Exploration of the growth parameter space for MBE-grown GaN_{1-x}Sb_x highly mismatched alloys

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Abstract

Highly mismatched GaN_{1-x}Sb_x alloys were grown under N-rich conditions at low substrate temperatures (325-550 °C) at a growth rates of ~ 0.09 μm/hr on sapphire. The alloys ranged in Sb composition from 0 – 16%, with the bandgap shifting from 3.3 to 1.6 eV in accordance with the band anticrossing (BAC) model. We compare these results to growths from another chamber, having a different N source, and using a faster growth rate (~0.24 μm/hr), much lower substrate temperatures (as low as 80 °C), different III/V ratios and absolute fluxes. Despite the range of morphologies obtained, all alloys follow the predictions of the BAC model with the bandgap only depending on the Sb composition.

Introduction

Highly mismatched alloys (HMAs) based on GaN have small fraction of a group V element, such as As or Sb incorporated in the N sublattice. The ‘mismatch’ refers to the large difference in electronegativity and/or size between the anion of the host alloy (N) and the minority incorporant (As or Sb). Although adding such mismatched components invokes challenges such as phase segregation and the introduction of strain, there are benefits in terms of the drastic increase in the range of the bandgaps normally inaccessible to GaN-based compounds. In accordance with the band anticrossing (BAC)¹ model, first-principle density functional theory (DFT)², and with experimental evidence, very small amounts of Sb (5%), for instance, reduce the bandgap of the alloys from ~3.4 eV to 2.0 eV. This is a bandgap size that is of interest for solar water splitting applications, which require an inert, robust material like GaN.

The challenge of growing GaN based HMAs involves an enormous, largely unexplored parameter space. The N source type and efficiency is a major parameter, as are the power it is operated at and the N flow rate. The Sb or As absolute flux and III/V ratios, and the Ga growth rate are also major factors. Even the substrate choice is not obvious. Since the bandgap properties seem to be unaffected by the crystal morphology³, and since we are growing at substrate temperatures that are well below what it is typical for high quality GaN, we are exploring the other numerous growth parameters using relatively inexpensive sapphire substrates. Certain device properties, however, may ultimately require that this technology be refined on better quality SiC substrates with buffer layers or GaN templates.

Experiment

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The samples from our previously published studies⁴⁻⁵ were grown in a MOD-GENII system with a HD-25 Oxford Applied Research rf activated plasma source to provide active nitrogen, and elemental Ga and Sb was used as the other sources. We are now growing these samples in an additional GENII system with a Veeco Uni-bulb plasma source to provide active N, elemental Ga and a Veeco valved cracker-sources for Sb. In both systems the uncoated sapphire substrate temperature was set by the thermocouple. The source and pumping arrangement in the second system produces significantly less atomic N; therefore we have to grow at a lower rate. Samples produced in this second chamber are the subject of this paper.

Because phase separation is a likely problem for growths at typical (~800 °C) GaN temperatures, we have focused on much lower growth temperatures, with many of our published studies discussing samples grown at 80°C⁴⁻⁵. For this paper, we are exploring samples grown at somewhat higher temperatures, typically from 325 °C to 550 °C. Previously we have shown that under Ga-rich conditions growth condition at low growth temperature (~80°C), the optical properties of GaN was dominated by a defect state and it was not possible to control the bandgap by increasing the Sb-concentration in the alloy. In this study, we have grown all subsequent samples under N rich conditions. We note that growing under group V rich conditions is advantageous for most III-V semiconductors, such as GaAs, but it is not typically used for high quality GaN films⁶. The composition of the films was determined by Rutherford Backscatter Spectroscopy and the bandgaps determined from optical transmission measurements by linear extrapolation of the absorption coefficient to zero intensity.

Results and Discussion

Our past studies from samples grown at higher growth rates (~0.24 µm/hr) showed that GaN grown at 80 °C was polycrystalline and columnar, and that the crystallinity markedly decreased as any Sb was incorporated and the films eventually became amorphous for Sb compositions exceeding 7%^[4-5]. We find that for slower growth rates (~ 0.09 µm/hr), the crystallinity is maintained for higher Sb incorporations as the substrate temperature is raised. For instance, at 325° C, we incorporated up to 16% Sb, and the polycrystalline morphology was maintained, although the preferential alignment with the substrate diminished.

