Topical Review

Highly mismatched GaN$_{1-x}$Sb$_x$ alloys: synthesis, structure and electronic properties

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Abstract

Highly mismatched alloys (HMAs) is a class of semiconductor alloys whose constituents are distinctly different in terms of size, ionicity and/or electronegativity. Electronic properties of the alloys deviate significantly from an interpolation scheme based on small deviations from the virtual crystal approximation. Most of the HMAs were only studied in a dilute composition limit. Recent advances in understanding of the semiconductor synthesis processes allowed growth of thin films of HMAs under non-equilibrium conditions. Thus reducing the growth temperature allowed synthesis of group III-N–V HMAs over almost the entire composition range. This paper focuses on the GaN$_{1-x}$Sb$_x$ HMA which has been suggested as a potential material for solar water dissociation devices. Here we review our recent work on the synthesis, structural and optical characterization of GaN$_{1-x}$Sb$_x$ HMA. Theoretical modeling studies on its electronic structure based on the band anticrossing (BAC) model are also reviewed. In particular we discuss the effects of growth temperature, Ga flux and Sb flux on the incorporation of Sb, film microstructure and optical properties of the alloys. Results obtained from two separate MBE growths are directly compared. Our work demonstrates that a large range of direct bandgap energies from 3.4 eV to below 1.0 eV can be achieved for this alloy grown at low temperature. We show that the electronic band structure of GaN$_{1-x}$Sb$_x$ HMA over the entire composition range is well described by a modified BAC model which includes the dependence of the host matrix band edges as well as the BAC model coupling parameters on composition. We emphasize that the modified BAC model of the electronic band structure developed for the full composition of GaN$_{1-x}$Sb$_x$ is general and is applicable to any HMA.

Keywords: highly mismatched alloys, nitride, band anticrossing, electronic band structure, photoelectrochemical water splitting

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1. Introduction

Alloying of semiconductors offers the ability to tailor the bandgap and even the conduction and valence band edge positions through the manipulation of the composition of the resulting alloy. This greatly expands the applications of these materials in electronic, optoelectronic, photovoltaic and photoelectrochemical devices. The degree to which the alloy band structure is modified with a change in composition is largely determined by the mismatch in the two endpoint materials. With advances in thin film growth techniques, an increasing array of semiconductor alloys may be synthesized with increasingly mismatched constituents. It is well known that alloys composed of two compounds of similar character can be treated within the scheme of the virtual crystal approximation (VCA), where the potential of the periodic crystal is taken as an average of the atomic potentials of the constituents [1–3]. Within the VCA the composition dependencies of the band gaps as well as band offsets are given by a linear interpolation between the values for the end point component semiconductors. However it has been found that, in most instances, a better approximation for these dependencies is obtained assuming a small deviation from the linear approximation. Thus the energy gap of a semiconductor alloy $A_xB_{1-x}$ with band gap $E_A$ and $E_B$, respectively, can be well approximated by the expression:

$$E_G(x) = xE_A + (1-x)E_B - bx(1-x),$$

where $x$ is the atomic fraction of $A$, and $b$ is the bowing parameter describing deviation of the band gap dependence from the linear interpolation. Typically, this approximation is acceptable only if the bowing parameter is smaller than the band gaps of the constituent materials. Note that there are ternary alloys, e.g. AlGaN [4] where the bowing parameter was found to be large and composition dependent due to local strain and built-in fields in the alloy.

Progress in preparation methods for semiconductor materials now allows synthesis of semiconductor alloys of constituents whose component atoms are distinctly different in terms of size, ionicity and/or electronegativity. The electronic properties of such highly mismatched alloys (HMAs) deviate significantly from an interpolation scheme based on small deviations from the VCA [5–7]. Compared to conventional ternary or quaternary alloys which require large composition alloying to achieve band gap tuning, HMAs have the unique advantage of drastically lowering the bandgap by the substitution of a small fraction (a few percent) of anions with an isovalent element. Moreover, by selecting different anion substituents we can preferentially move the conduction band or valence band of the HMA. This is particular important for photoelectrodes for photoelectrochemical water splitting where not only the band gap but also positions of the conduction and valence band are essential for efficient operation of the device.

