GaN$_{1-x}$Bi$_x$: Extremely mismatched semiconductor alloys

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Through nonequilibrium low-temperature molecular beam epitaxy, we have grown GaN$_{1-x}$Bi$_x$ alloys on sapphire substrates with x up to 0.11. The GaN$_{1-x}$Bi$_x$ alloys are found to be amorphous with GaN crystals distributed throughout the film. A dramatic reduction in the optical band gap from 3.4 eV in GaN to as low as 1.2 eV for $x \sim 0.11$ was qualitatively explained by formation of a narrow band originating from anticrossing interaction between Bi localized states and the extended states of the GaN matrix. © *2010 American Institute of Physics.* [doi:10.1063/1.3499753]

Semiconductor alloying is a common method for tailoring material properties for specific applications. The most common semiconductor alloys are composed of isoelectronic elements that are relatively well matched in terms of atom size, ionicity, and electronegativity, e.g., SiGe, AlGaAs, GaAsP, etc. However, there is a class of semiconductors known as highly mismatched alloys (HMAs), which contain isoelectronic elements with very different properties. These alloys are generally difficult to synthesize due to large miscibility gaps but they can have unique and interesting electronic properties.[1,2] Extensive work has been conducted on GaN$_{1-x}$As$_x$ and As-rich GaAs$_{1-x}$Bi$_x$ HMAs where the electronic bands are strongly restructured due to the isoelectronic substitution of a host anion with a mismatched anion.[3–9] As-rich GaN$_x$As$_{1-x-y}$Bi$_y$ has been studied for photovoltaic applications for the development of a 1 eV band gap material that is lattice matched to GaAs.[10–12] In addition, Bi in group III-V semiconductors has been used as a surfactant during growth to improve surface morphology.[13,14] Given the electronegativity, N (3.0) and Bi (1.8), as well as atomic radius, N (75 pm) and Bi (155 pm), mismatches are the largest among all group V elements, a dramatically different electronic band structure is expected to result from an N-rich GaN$_{1-x}$Bi$_x$ alloy.[15]

A wide variety of crystalline semiconductor alloys have been applied to a range of technologies but silicon-based alloys have dominated the application of amorphous semiconductors. Amorphous GaN has been theoretically predicted to be a technologically useful electronic material due to the lack of deep gap states common in amorphous III-V semiconductors caused by metallic bonds.[16] Therefore, the amorphous nitride-based ternary alloys could also have technical potential.

Recently, GaN$_{1-x}$As$_x$ semiconductor alloys have been grown as a HMA across the entire composition range by nonequilibrium low temperature molecular beam epitaxy (LT-MBE).[17,18] In the composition range $(0.15 < x < 0.75)$ these GaN$_{1-x}$As$_x$ alloys are found to be amorphous. Despite the amorphous nature these GaN$_{1-x}$As$_x$ alloys exhibit sharp absorption edges indicative of local structural order.[19] At-

tempts to grow Bi-doped GaN at high temperatures did not achieve significant incorporation of the concentrations of the mismatched element Bi.[20] In this work, we demonstrate that GaN$_{1-x}$Bi$_x$ alloys with up to $x \sim 0.11$ can be grown by LT-MBE.

The GaN$_{1-x}$Bi$_x$ films in this study were grown on 2″ c-plane sapphire substrates by plasma-assisted MBE in a MOD-GENII system. Elemental sources were used for Ga and Bi fluxes and an HD-25 Oxford Applied Research rf-activated plasma source provided the active nitrogen. For the growth of GaN$_{1-x}$Bi$_x$ films, the same active N flux with a total N beam equivalent pressure (BEP) of 1.7×10^{-5} Torr, and constant Ga and Bi fluxes of 2.4×10^{-7} Torr and 7×10^{-8} Torr BEP, respectively, were used for a 2 h deposition time. Since uncoated transparent sapphire substrates were used, the pyrometer measured the temperature of the substrate heater instead of the substrate. Therefore, our estimate of the growth temperature is based on the thermocouple reading on the substrate heater. The films were grown without substrate rotation in order to investigate a wide range of III:V ratios in a single growth.

