growth, the 6H-SiC substrates were annealed in hydrogen at 1000 °C for 10 minutes. Trimethylgallium (TMG) and ammonia (NH$_3$) were Ga and N source gases, and hydrogen was the carrier gas. The boron precursor was 0.01% diborane (B$_2$H$_6$) diluted in H$_2$. Diborane and ammonia have been commonly used to produce BN [5]. The B$_2$H$_6$ and NH$_3$ were separately introduced into the reactor and mixed just above the susceptor to avoid their parasitic gas phase reaction at room temperature [6]. A GaN buffer layer with 20-30 nm thickness was grown at 565 °C and ramped to 950 °C for crystallization. This buffer layer was essential for wetting the 6H-SiC substrates for later continuous film growth. The growth temperature was increased to 950 °C for the growth of B$_x$Ga$_{1-x}$N. The TMG and NH$_3$ were fixed at 18 µmol/min and 1.5 sdm, respectively. The B/Ga ratio in the gas phase was varied from 0 to 0.2.

The B$_x$Ga$_{1-x}$N composition was determined using a PHI 660 scanning Auger microprobe (SAM) after bombarding the surface with argon ions for several seconds to remove surface contamination. The crystal structure of B$_x$Ga$_{1-x}$N was examined by X-ray diffraction (XRD) and its quality was obtained from the full width at half maximum (FWHM) of x-ray rocking curves.

The surface morphology of the samples was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The thickness of films was measured by cross-sectional SEM, but for very thin layers, the growth rate was estimated from the argon-ion sputtering rate during Auger measurements. Photoluminescence (PL) measurements were performed at 10 K to study the optical properties of the films and determine the band edge emission of the samples.

**RESULTS AND DISCUSSION**

The influence of the B/Ga ratio in the gas phase on the B$_x$Ga$_{1-x}$N growth rate is plotted in Fig. 1. The growth rate sharply decreased from 1.8 to 0.4 µm/hr as the B/Ga was increased from 0.01 to 0.02; otherwise, the growth rate was fairly constant for B/Ga ratios in the 0-0.1 and 0.02-0.1 ranges. For B/Ga ratio higher than 0.2, the growth rate of B$_x$Ga$_{1-x}$N dropped to zero and only BN layer was produced. Apparently, higher concentration of diborane in the gas phase prevented...
the formation of $B_xGa_{1-x}N$, but favored pure BN growth. The drop-off in the growth rate is attributed to the growth of different structure in the deposited films; highly-faceted big crystals were produced at $B/Ga \leq 0.01$, while tiny irregular shape particles with very smooth surface were observed as $B/Ga$ ratio was higher than 0.02.

Figures 2(a) and 2(b) show SEM images of $B_xGa_{1-x}N$ with B/Ga ratio of 0.005 and 0.01, respectively. Well-faceted crystals are seen in both samples. However, the crystal size and size distribution in Fig. 2(a) are much smaller than in Fig 2(b). As shown in Fig. 2(b), the surface of the film contained the matrix film and two distinct shapes: well (0001) oriented epicrystals and agglomerated crystals on top of the surface. Some of the agglomerated crystals also showed a hexagonal structure, but the [0001] growth direction was roughly parallel to the substrate surface. These features strongly suggest that phase separation occurred in the film deposited at $B/Ga=0.01$, while single crystals of $B_xGa_{1-x}N$ were formed at $B/Ga=0.005$.

Figure 2. SEM images of $B_xGa_{1-x}N$ films deposited at different B/Ga ratios. (a) $B/Ga=0.005$; (b) $B/Ga=0.01$. 
The Auger spectra of $B_xGa_{1-x}N$ grown at different B/Ga ratios are shown in Figs. 3 and 4. The spectra shown in Fig. 3 is the film deposited at B/Ga=0.01. As described in the SEM section, this film was composed of hexagonal crystals, agglomerated crystals, and matrix material. The relative atomic concentrations of the three elements- B, Ga, and N- are shown above each spectrum, which were calculated using the sensitivity factor of 0.11, 0.22 and 0.17 for B, Ga, and N, respectively. The main gallium, nitrogen, and boron peaks occur at 1067, 384 and 179 eV, respectively. The matrix material was a B-rich phase with relatively high concentration of boron (Fig. 3(a)). The agglomerated crystals were $B_xGa_{1-x}N$ alloy (Fig. 3(b)) and the well-orientated hexagonal crystals just pure GaN (Fig. 3(c)). These results confirmed that the phase separation occurred in the film grown at B/Ga=0.01. The oxygen and carbon peaks were detected in all samples but decreased with the depth away from the surface. Figure 4 displays the Auger spectra of the films deposited at higher B/Ga ratio. The boron concentration in the samples increased with increasing B/Ga ratio. However, the Ga peak disappeared and only BN was produced at B/Ga=0.2.