The absolute Ga and Sb fluxes were determined from reflection high-energy electron diffraction (RHEED) oscillations: Assuming unity sticking, the GaSb growth rate was recorded as a function of decreasing Sb over pressure and the 1:1 flux defined at the point when the rate began to decrease (the onset of group V limited growth). The growth rate was converted to flux using the known lattice constant of the substrate. In another experiment the (fixed) N-flux was determined from the chemical composition of GaN as a function of a linearly increasing Ga-flux, using in-situ Auger electron spectroscopy. The 1:1 flux was defined at the point when the N-signal began to disappear due to formation of metallic Ga⁷. The Ga-flux as a function of temperature was known from the mentioned GaSb RHEED experiment.

For the first series of HMAs samples, we fixed the substrate temperature at 325 °C, the N flux at 2.00×10^{18} at/(m²s), the Ga flux at 2.35×10^{18} at/(m²s), and the Sb flux ranging from 0 to 7.82×10^{18} at/(m²s). The Sb mole fraction (x) in GaN_{1-x}Sb_x as a function of Sb/N is plotted in Figure 1a, and the region in the inset is expanded in Figure 1b. As with any alloy system, to first order, the Sb concentration can be

described by $[Sb] = \frac{f\Phi_{Sb}}{f\Phi_{Sb} + \Phi_N}$ where Φ_{Sb} and Φ_N refer to the Sb and N flux, respectively, and f is an

interaction parameter that describes the deviation from ideal incorporation. The solid lines in Fig. 1 represent calculations using $f=1$ and $f=0.62$. Up to the Sb/N flux ratio of 0.2, the incorporation is well-behaved with an interaction parameter slightly below 1. However, it appears that the Sb composition dramatically levels off at about 18% at this growth temperature. In contrast, we had earlier been able to grow across the composition spectrum at 80 °C⁵. It is unclear if the Sb composition is limited by the increased substrate temperature, or if it is because of the difference in absolute fluxes, etc, used in the two different MBE systems.

In a second series of growths, we fixed the Sb flux at 2.24×10^{17} At/(m² s), the Ga at 2.36×10^{18} At/(m² s) and the N at 2×10^{18} At/(m² s), and we varied the substrate temperature between 325 °C and 550 °C. The Sb incorporation decreases linearly with substrate temperature, as shown in Fig. 2 and in qualitative agreement with N-rich growth in the first MBE system⁸.

Despite differences between samples grown in the two MBE systems, the behavior of the bandgap with Sb composition follow closely and agree with the trend predicted by the BAC model. All of the samples shown in Figure 3 were grown at 325 °C, and are polycrystalline with Sb compositions ranging from 0 to 16%. The samples from Fig. 2 with the lowest composition are not included in Fig. 3 due to the difficulty of determining a bandgap from transmission measurements since the density of states of the Sb-derived valence band is quite small in the very dilute regime.

Conclusion

We have grown N-rich GaN_{1-x}Sb_x highly mismatched alloys with various Sb fluxes and substrate temperatures. Samples grown in two chambers with different N sources and various substrate temperatures, III/V ratios, absolute fluxes, and growth rates have different morphologies, but all follow the predictions of the band anticrossing model. Although the growth parameter space is enormous, the sole factor for obtaining specific bandgaps is dictated by the Sb composition. The control of many other materials properties required for device applications need to be studied and optimized separately.

Figure 1. (a) The Sb mole fraction (x) in $\text{GaN}_{1-x}\text{Sb}_x$ as a function of Sb/N flux with the inset expanded in (b). The symbol f refers to the interaction parameter between N and Sb.

Figure 2. The Sb mole fraction as a function of substrate temperature for N and Ga rich samples grown in chamber 1 (subject of prior studies) and N rich samples grown in chamber 2 (this publication).

Figure 3. Bandgap as a function of Sb composition for N-rich samples grown at 325 °C, with the line indicating the fit according to the BAC model.

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