The composition of the films was determined using Rutherford backscattering spectrometry (RBS) with a 2.13 MeV He^{2+} beam. RBS analysis revealed that films with a III:V ratio of 1:1 and compositional uniformity in the growth direction were achieved under a Ga-rich growth condition and on the part of the wafer away from the metal source. Here, we limit discussion to the most uniform and stoichiometric samples within the +/−5% accuracy limit of RBS. Oxygen resonance RBS using a 3.05 MeV He^{2+} beam showed that except for a very thin surface layer (<5 nm) no significant amount of O ($<0.5\%$) was incorporated in the films. Figure 1 shows the monotonic increase in Bi concentration in the GaN$_{1-x}$Bi$_x$ films as a function of decreasing thermocouple temperature, T_{TC}, with a representative RBS spectrum in the inset. The amount of Bi in the film appears to saturate for a given BEP but this could be overcome by increasing the Bi flux. No measurable Bi ($<0.01\%$) can be detected for samples grown at a T_{TC} above 670 °C. Although the T_{TC} varied from 100–700 °C, the growth rate was relatively constant and the sample thicknesses were between 600–750
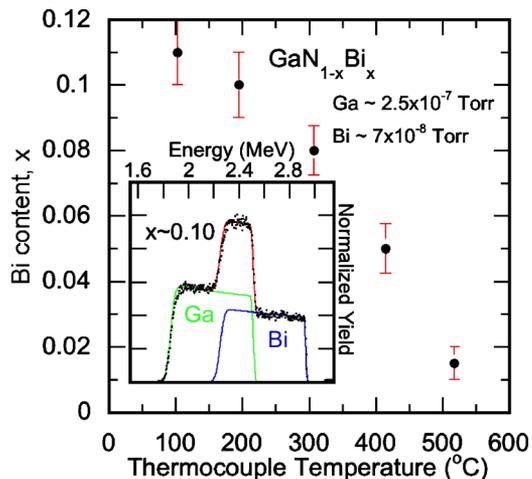
FIG. 1. (Color online) The bismuth composition in $GaN_{1-x}Bi_x$ measured by RBS as a function of LT-MBE thermocouple temperature. The III-V ratio was approximately 1:1 and the films were homogeneous in the growth direction within the resolution limit of RBS. Inset contains a representative RBS spectrum for a film with $x \sim 0.10$. The blue, green, and red lines correspond to the Bi, Ga, and total simulated contributions to the spectrum.

nm. All Bi containing $GaN_{1-x}Bi_x$ films were highly electrically resistive.

The $GaN_{1-x}Bi_x$ films were then further examined using x-ray diffraction (XRD) (Siemens D5000 x-ray diffractometer) and optical absorption spectroscopy (Perkin–Elmer Lambda 950 Spectrometer). The XRD patterns in Fig. 2 show the presence of a GaN phase with decreasing crystallinity with lowering growth temperature. There is no shift in the GaN (0002) peak indicating low Bi incorporation into this crystalline phase, in contrast with the less mismatched N-rich $GaN_{1-x}As_x$ system.[17–19] Since no other XRD peaks of a new crystalline phase were observed, we conclude that Bi is distributed in an amorphous $GaN_{1-x}Bi_x$ alloy phase. Due to the high atomic scattering factor of Bi we expect XRD to be able to detect crystalline Bi precipitate in the atomic percent range. The GaN peak can come from three potential sources: GaN crystallites inside the amorphous $GaN_{1-x}Bi_x$ phase, a thin GaN layer formed during initial stages of $GaN_{1-x}Bi_x$
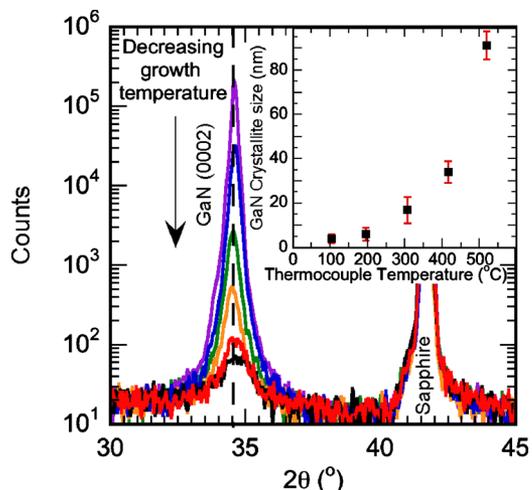
FIG. 2. (Color online) XRD patterns from the GaNBi films grown at various temperatures. Crystalline GaN with no Bi incorporated is present even at the lowest growth temperature. GaN Crystallite size as a function of growth temperature determined from peak breadth contained in inset.
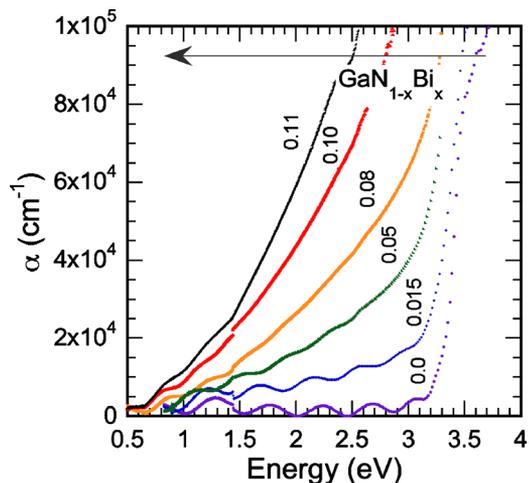
FIG. 3. (Color online) The absorption spectra for $GaN_{1-x}Bi_x$ films grown at different growth temperatures. The composition of each film is given in the figure.