The most extensively studied classes of HMAs are based on group III–V and II–VI semiconductor alloys in which metallic (electronegative) anions are replaced by isovalent electronegative (metallic) atoms. A prototypical and most notable example of an HMA has been As-rich GaN$_{1-x}$As$_x$ in which a small fraction (a few percent) of highly electronegative N replaces the host As atoms. A striking feature of this alloy was a strong dependence of the band gap energy on the N content. A band gap reduction by as much as 180 meV per mole percent of N has been observed in the low N composition range [8–13]. The strong effect of the N content on the electronic structure and the energy band gap have made GaAs based dilute nitrides important materials for a variety of applications, including long wavelength optoelectronic devices [14, 15], high efficiency tandem [16, 17] and intermediate band solar cells [18–20]. Although, most of the initial work has been focused on the GaAs based HMA it has been also shown that similar modifications of the electronic band structure is observed in other group III–V dilute nitrides including InN$_{1-x}$P$_x$, GaN$_{1-x}$As$_x$, GaN$_{1-x}$Sb$_x$ [21–26]. Also, comparable or even larger band gap reductions were observed in materials like GaAs$_{1-x}$Bi$_x$ [27, 28], GaN-rich GaN$_{1-x}$As$_x$ [29] in which electronegative anions are partially replaced by more metallic atoms. Similarly, a large variety of group II–VI based HMAs have been studied including dilute oxides e.g. ZnO$_{1-x}$O$_x$ and ZnO$_{1-x}$Te$_x$ [31–34] where a small portion of metallic Se or Te is replaced with electronegative O, or dilute selenide ZnSe$_{1-x}$Te$_x$ [35] or tellurides ZnTe$_{1-x}$O$_x$ [36] in which a fraction of O anions is replaced with Se or Te, respectively.

The unusually strong dependence of the fundamental gap on the N content in the group III–N–V alloys has been the subject of many theoretical investigations [8, 13, 37, 38]. Calculations based on ‘ab initio’ methods faced a difficulty with properly treating the dilute alloy limit as they required large size of supercells. Also such calculations were not capable of accurately determining the dispersion relations at the band edges. Inspired by the observed splitting of the conduction band of GaInNAs alloys a phenomenological model of the electronic band structure has been proposed [10]. The model considers repulsive interaction between the localized level of the minority element (N) and the extended states of the majority semiconductor phase (GaN). This band anticrossing model (BAC) [5–7, 10] has been successful in explaining the experimentally observed electronic band structure of the dilute As-rich GaN$_{1-x}$As$_x$ alloys. The salient feature of the model i.e. splitting of the conduction band into two nonparabolic subbands $E_1(\mathbf{k})$ and $E_2(\mathbf{k})$ have been confirmed by pressure dependent photomodulated reflectance measurements [10]. The downward shift of the lower subband ($E_1$) is responsible for the observed large reduction of the fundamental band gap.

The large difference in the size and electronegativity of the constituent atoms severely restricts solubility limits and the attainable composition range of HMAs. Most of the alloys were only studied in a dilute composition limit. Recent advances in understanding of the semiconductor synthesis processes allowed...
growth of thin films of HMAs under non-equilibrium conditions. Thus reducing the growth temperature allowed synthesis of group III–N–V HMAs over almost the entire composition range. The unusual evolution of the band gap and the conduction and valence band energies generated interest in potential applications of these HMAs for solar power conversion applications [39]. This review focuses on the GaN$_{1-x}$Sb$_x$ HMA which has been suggested as a potential material for solar driven water dissociation [40, 41]. However it should be emphasized that the BAC model of the electronic band structure developed for the full composition of GaN$_{1-x}$Sb$_x$ is general and is applicable to any HMA. The paper is organized as follows. In the second chapter we introduce and discuss key general aspects of the BAC model that are applicable for HMAs in the entire composition range. Then the general aspects of the low temperature molecular beam epitaxy (LT-MBE) technique is described. In particular, properties of LT-MBE grown GaN$_{1-x}$As$_x$ HMA over the entire composition range are discussed as an example. Chapter 4 is devoted to discussion of the growth and various properties of GaN$_{1-x}$Sb$_x$ HMA. Finally, the potential of GaN$_{1-x}$As$_x$ HMA as a viable photoelectrode for photoelectrochemical (PEC) water splitting applications is discussed in chapter 5.

