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Non-equilibrium GaNAs alloys with band gap ranging from 0.8-3.4 eV

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A new alloy system, the $GaN_{1-x}As_x$ alloys in the whole composition range was successfully synthesized using the non-equilibrium low temperature molecular beam epitaxy method. The alloys are amorphous in the composition range of $0.17 < x < 0.75$ and crystalline outside this region. The amorphous films have smooth morphology, homogeneous composition and sharp, well defined optical absorption edges. The bandgap energy varies in a broad energy range from ~3.4 eV in GaN to~0.8 eV at x~0.85. The reduction of the band gap can be attributed primarily to the downward movement of the conduction band for alloys with $x > 0.2$, and to the upward movement of the valence band for alloys with $x < 0.2$.

1 Highly mismatched III-V alloys Semiconductor alloys formed through substitution of atoms with very different electronegativity and/or size have been known as highly mismatched alloys (HMAs) [1]. Because of large miscibility gaps, typically HMAs consist of a semiconductor matrix (elemental or compound) with the substitution of only a small amount (up to several percents) of distinctly different isovalent atoms. The HMAs show large band gap reduction and their electronic structures are drastically different from their host materials. A most notable example of HMAs is the As-rich GaN_xAs_{1-x} in which strong band gap reduction by as much as 180 meV per mole percent of N has been observed [2,3].

The unusually strong dependence of the fundamental gap on the N content in the group III-N-V alloys has been well described by the anticrossing interaction between localized N states and the extended conduction band states of the III-V matrix – the band anticrossing model (BAC) [1,3,4]. More recently, the BAC model has also been extended to HMAs where a small fraction of metallic isovalent atoms substitute more electronegative host atoms as occurs in the dilute N-rich $GaN_{1-x}As_x$ alloys. In this case due to the substantial difference in the ionization energies of the As and N anions, the As derived localized states interact strongly with the extended valence band states of the host. The interaction splits the valence band into a series of sub-bands with dispersion relations that are dependent on the As concentration [4,5].

2 Synthesis of GaNAs alloys Due to the large miscibility gap for the Ga-N-As system, GaNAs alloys with large compositions have not been achieved. It is known that in molecular beam epitaxy the As solubility limit in $GaN_{1-x}As_x$ alloys is increasing with decreasing growth temperature [6]. In this study low temperature MBE (LT-MBE) has been employed to overcome the miscibility gap in the $GaN_{1-x}As_x$, allowing the synthesis of $GaN_{1-x}As_x$ thin films over the whole composition range.

All GaNAs samples were grown on 2 inch sapphire (0001) substrates by plasma-assisted MBE at 100-600 °C. The same active N flux with the total N beam equivalent pressure (BEP) ~1.5 10^{-5} Torr and the same deposition time (2hr) were used for the majority of the films [7].

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The composition of the films was measured by Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE). Compositon mapping by wavelength-dispersive x-ray spectroscopy with ~1 μm resolution further confirms the composition and found no discernable compositional variation over a 256x256 μm region in the films. Figure 1 shows the As composition in $GaN_{1-x}As_x$ films as a function of growth temperature. The Ga and As_2 flux in these growths were kept constant with BEP ~$1.5x10^{-7}$ and ~$7.5x10^{-6}$ Torr, respectively. A monotonic increase in the As incorporation in the film is observed as the growth temperature is reduced. We note that as the growth temperature decreases, along with the increase in As content in the film, the film loses its crystallinity and becomes amorphous (close circle symbols in Fig. 1).

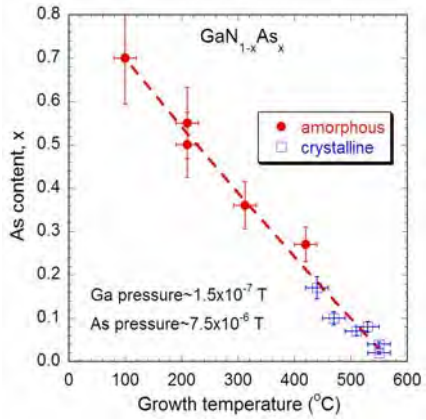

Figure 1 The Arsenic composition in $GaN_{1-x}As_x$ films grown by LT-MBE measured by RBS/PIXE as a function of growth temperature.