Figure 5 shows θ-2θ XRD spectra of films with B/Ga of 0.005, 0.01 and 0.05. The $B_xGa_{1-x}N$ alloys were detected and the (0002) peak shifted toward the SiC (0006) reflection in Figs. 5(a) and 5(b), which indicated the c lattice parameter was reduced with the increase of boron in GaN. The concentration of boron was 0.015 and 0.30 in Fig. 5(a) and Fig. 5(b), respectively, which was determined by the relative shift of the $B_xGa_{1-x}N$ peak with respect to the GaN (0002) peak.
applying Vegard’s law. The sample grown at B/Ga=0.005 was a single crystal alloy of B$_{0.015}$Ga$_{0.985}$N with wurtzite structure. However, the sample produced at B/Ga=0.01 showed a phase separation of GaN and B$_{0.3}$Ga$_{0.7}$N. When the B/Ga ratio was increased to 0.05, no B$_x$Ga$_{1-x}$N peak was detected and only a broad and low intensity of GaN (0002) peak was observed. The decrease in x-ray peak density and increase in peak width shown in Fig. 5c indicate that the quality of film became poor at high B/Ga ratio.

The PL spectra measured at 10 K for the films with B/Ga ratios of 0, 0.005, 0.05 and 0.1 are given in Fig. 6. The band edge emission of pure GaN shown in Fig. 6(a) was 3.451 eV with FWHM of 39.2 meV, which was ascribed to the neutral donor bound exciton recombination labeled I$_2$. The I$_2$ line increased to 3.465 eV with FWHM of 35.1 meV when the B/Ga ratio was equal to 0.005. Two weak peak transitions at 3.267 and 3.178 eV shown in Fig. 6(b) were attributed to donor-acceptor (D-A pair) recombination. The narrower FWHM of B$_x$Ga$_{1-x}$N at B/Ga ratio of 0.005 (x=0.015) compared with B/Ga=0 (pure GaN epilayer) suggests that the quality of GaN epilayer was improved with small amount of boron incorporation. It seems that the band edge transition of B$_x$Ga$_{1-x}$N shifted to high energy with increasing B/Ga ratio. However, when the B/Ga ratio was increased to 0.05, two peaks appeared at 3.358 eV and 3.323 eV as shown in Fig. 6(c). The emission peaks at 3.358 eV and 3.323 eV were possibly due to band edge transitions and impurity related transitions, respectively. As the B/Ga ratio increased to 0.1, the PL spectrum shows a much broader emission band, indicating poor crystalline quality at high B/Ga ratio.

Figure 5. XRD $\theta$-2$\theta$ scans of films deposited at different B/Ga ratios. (a) B/Ga=0.005; (b) B/Ga=0.01; (c) B/Ga=0.05.

Figure 6. PL spectra of films measured at 10 K at different B/Ga ratios. (a) B/Ga=0; (b) B/Ga=0.005; (c) B/Ga=0.05; (d) B/Ga=0.1.
CONCLUSIONS

We have grown $\text{B}_x\text{Ga}_{1-x}\text{N}$ films on 6H-SiC (0001) substrates at 950 °C by MOVPE. These studies show that single phase, single crystal of $\text{B}_x\text{Ga}_{1-x}\text{N}$ can be produced at B/Ga ratio of 0.005. Phase separation occurred in the films when the B/Ga ratio was above 0.01. The boron concentration in the solid phase was as high as 30% reported for the first time. The quality of the GaN epilayer can be improved with small amount of boron addition.

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