2. BAC model for HMAs

Well matched semiconductor alloys (such as In$_x$Ga$_{1-x}$As and Al$_x$Ga$_{1-x}$As) have been extensively studied and are relatively easy to synthesize in the whole composition range. In contrast, synthesis of HMAs is much more difficult and, in many instances there are severe solubility limits for these materials. However, following the original success in synthesis of GaN$_{1-x}$As$_x$ with a few % of N, new methods have been developed to synthesize a large variety of HMAs [22, 31, 32, 42].

The BAC model has been developed to calculate energy band structure in a system of extended band states interacting with highly localized states. In the first studied case of a HMA, host metallic As atoms were partially replaced with more electronegative N to form GaN$_{1-x}$As$_x$ alloys [10]. Substitutional N atoms produce highly localized states in the conduction band of the GaAs matrix. The repulsive, anticharging interaction of these localized states with the extended, conduction band states leads to a drastic modification of the electronic band structure close to the conduction band edge (CBE). The interaction splits the conduction band into two subbands ($E_+$ and $E_-$.). In the coherent potential approximation for spin independent interaction the dispersion relations for the two subbands are given by simple expressions obtained from a quantum mechanical solution of two sets of interacting states [5]. It has been shown that the BAC model applies to all group III–V dilute nitrides [6, 7, 10, 21, 22, 24] as well as group II–VI dilute oxides [30–34] or any HMA in which metallic atoms are partially substituted with more electronegative atoms [43]. It provides a description of the conduction band structure for the cases with localized levels in the band as well as with localized levels located in the band gap close to the CBE of the host material. For the specific case Sb-rich GaN$_{1-x}$Sb$_x$, the dispersion relation for the two CBE subbands are given by [10]:

$$E_{\pm} = \frac{1}{2} \left\{ (E_C(k) + E_N) \pm \sqrt{(E_C(k) - E_N)^2 + 4C_N^2x(1-x)} \right\},$$

where $E_C(k)$ is the CBE dispersion of the GaSb and $E_N$ the energy of localized N derived states. The coupling parameter $C_N$ describes the interaction between the two states, and $x$ is the N content.

In the opposite case, a partial substitution of electronegative atoms with more metallic atoms leads to the formation of localized states in the valence band or in the band gap close to the VBE. For example, partial replacement of N with As or Sb in the GaN matrix leads to formation of a localized state at about 0.8 or 1.2 eV above the VBE, respectively. As both the extended valence band and the substitutional As or Sb states have p-symmetry the BAC interaction is more complicated, with the band structure of the VBE described by solutions of a $12 \times 12 k \cdot p$ matrix [29]. The problem can be simplified by ignoring spin-effects and separating the resulting $6 \times 6$ problem into three $2 \times 2$ problems. Thus for the example of N-rich GaNSb the dispersion relation of the two sub-bands can be described as [6, 44]:

$$E_{\pm} = \frac{1}{2} \left\{ (E_V(k) + E_{\text{Sb}}) \pm \sqrt{(E_V(k) - E_{\text{Sb}})^2 + 4C_{\text{Sb}}^2x(1-x)} \right\},$$

where $E_V(k)$ denotes the valence band dispersion and $E_{\text{Sb}}$ the energy of localized Sb derived states. The coupling parameter $C_{\text{Sb}}$ describes the interaction between the two states.
Examples of the CBE and VBE splitting in Sb-rich and N-rich alloys are shown in figure 1. The N level is at $E_N = 0.45 \text{eV}$ above the CBE of GaSb, the Sb level at $E_{\text{Sb}} = 1.2 \text{eV}$ above the VBE of GaN. As can be seen in the figure, dilute concentrations of either of the substitutional elements causes the band gap of the alloys to decrease substantially.

### 2.1. BAC of HMAs for the entire composition range

In its simple form the BAC model is applicable only to dilute alloys in which the effects of the minority constituents can be treated as a small perturbation. However a good description of the electronic structures of HMAs across the entire composition range requires modification of the BAC model. In the first approximation it was proposed that the BAC model can be extended to the whole composition range by compositional weighting of the BAC results obtained in the dilute limits [29]. This approach has been developed for GaN$_{1-x}$As$_x$ [39]. As will be discussed later in section 3.3 in a study of the composition dependence of the bandgap of GaN$_{1-x}$As$_x$ over the entire composition range at dilute concentration limits (dilute-N GaAs and dilute-As GaN), the calculated band gap is in a reasonably good agreement with the experimentally determined optical band gaps [11, 29, 39] (figure 8(b)).

