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Universal Bandgap Bowing in Group III Nitride Alloys

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The energy gaps of MBE-grown wurtzite-structure $\text{In}_{1-x}\text{Al}_x\text{N}$ alloys with $x \leq 0.25$ have been measured by absorption and photoluminescence experiments. The results are consistent with the recent discovery of a narrow bandgap of ~ 0.8 eV for InN. A bowing parameter of 3 eV was determined from the composition dependence of these bandgaps. Combined with previously reported data of InGaN and AlGaN, these results show a universal relationship between the bandgap variations of group III nitride alloys and their compositions.

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Group III nitrides and their alloys are attracting much research attention in part because of applications in optoelectronic devices [1, 2]. Particularly, GaAlN ternary alloys have room-temperature bandgap energies tunable continuously from ~ 3.42 eV for GaN to ~ 6.2 eV for AlN [3]. Ga-rich InGaN alloys are under intense investigations as a highly efficient blue light emitting material [1]. It has been discovered recently that wurtzite-structure InN is actually a narrow gap semiconductor, with a minimum bandgap energy equal to ~ 0.77 eV [4, 5]. The studies of In-rich InGaN have shown that the optical properties of these alloys are consistent with the observed narrow gap of InN, and with the relatively high luminescence efficiency as it is found in the Ga-rich InGaN alloys [5, 6]. The bandgap of the InGaN ternary system thus covers a very wide range of the optical spectrum from the infrared for InN to the ultraviolet for GaN.

Similar to the case of InGaN, studies of InAlN alloys have concentrated on the wide-gap, Al-rich side due to the difficulties in the epitaxial growth of high-quality In-rich materials [7, 8]. However, the optical properties of InAlN over the entire composition range are of great interest as this alloy system offers an exceptionally large bandgap tunability and a wide range of lattice constant variation. In this letter, we report studies of the optical properties of In-rich $\text{In}_{1-x}\text{Al}_x\text{N}$ with x up to 0.25. It is shown that the energy range covered by the bandgap of the InAlN ternary system extends continuously from the infrared for InN to the deep ultraviolet for AlN. The bandgap bowing parameter has been determined to be 3.0 eV. Combining these results with recently reported data on the bandgap energies of other group III-nitride alloys, we have found that the bandgap bowing parameters scale with the energy gap difference between the end-point compounds. This allows expressing the composition dependence of the bandgap in terms of a universal dependence applicable to all group III-nitride ternaries. Band edge offsets in group III-N alloys are also discussed in the context of these findings.

The $\text{In}_{1-x}\text{Al}_x\text{N}$ films (250 \sim 300 nm, $0 \leq x \leq 0.25$) were grown on (0001) sapphire substrates by molecular beam epitaxy using an AlN buffer layer (~ 200 nm). The growth temperature was about 470 °C. The growth method and conditions were similar to those described in Ref. [9]. The Al atomic fraction was determined by X-ray diffraction (XRD) using the AlN (0002) peak as the reference peak. The XRD analysis showed that high-quality wurtzite-structure $\text{In}_{1-x}\text{Al}_x\text{N}$ epitaxial layers formed with their c-axis

perpendicular to the substrate surface. Typical Hall mobility of these samples was several hundred cm^2/Vs , and the sheet free electron concentration was slightly below 10^{14} cm^{-2} . The samples were characterized by conventional optical absorption and photoluminescence (PL) spectroscopy. The optical absorption measurements were performed on a CARY-2390 NIR-VIS-UV spectrophotometer. The PL signals were generated in the backscattering geometry by excitation with the 515 nm line of an argon laser. The signals were then dispersed by a SPEX 1680B monochromator and detected by a liquid-nitrogen cooled Ge photodiode.