growth on the sapphire substrate, and/or GaN crystals formed on the surface of the $GaN_{1-x}Bi_x$ layer from the excess liquid Ga during postgrowth cooling. RBS measurements did not detect such a GaN layer at the interfaces. This may suggest that in these $GaN_{1-x}Bi_x$ films, GaN crystals are present in an amorphous $GaN_{1-x}Bi_x$ matrix. However, the presence of small crystals of GaN on the film surface and/or at the interface cannot be ruled out. Cross-sectional transmission electron microscopy studies to resolve this issue are currently underway. The monotonic decrease in the GaN (0002) peak intensity and increase in the peak width as T_{TC} decreases suggest that the fraction and size of these GaN crystals decreases with decreasing growth temperature. The crystallite size was estimated using the Scherrer equation, and the result is contained within the Fig. 2 inset.[21] The breadth of the GaN (0002) peak from the highest temperature growth was attributed to instrumental broadening and was subtracted from the breadth of the other peaks. At the lowest growth temperature ($T_{TC} \sim 100\ °C$) GaN nanocrystals (~ 5 nm diameter) are present.

Figure 3 shows the effect of Bi content on the absorption characteristics of the material. A low energy tail of relatively weak subband-gap absorption is observed in the low x ($x = 0.015$) $GaN_{1-x}Bi_x$. The appearance of the Fabry–Perot oscillations indicates that the films are smooth and uniform but they also limit the accuracy of the absorption measurement to absorption coefficients higher than $\sim 10^4$ cm^{-1}. The absorption spectra in the samples with $x \geq 0.05$ clearly show an onset of strong absorption ($> 10^4$ cm^{-1}) at photon energies ranging from about 1.5 eV for $x = 0.05$ to 1 eV for $x = 0.11$. Taking into account unavoidable absorption edge broadening effects of the order of 0.2 eV the actual average absorption edge is located close to 1.2 eV for $x = 0.11$.[22] Although RBS is limited to identifying the physical presence of the Bi atoms, the chemical interaction of Bi with GaN and formation of $GaN_{1-x}Bi_x$ is confirmed by the modification of the density of states. Therefore, it is likely the shift in the absorption is attributed to higher concentrations of Bi in $GaN_{1-x}Bi_x$.

The observed optical absorption spectra can be qualitatively understood in terms of the band anticrossing (BAC) model of HMAs. Previous experiments have determined that the bismuth energy level (E_{Bi}) is located 0.1 eV above the

valence band edge of GaP.[23] Applying the transitivity rule of semiconductor band offsets, we can predict that E_{Bi} will be near midgap in GaN at 1.7 eV above the valence band edge.[24] Similar to the case of As in GaNAs or Se in ZnOSe, the localized Bi states form a narrow fully occupied band through the anticrossing interaction with the extended states of the valence band of GaN matrix.[7,22] Consequently the lowest energy optical transitions start at about 1.7 eV at low Bi contents. The absorption edge energy decreases with increasing Bi concentration due to two effects: a downward shift of the conduction band toward GaBi, and the widening of the Bi-derived midgap band. Following the arguments of Ref. 3 the conduction band offset between GaN and GaBi amounts to about 2.3 eV.[8,11] Therefore for $GaN_{1-x}Bi_x$ with $x = 0.11$ the conduction band edge and thus also the absorption edge will shift downward by at least 0.25 eV. The remaining 0.25 eV part of the total shift of the absorption edge from the bismuth level energy, $E_{Bi} = 1.7$ eV to about 1.2 eV at $x = 0.11$ can be attributed to the anticrossing induced widening of the Bi-derived band. According to the BAC model the width of the Bi-derived band is equal to $(\sqrt{E_{Bi}^2 + 4C^2 x} - E_{Bi})/2$. A coupling constant $C = 2$ eV is required to account for the band widening of 0.25 eV. This value is quite reasonable compared with $C = 1.6$ eV found in the significantly less mismatched GaAsBi HMA.[3] This qualitative agreement between experiment and the BAC model confirms the previous findings in GaNAs alloys that have shown applicability of the model to the analysis of the absorption edge of amorphous HMAs.[19]

Accurately determining the exact band gap of semiconductors with such diffusive absorption spectra is nontrivial since the Tauc[25] formula does not explicitly apply for amorphous semiconductors. The absorption characteristics are further complicated by multiple-band hybridization according to the BAC theory,[1,7] the large spin-orbit splitting as confirmed in $GaAs_{1-x}Bi_x$,[3,5] and the disorder in amorphous materials.[26]

In summary, $GaN_{1-x}Bi_x$ films were grown on sapphire substrates by LT-MBE with compositions up to $x \sim 0.11$. The incorporation of Bi into GaN results in a $GaN_{1-x}Bi_x$ amorphous alloy with a small density of GaN nanocrystals. A monotonic, rapid shift in the optical absorption to energies as low as ~ 1.2 eV is observed as x increases. The significant band gap change is consistent with the large mismatch between Bi and N, agreeing with previous work on HMAs. A detailed transmission electron microscopy investigation of the microstructure of these films and thorough absorption spectra analysis will be reported in a future publication.

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