The compositionally weighted BAC model has been also used to calculate the band gap of the group II–IV HMAs including ZnO$_{1-x}$S$_x$ [45], ZnO$_{1-x}$Se$_x$ [35], and ZnO$_{1-x}$Te$_x$ [36]. In general the BAC model describes the electronic band structure for dilute group II–IV and III–V HMAs very well. However for alloys with mid-range compositions, the model tends to overestimate the band gap reductions.

### 2.2. The modified BAC model

The BAC model provides an accurate description of the electronic band structure of dilute group III–V and II–VI HMAs. However the extension of the model to the whole composition range by compositional weighting of the BAC models for the conduction and the valence band is not well justified. The main deficiencies of the compositionally weighted BAC model are that it ignores direct dependence of the coupling parameter on composition and that it uses the end-point CBE and VBE energies as the host matrix values. In order to address these deficiencies we have proposed a new hybrid BAC model [46] in which the composition dependence of CBE and VBE is separated into two contributions: the band edge shifts originating from a change of crystalline potential in the VCA and from a BAC interaction between localized states and the virtual crystal as a host matrix. This allows the BAC interactions to be treated as perturbations. In the VCA the BVE and CBE for GaN$_{1-x}$Sb$_x$ are given by linear interpolation between the end point compounds:

$$E_V(x, k = 0) = \langle f \rangle (1 - x) E_V^{\text{GaN}} + x E_V^{\text{GaSb}}$$

$$E_C(x, k = 0) = \langle f \rangle (1 - x) E_C^{\text{GaN}} + x E_C^{\text{GaSb}}$$

$E_{V,\text{GaN}}$ and $E_{V,\text{GaSb}}$ denote the VBEs, and $E_{C,\text{GaN}}$ and $E_{C,\text{GaSb}}$ of the CBEs of GaN and GaSb, respectively.

$V_{\text{cc}}(x) = (1 - x) V_N + x V_{\text{Sb}}$,  

where $V_N$ and $V_{\text{Sb}}$ are the potentials of the lattice sites occupied by N and Sb atoms, respectively. In this approximation the coupling parameter for the N atom substituting a virtual crystal site is given by the matrix element

$$C_N(x) = \langle f \rangle V_N (1 - x) + x V_{\text{Sb}} - V_N(f) = x C_{\text{No}},$$

where $\langle f \rangle$ is the Bloch wavefunction obtained in the VCA and $C_{\text{No}} = \langle f \rangle V_{\text{Sb}} - V_N(f)$ is the coupling constant in the dilute N limit. In a similar manner it can be shown that the composition dependence of the coupling constant for the BAC interaction between the valence band and the localized Sb level is given by $C_{\text{Sb}}(x) = (1 - x) C_{\text{Sb}}$ where $C_{\text{Sb}}$ is the coupling constant in the dilute Sb limit.

Figure 2 shows the electronic band structure close to the VBE and CBE for GaN$_{1-x}$Sb$_x$ with several different alloy compositions calculated using the modified BAC model. The arrows in the figure illustrate the linear dependence of the VCA matrix band edges on the Sb concentration. The band gap is given as the energy difference between the $E^C$ and the $E^V$ bands. Here, for illustrative purposes, we have used a simplified valence band structure by ignoring spin–orbit splitting of the valence band and the localized Sb level. However as we will discussed later the spin–orbit splitting has to be included in the fitting of the optical absorption curves for the accurate determination of the composition dependent band gap. As can be seen in the figure, the drastic narrowing of the bandgap of GaN-rich GaN$_{1-x}$Sb$_x$ HMA arises primarily from the modification of the valence band due to the BAC interaction between the GaN valence band with the Sb localized levels. On the other hand, the BAC interaction between the conduction band of GaSb and the localized N levels has a dominant effect on the band gap in the GaSb-rich alloys.
3. Low temperature MBE growth of N-rich HMAs