As a typical example, the inset of Fig. 1 shows the PL and absorption curves of an $\text{In}_{0.75}\text{Al}_{0.25}\text{N}$ sample obtained at room temperature. A photo-modulated reflectance (PR) curve is also shown for comparison. The sample emits an intense PL signal with the peak position observed at the edge of the absorption tail at 1.15 eV. The extrapolation of the linear part of the squared absorption leads to a bandgap energy at 1.55 eV, which is in reasonable agreement with the critical energy determined by the PR spectrum. Similar to the behavior of In-rich InGaN alloys [6], a large Stokes shift is also observed here and is mainly attributed to composition fluctuations. Figure 1 shows the absorption curves for the $\text{In}_{1-x}\text{Al}_x\text{N}$ samples with the Al fraction x ranging from 0 to 0.25. A blue shift of the energy gap with increasing AlN fraction is clearly visible, a result expected from the effect of alloying with wide-gap AlN. Considering the thickness of these films, an absorption coefficient as large as $6 \times 10^4 \text{ cm}^{-1}$ at photon energy of $\sim 0.5 \text{ eV}$ above the bandgap is estimated for these films, which is a typical absorption intensity for direct-gap semiconductors.

The PL peak energies and the energy gaps derived from the absorption experiments are plotted as a function of x in the inset of Fig. 2. Some previously reported data on the Al-rich side are also shown on the same plot [7]. It can be seen from this plot that the energy gap of the InAlN ternary alloy covers a wide portion of the optical spectrum, ranging from the infrared for InN to the deep ultraviolet for AlN. The composition dependence of the bandgap can be described by the standard bowing equation,

$$E_g^{\text{InAlN}}(x) = E_g^{\text{AlN}} \cdot x + E_g^{\text{InN}} \cdot (1-x) - b \cdot x \cdot (1-x). \quad (1)$$

A best fit leads to a bowing parameter of $b = 3.0 \text{ eV}$.

It is interesting to compare the values of bowing parameter of different group III nitride ternaries. A bowing parameter of 1.43 eV has been found for InGaN [6]. We have also measured the composition dependence of the bandgap of wurtzite GaAlN alloys grown by the same method. Our results show that the bandgap energy as a function of composition can be well fit with a bowing parameter of 1.4 eV. This value is in good agreement with the value of 1.33 eV reported by Shan *et. al.* [10]. Considering the bandgap difference between the end-point nitrides for each ternary, we note a proportional relationship between the bowing parameter and the bandgap difference. To illustrate this relationship, we define, for the alloy of the form AB, a normalized bowing parameter $\mathbf{b} \equiv b / |E_g^A - E_g^B|$, and a dimensionless bandgap variation as $\mathbf{a}(x_A) \equiv |E_g^{AB}(x_A) - E_g^B| / |E_g^A - E_g^B|$. The standard bowing equation, Eq.(1), can be rewritten as

$$\mathbf{a}(x) = x - \mathbf{b} \cdot x \cdot (1 - x). \quad (2)$$

In this equation, the dimensionless parameter \mathbf{b} describes the degree of the bandgap bowing relative to the bandgap difference of end-point materials. It is found that the value of \mathbf{b} is essentially the same for these three group III-N alloys. It only varies from 0.50 for AlGa_xN to 0.55 for InAl_xN alloys. Shown in Fig. 2 is the data of \mathbf{a} plotted as a function of x for In_{1-x}Al_xN measured in this work and from a previous report [7], for Ga_{1-x}Al_xN measured in this work, and for In_{1-x}Ga_xN [6, 11, 12] adopted from the literature. It can be seen that although these gap energies were measured on different alloy systems and reported by different groups, they all fall into one single curve when expressed in the reduced form of Eq. (2). A common normalized bowing parameter of $\mathbf{b} = 0.54$ well describes the universal composition dependence, as depicted by the curve in Fig.2. This scaling relationship is not surprising, though, because the main contribution to the bandgap bowing is due to the effects of composition disorder on the conduction and valence band edges [13]. Given the similar degree of disorder in space, for a larger bandgap difference between alloy constituents, the potential perturbation caused by the composition fluctuations is larger; consequently the bandgap bowing effect is expected to be proportionally stronger.