3 Structural and optical properties X-ray diffraction measurements show that as the growth temperature is reduced from ~600 to 100 °C, along with the increase in the As incorporation from x~0.02 to 0.7, the structure of the $GaN_{1-x}As_x$ film transforms from crystalline (wurtzite) to amorphous (<410 °C). This is further confirmed by selective area electron diffraction (SAD) studies shown in Fig. 2. The SAD results unambiguously illustrate that the $GaN_{1-x}As_x$ alloys go from single crystalline spot pattern (T_g=550 °C) to polycrystalline ring pattern (400 °C < T_g < 500 °C) to amorphous diffuse ring pattern (T_g<400 °C; x > 0.2). The diffuse ring patterns for $GaN_{1-x}As_x$ alloys with x in the range of ~0.2 to 0.75 confirm the amorphous structure of these alloys. The As content in the amorphous film can also be increased by increasing the As flux during growth. This is shown in Fig. 2 with the SAD patterns from two amorphous samples grown at 210 °C: the sample with 45% As was grown with ~6X higher As flux as the sample with 27% As. High resolution transmission electron microscopy on the high As content $GaN_{1-x}As_x$ layer (45% As) clearly shows a homogeneous, amorphous film with no observable composition segregation.

As the alloy composition is pushed to the As-rich side (x > 0.75) the films becomes crystalline again with a cubic structure. The SAD pattern for the As-rich $GaN_{1-x}As_x$ film with x= 0.86 grown at ~200 °C is shown in Fig. 2. The ring pattern of this sample is consistent with the XRD result that shows a cubic polycrystalline phase of $GaN_{1-x}As_x$ for As-rich alloys ~ 14% N substituting the As sublattice.

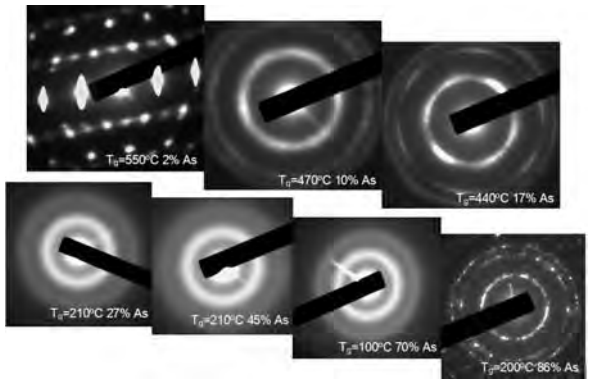

Figure 2 A series of selective area electron diffraction pattern (SAD) from $GaN_{1-x}As_x$ alloys with increasing As content as a result of decreasing growth temperature from 550 to 100 °C.

Optical absorption measurements show a strikingly sharp band gap absorption in all films. Despite the crystalline and amorphous transition a continuously monotonic decrease in the band gap is observed as the As content increases. This also supports the claim that the films are single phase with no phase separation in the crystalline state, and no composition non-uniformity in the amorphous state.

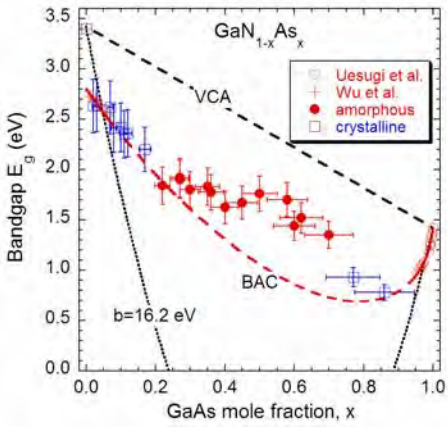

Figure 3 Dependence of the optical band gap energy obtained by absorption measurements on the value of x for crystalline and amorphous $GaN_{1-x}As_x$ alloys.