3.1. Low temperature MBE

Under most conventional growth conditions, GaN crystallizes in the wurtzite structure, which has a hexagonal symmetry. High quality GaN for device applications are typically grown by metal organic chemical vapor phase deposition (MOCVD), hydride vapor phase epitaxy, and molecular beam epitaxy (MBE). Of these methods, MBE is inherently slower, but affords advantages of atomic and chemical precision. MBE allows the formation of metastable phases of GaN, and also allows lower temperature growth, whereas the CVD processes require high growth temperatures exceeding 1000 °C to crack the ammonia molecules. The first few decades of GaN research was hindered by the lack of suitable bulk GaN substrates onto which lattice-matched group III-nitride films could be grown. GaN has been grown on non-lattice-matched and non-isomorphic sapphire [47], SiC [48], GaAs [49] and Si [49, 50]. Crystalline GaN templates now exist [51–53], but even today devices fabricated from GaN based compounds are grown on non-native substrates [54, 55]. Examples include commercially available LEDs, produced from GaN or InGaN grown on SiC or sapphire, and GaN power transistors, which use sapphire substrates.

High temperatures of 800 °C–1000 °C were traditionally and are currently used for GaN growth in both MBE and MOCVD to mitigate the energy barriers to precursor adsorption and surface adatom migration [56]. Such high growth temperatures, however, prevent the incorporation of substantial amounts of highly mismatched isovalent elements in the crystal lattice of GaN. For the synthesis of materials with constituents having drastically different chemical or physical properties at compositions or structures far exceeding their thermodynamic solubility limits, extreme nonequilibrium techniques are required. The atomic diffusion length in these nonequilibrium processes has to be long enough to form crystalline lattices with uniform compositions, but short enough to avoid equilibrium phase segregation. This has been recently demonstrated in the growth of single phase ferromagnetic Ga1−xMnAs with Mn concentration as high as 16% using the LT-MBE technique [57, 58]. Figure 3 shows a schematic ‘phase diagram’ relating the MBE growth temperature with the different phases observed in Ga1−xMnxAs alloys [57].

It has been shown previously that MBE growth of GaAs at low temperature (LT-MBE) in the range of 200 °C–350 °C resulted in materials with many interesting properties such as a high defect concentration and high electrical resistivity. LT-MBE-GaAs layers grown at substrate temperatures in the range of 200 °C–250 °C are good quality single crystals with >1 at% excess arsenic [59, 60]. Electron paramagnetic resonance measurements on LT-MBE-GaAs layers showed that these layers have ~5 × 1018 cm−3 arsenic antisite defects [59]. The short lifetime allows for ultrafast switching, with mobilities that are still sufficient for good switch responsivity. This material found applications as buffer layers to eliminate the backgating effect for GaAs FET’s [61], as ultrafast photoconductive switches [62], and in quantum cascade lasers for THz spectroscopy applications [63].

3.2. LT-MBE grown GaN

Because of the technological potential of LT-MBE GaAs, a lot of work has been performed on understanding the defects in this material [59–61, 64–67]. In contrast only a few reports have been published on gallium nitride grown at low temperature [68, 69]. Most of these previous studies focused on the structural properties of GaN synthesized at low temperatures (<300 °C) by radio frequency sputtering. In MBE high quality GaN thin films for optoelectronic applications are typically grown at a growth temperature >800 °C. Recently as part of our investigation on the low temperature synthesis of highly mismatched GaN1−xAsx [39] and GaN1−xSbx [41, 70] alloys, we explored LT-MBE synthesis of GaN thin films grown at temperatures ranging from ~80 °C to 500 °C under a wide range of Ga:N flux ratios [71].

It is now well established that there are three main regimes for plasma assisted (PA)-MBE growth of GaN; N-rich growth when the active nitrogen flux is larger than the Ga-flux, Ga-rich growth when the active nitrogen flux is less than the Ga-flux, and extremely Ga-rich growth when the active nitrogen flux is much less than the Ga-flux. In the latter case Ga droplets are formed on the film surface. The most common approach for determining the conditions at which the Ga- and N-fluxes are the same is to fix the N-growth condition and to grow a series of films for equal amounts of time, each one with increasing Ga-flux, and then to measure the resulting film thicknesses. As long as there is an excess of N, the GaN growth rate is proportional to the Ga-flux. This produces films with increasing thicknesses up to the point where the Ga and N fluxes are equal. For higher Ga-fluxes, GaN cannot form resulting in metallic Ga coverage. This is obviously a time-consuming method and alternative approaches such as analysis of reflection high-energy electron
diffraction (RHEED) patterns have also been employed. The latter, however, requires growth at the high temperatures that usually employed for growth of GaN, and therefore would not be an easily amenable technique for the low growth temperatures used for the HMA.