The origin of the universal relationship describing the composition dependence of the bandgaps of group III-nitride alloys strongly suggests that similar arguments may be also used in the considerations of the composition dependence of the band offsets. Since the total change of the bandgap is a sum of shifts of the conduction and the valence band edges, it could be argued that the relationship given by Eq. (2) is also a proper scaling function for the band offsets. Namely, for any group III-nitride alloy system, the composition dependence of the conduction or the valence band offset is given by the band offsets of the end-point compounds multiplied by the universal scaling function in Eq. (2). This formula provides a method to estimate the band edge offsets between different group III-nitride alloys, which is an important issue in the design of heterostructure devices. Figure 3 shows the dependence of the bandgaps on the in-plane lattice constant obtained assuming a linear relationship between the lattice constant and the composition according to Vegard's law. The inset in Fig. 3 shows the conduction and the valence band offsets calculated using the scaling function given by Eq. (2) and the experimentally determined valence band offsets of 1.05 eV for InN/GaN, and 0.70 eV for GaN/AlN [14].

The results shown in Fig. 3 suggest that a large gap difference is expected between GaN and the lattice matched $\text{In}_{0.18}\text{Al}_{0.82}\text{N}$. Also, it is important to note that most of the bandgap difference is accommodated by a large conduction band offset of almost 1 eV. This offers an interesting possibility of using $\text{In}_{0.18}\text{Al}_{0.82}\text{N}/\text{GaN}$ heterostructures to confine the two-dimensional electron gas in lattice-matched GaN quantum wells. Such a heterostructure design would eliminate strain-induced polarization effects that are known to be partially responsible for the transfer of electrons from surface defects into the GaN quantum well in standard AlGaN/GaN high electron mobility transistors [15]. A reduction of the piezoelectric field induced charge transfer could provide a better control of the heterostructure characteristics by enhancing the role of intentional doping of the barrier.

In conclusion, the bandgap energy of In-rich InAlN alloys has been measured as a function of composition. The bowing parameter is found to be 3.0 eV. The bandgap bowing in group III nitride alloys was found to be proportional to the bandgap difference between the end-point compounds.

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Figure Captions

Fig. 1 Representative absorption curves of $\text{In}_{1-x}\text{Al}_x\text{N}$ with x in the range of 0 to 0.25. The inset shows the squared absorption (abs), the PL and PR signals of $\text{In}_{0.75}\text{Al}_{0.25}\text{N}$ taken at room temperature.

Fig.2 Normalized bandgap variations shown as a function of x for $\text{In}_{1-x}\text{Ga}_x\text{N}$, $\text{In}_{1-x}\text{Al}_x\text{N}$ and $\text{Ga}_{1-x}\text{Al}_x\text{N}$. The curve is a fit based on Eq.(2) using $\mathbf{b} = 0.54$. Inset, the measured bandgap and PL peak position as a function of Al fraction for $\text{In}_{1-x}\text{Al}_x\text{N}$.

Fig. 3 Bandgaps of group III-nitride alloys as a function of in-plane lattice constant. Each curve between two end-points is the quadratic dependence of the bandgap of corresponding ternary alloy described by Eq. (1). Inset, the calculated valence and conduction band edges of group III-N ternary alloys as a function of lattice constant. The points at lattice constants of 3.11, 3.19, and 3.54 Å represent AlN, GaN and InN respectively. All the band edge energies are referenced to the top of the valence band of InN.