Figure 3 summarizes the composition dependence of the optical band gap energy for both crystalline (open

symbols) and amorphous (solid symbols) $GaN_{1-x}As_x$ alloys. These experimental data are compared directly with calculated composition dependence of the band gap. It is obvious that these data cannot be explained by a virtual crystal approximation (VCA) represented by the dashed line. The dotted line in Fig. 3 shows a forced quadratic fitting to the experimental gap energies on dilute alloys with a single bowing parameter of b=16.2 eV. Excellent agreement can be observed between the band gap values for the crystalline alloys and the BAC model. The deviation of the experimental results from the BAC calculations found for the amorphous alloys is not unexpected as the model has been developed for crystalline materials.

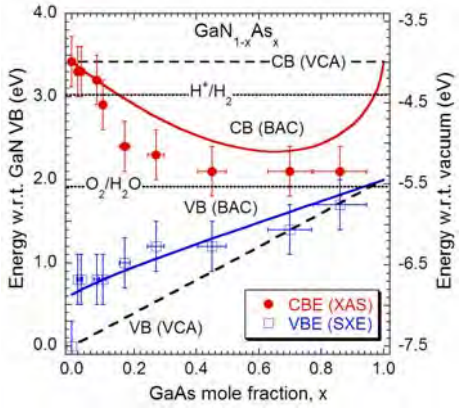

Figure 4 Composition dependence of the conduction band minimum (CBM) and the valence band maximum (VBM) energies for $GaN_{1-x}As_x$ alloys as measured by XAS and SXE, respectively.

To directly measure the band positions we used the combination of soft x-ray emission (SXE) and absorption (XAS) spectroscopies. XAS and SXE directly probe the partial density of states (DOS) of the conduction band and valence band, respectively [8]. The composition dependence of the CBE and the VBE energies for $GaN_{1-x}As_x$ alloys as measured by XAS and SXE, respectively, is shown in Fig. 4 together with the BAC predicted values. The linear interpolations of CBE and VBE (VCA) between end point binary compounds (GaN and GaAs) are also shown. Figure 4 shows that both CBE and VBE are shifted as x increases. In general, the experimental CBE and VBE values significantly but follow the trend of the BAC prediction, although the alloys with composition in the range of x~0.2-0.75 are amorphous.

4 Conclusion We have successfully synthesized $GaN_{1-x}As_x$ alloys in the whole composition range using low temperature molecular beam epitaxy. Alloys in the composition range of $0.17 < x < 0.75$ are amorphous with no indication of composition non-uniformity. Optical absorption measurements show sharp absorption edges with a gradual decrease of the bandgap from ~3.4 eV to < 1 eV with increasing As content. The energy gap reaches its minimum of ~0.8 eV at x~0.8. The composition dependence of the band gap of the crystalline $GaN_{1-x}As_x$ alloys ($x < 0.2$ and $x > 0.8$) follows the prediction of the band anticrossing model well while the amorphous alloys show higher band gaps than predicted (by as much as ~0.6 eV). The reduction of the band gap can be attributed primarily to the downward movement of the conduction band minimum for alloys with $x > 0.2$, and to the upward movement of the valence band maximum for alloys with $x < 0.2$.

The unusual electronic structure and capability for controlling the locations of the conduction and valence band edges offer unprecedented opportunity for using these alloys for novel solar power conversion devices. For example, we propose that the N-rich $GaN_{1-x}As_x$ alloys can be promising materials for the photoanodes for the direct conversion of sunlight into hydrogen by photoelectrochemical (PEC) water-splitting. Moreover, the wide band gap tuneability of this alloy system covering a spectral range of ~0.8 to 3.4 eV provides an almost perfect match to the solar spectrum. This offers the opportunity to design high efficiency multijunction solar cells using a single ternary alloy system.

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