To quickly determine the fluxes at temperatures required for HMA growth we have employed a new in situ Auger electron probe that allows chemical analysis during deposition [72]. In these experiments we fix the N flux and program a linear Ga-flux ramp, while observing the emitted Auger electrons from nitrogen that are excited by the RHEED electron gun. The intensity of the signal is proportional to the concentration of nitrogen within the escape depth of the material which is on the monolayer scale. Thus plotting the N electrons from nitrogen that are excited by the RHEED electron probe that allows chemical analysis during deposition of GaN. Once the film thickness exceeds the escape depth the signal saturates at a constant level while the Ga-flux is less than the N-flux. Right after the Ga-flux reaches the point where it is equal to the N-flux, the N-Auger signal starts dropping. This is because the surface now exhibits an accumulation of Ga droplets which prevent an increasing fraction of the N-Auger electrons from escaping.

The time for the experiment is a trade-off between Ga-cell control and sampling rate of the probe. We have found that a two-hour ramp gives reliable data for determining the 1:1 transition point. This is a marked improvement over growth and thickness analysis of multiple samples, which would take several days. In our current study, a constant N flux corresponding to a total N beam equivalent pressure (BEP) \(\sim 1.5 \times 10^{-5}\) Torr, RF power 200 W was maintained. We have determined that N-rich and Ga-rich conditions correspond to Ga BEP <2 \(\times 10^{-7}\) and \(\geq 2 \times 10^{-7}\) Torr, respectively.

We found that reduction of the growth temperature to 200 °C results in epitaxial GaN films with a high density of dislocations and small size (30–50 nm) columns. At an even lower growth temperature of 80 °C, GaN films still exhibit a polycrystalline columnar morphology with high c-axis orientation and average widths varying from 10 nm near the sapphire interface to 14 nm near the surface. This can be attributed to the high ionicity of GaN that prevents the material from becoming amorphous. From x-ray diffraction (XRD) studies we estimated that at \(T_g \sim 80\) °C the c-axis lattice parameter c increases by 0.44%. The reduction of the diffraction peak intensity and an increase in the peak width also suggest that the crystallinity of the films decreases strongly as the \(T_g\) decreases. It is estimated that the grain size decreases from 100 nm \((T_g \sim 540 \) °C) to 30 nm \((T_g \sim 80 \) °C). Figure 4 shows a cross sectional transmission electron microscopy (TEM) from a GaN samples grown at 80 °C under N-rich (Ga BEP \(\sim 1.6 \times 10^{-7}\) Torr) conditions. Despite the extremely low growth temperature, the sample has a polycrystalline, columnar morphology. Similarly films grown under Ga-rich conditions with much higher Ga BEP exhibit very similar microstructures (not shown). The selected area diffraction (SAD) pattern shows clear polycrystalline rings, confirming the XRD results. The high-resolution image in figure 4 show that most of the grains are aligned with the c-plane normal or at a slight angle to the growth direction.

The optical absorption properties of GaN films grown at low temperature under N-rich condition are similar to normal GaN. The LT-MBE GaN films grown under Ga-rich (Ga BEP \(\geq 2 \times 10^{-7}\) Torr) conditions are found to be conducting with resistivity in the range of \(10^{-1}\)–\(10^{-3}\) Ω cm. The charge transport was determined by thermopower measurements to be dominated by holes. However it was also found that for the constant Ga BEP of 2.2 \(\times 10^{-7}\) Torr there is a change of the thermopower type from p to n for \(T_g \geq 350\) °C.

The absorption coefficient \(\alpha\) of GaN films was determined from transmission and reflection measurements in the wavelength range of 200–2600 nm. Figure 5(a) shows \(\alpha\) for GaN films grown at 80 °C under different Ga fluxes. A monotonic increase in low energy absorption is observed when the Ga BEP increases during growth. Strong absorption at energies as low as 1 eV is observed for samples grown under very high Ga BEP \(\geq 2.2 \times 10^{-7}\) Torr. The high absorption coefficient \((\alpha > 10^6\) cm\(^{-1}\)) at low energy for Ga-rich grown films combined with the observations of extremely low carrier mobility and growth conditions dependent polarity of the thermopower indicate the presence of a large density of native defect states in the band gap.