Figures

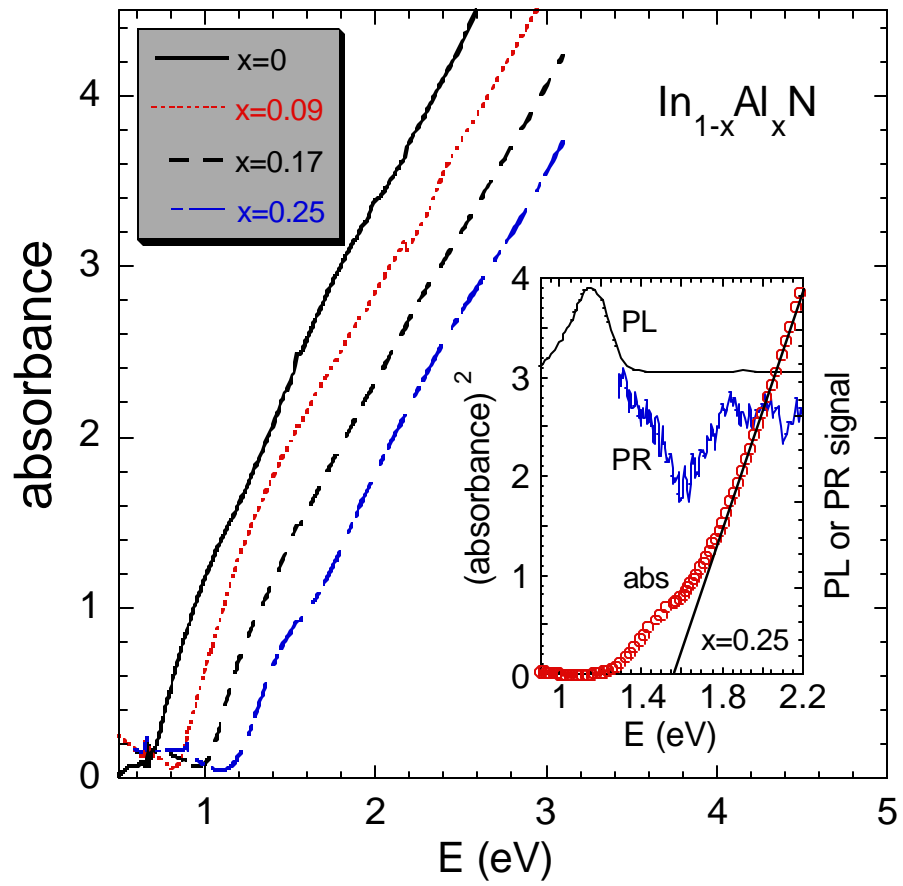


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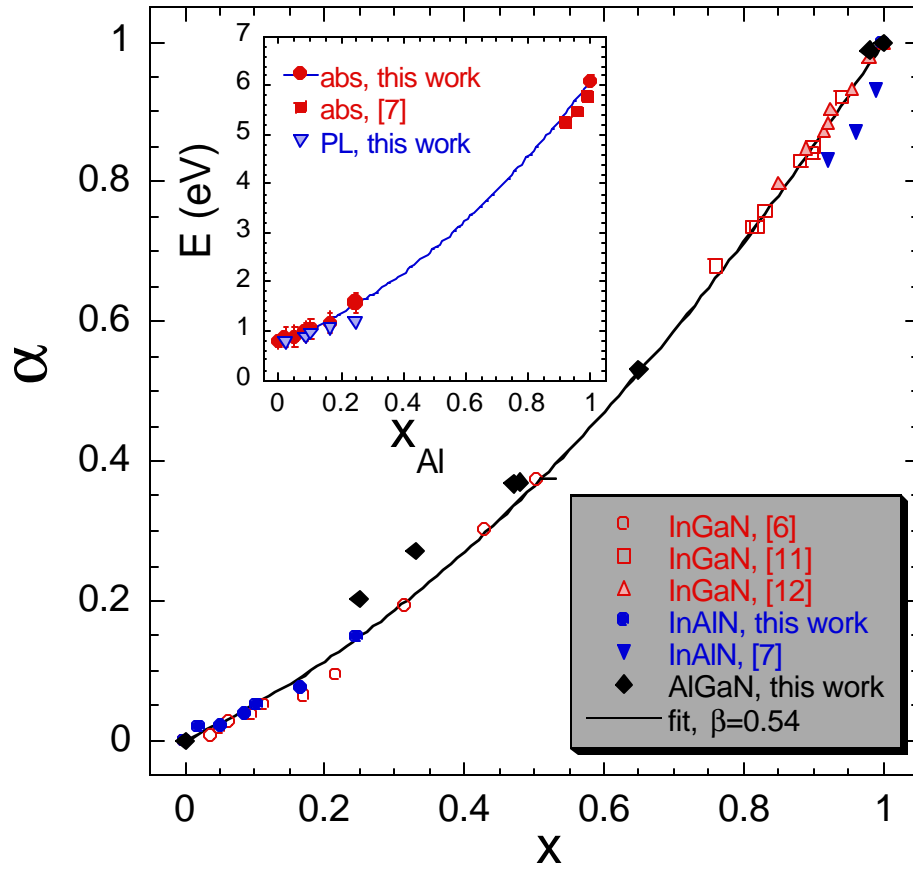