Figure 5(b) shows soft x-ray absorption (XAS) and emission (XES) spectra for LT-GaN samples grown with different Ga fluxes. The appearance of a near zero gap for the Ga-rich LT-GaN film suggests that there is a very small energy separating occupied from unoccupied states. This is consistent with the presence of a large concentration of \(\text{Ga}_N\) defects, forming a partially occupied band located at \(\sim 1.2\) eV below the conduction band minimum (CBM) of GaN and with the strong sub-bandgap optical absorption shown in figure 5(a). The XAS and XES results then correspond to the partial density of states of these \(\text{Ga}_N\) defect states hybridized with N 2p states. The p-type conductivity observed in the
Ga-rich samples can also be explained by a charge transport within this partially filled GaN defect band. A schematic diagram showing the location of the Ga antisites in GaAs and GaN is shown in the inset figure 5(b). The p-type conductivity of this defect band due to low temperature growth can be exploited for the fabrication of low resistivity p-type ohmic contacts on GaN devices.

3.3. LT-MBE grown GaN$_{1-x}$As$_x$ over the entire composition range

In contrast to the very extensively studied As-rich GaNAs alloys much less work has been devoted to HMAs on the N-rich side of this alloy system. It was found that GaN doped with As at low, impurity-like levels show a characteristic blue emission at room temperature. At higher As doping levels an abrupt decrease in the band gap of resulting GaN$_{1-x}$As$_x$ alloys was observed [73–75]. Wu et al [29] investigated the BAC in N-rich and As-rich GaNAs alloys with a limited range of composition and interpolated the composition dependence of the band gap of GaN$_{1-x}$As$_x$ alloys over the entire composition. The calculations predict a minimum band gap of 0.7 eV at $x \sim 0.8$. This is in a stark contrast to the composition dependence of the band gap predicted by the VCA and the quadratic fitting (equation (1)) with a large bowing parameter $b = 16.2$ eV. However, neither of these

Figure 5. (a) Absorption coefficient, $\alpha$ for GaN films with increasing Ga BEP content grown at 80 °C under different Ga flux. (b) The nitrogen K-edge XES (left side) and total fluorescence yield XAS (right side) of GaN films grown at 80 °C with different Ga BEP and a standard GaN thin film grown by plasma assisted MBE at ~800 °C. The threshold-excited elastic emission peak near 396 eV was used to align the XES spectra to the XAS. The inset is a schematic diagram showing the possible location of the Ga antisites in GaAs and GaN. Reprinted with permission from [71].

Figure 6. (a) A series of selective area diffraction patterns (SAD) patterns from GaN$_{1-x}$As$_x$, alloys with increasing As content as a result of decreasing growth temperature from 550 °C to 100 °C. (b) A cross-sectional TEM micrograph of an amorphous GaN$_{1-x}$As$_x$ film ($x = 0.45$; $T_g = 210$ °C). Reprinted with permission from [39]. Copyright 2009 AIP Publishing LLC.
predictions could be tested as there had been no experimental data for alloys in the middle 85% of the alloy composition.

Using highly non-equilibrium LT-MBE with growth temperatures as low as 200 °C we have synthesized GaN_{1-x}As, across the entire composition range [39, 76, 77]. The resulting alloys are amorphous in the intermediate composition range (0.10 < x < 0.75), with the transition between crystalline to amorphous structure depending on the growing substrate. For example, the N-rich alloy remains in the wurtzite structure for higher As concentrations when grown on sapphire instead of glass [77] and the As-rich alloy remains in the zinc blende structure for higher N concentrations when grown on silicon. We found that epitaxy of GaN_{1-x}As, under Ga-rich growth conditions at relatively high temperatures of ~600 °C results in phase separation into GaN:As and GaAs:N for x > 0.02. As the growth temperature is reduced from ~600 °C 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, film transforms from single crystalline to polycrystalline (~500 °C) to amorphous (<410 °C).

Figure 6(a) shows a series of SAD from alloys with increasing As content as a result of decreasing growth temperature from 550 °C to 100 °C. The SAD results unambiguously illustrate that the GaN_{1-x}As, alloys grow 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, alloys with x in the range of ~0.2–0.75 confirm that these alloys are amorphous with no observable nanoscale secondary phases. We also found that at the same growth temperature, the As content in the amorphous film increases with the As flux during growth. This is illustrated in figure 6(b) by the SAD patterns from two amorphous samples grown at 210 °C: the sample with 45% As was grown with ~6× higher As flux as the sample with 27% As. The SAD pattern for the As-rich GaN_{1-x}As, film with x = 0.86 grown at ~200 °C is also shown in figure 6(a). The ring pattern for this sample is consistent with the XRD result that cubic polycrystalline phase of GaN_{1-x}As, was formed for As-rich alloys [39].