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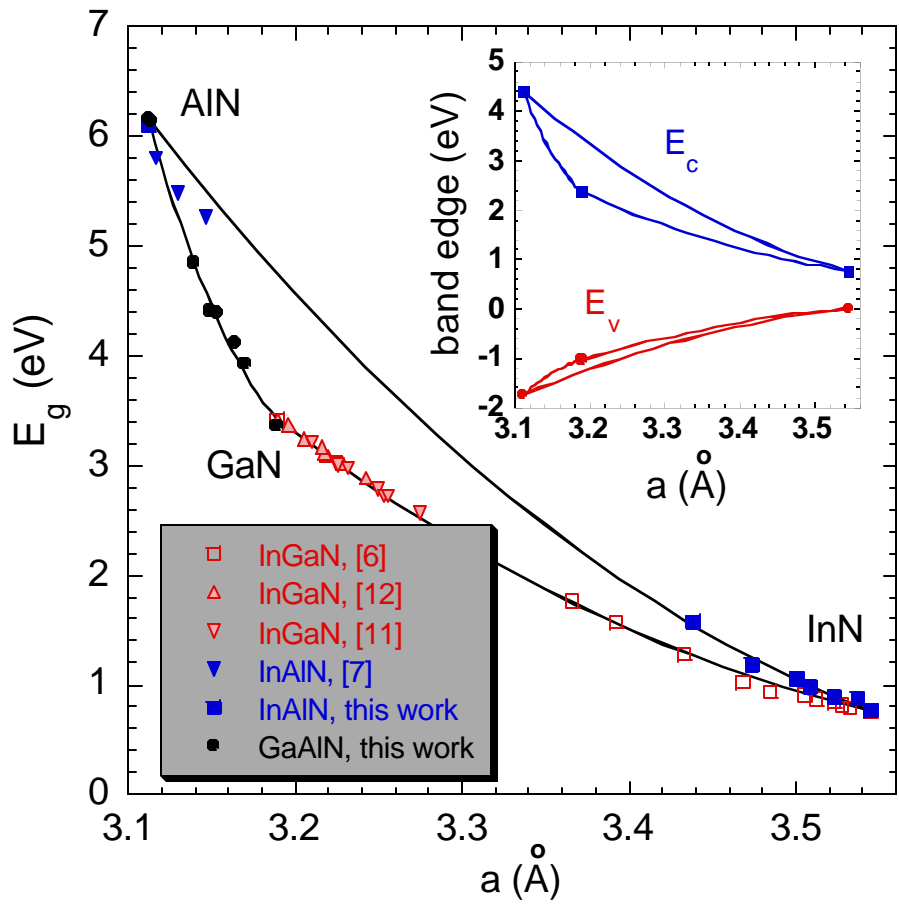


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