TEM micrograph of the crystalline 2% As film (not shown) reveals a columnar crystalline film with high density of planar defects. These columns are misoriented with respect to each other; therefore dislocations need to form to accommodate this misorientation. Figure 6(b) is a high resolution micrograph of an As rich amorphous film (x = 0.45; T_g = 210 °C) confirming the amorphous nature of this film with no observable composition segregation. We also note that the range of amorphous phase is dependent on the substrate used. When grown on sapphire substrates, the alloys are amorphous in the composition range of 0.17 < x < 0.75 and crystalline outside this region [39]. For the films grown on Pyrex substrates, the composition range for amorphous alloys extends to x ~ 0.1 [77]. The amorphous nature of these films were further confirmed by extended XAS fine structure measurements [78].

The E_g of GaN_{1-x}As, changes monotonically across the crystalline–amorphous boundary and as the amorphous phase composition is varied, in qualitative agreement with the band anti-crossing model for HMAAs. Taking into account both crystalline and amorphous phases, the band gap of the GaN_{1-x}As, alloy system goes from 0.8 to 3.4 eV. Figure 7(a) shows a series of photorelectance (PR) spectra from amorphous GaN_{1-x}As, samples with x = 0.15–0.45. A gradual decrease of the GaN_{1-x}As, band gap as x increases is clearly shown. These band gap values are further confirmed by optical absorption measurements that showed sharp absorption edges for all the amorphous films with absorption coefficient ~1 × 10^5 cm⁻¹ at ~0.5 eV above the band gap. The inset of figure 7(a) compares the PR and absorption spectra from a GaN_{0.75}As_{0.25} sample. The clear observation of the PR signal indicates an extended rather than localized nature of the band edge states. This is also consistent with an abrupt onset of the absorption edges and an absence of defused absorption tails that are typical in amorphous silicon.

The band gap as measured by PR on the GaN_{1-x}As, films grown on Pyrex are shown in figure 7(b) together with data taken from films grown on sapphire. Band gap values for dilute alloys (As-rich [11] and N-rich [29] GaNAs) from the literature are also presented. The composition dependence of the band gap of GaN_{1-x}As, alloys over the entire composition range shown in figure 7(b) was calculated by a weighted interpolation of the BAC calculated curves for N-rich and As-rich dilute alloys [29] as discussed in section 2.1. Comparing our experimental data (both on sapphire and Pyrex) directly with the BAC model we notice that the band gap values for the crystalline and amorphous GaN_{1-x}As, alloys are in good agreement with the BAC model. The results suggest that for this composition range the amorphous GaN_{1-x}As, alloys have short-range ordering that resembles random crystalline GaN_{1-x}As, alloys. Moreover, soft XAS and XES measurements revealed that this reduction in the bandgap indeed arises from the VB change due to valence N states hybridizing with an As impurity level just above the GaN valence band maximum (VBM). This observation is in excellent agreement with predictions of the BAC model in this dilute doping regime [39].

Due to the low growth temperature of 200 °C–320 °C and the amorphous structure, these GaN_{1-x}As, films can be grown on low cost glass substrates instead of expensive single crystal substrates. Despite the highly non-equilibrium composition of these alloys, they are remarkably stable for short excursions beyond 700 °C prior to phase segregation [79]. The thermal stability of these alloys is important for functionalization due to various high temperature semiconductor processing techniques (e.g. dielectric deposition). Furthermore, both p-type and n-type doping of a partially amorphous GaN_{1-x}As, (x ~ 0.55–0.65) have been demonstrated [80, 81]. We observed that the room temperature p-type conductivity of GaN_{1-x}As, increased monotonically with increasing of Mg content, up to a maximum value of about 35 S cm⁻¹ for 8 atomic % Mg content [80]. We have found that achieving the p-type doping of GaN_{1-x}As, requires growth under Ga-rich conditions. These conditions result in the formation of As-rich crystalline GaAs:N inclusions inside the amorphous GaNAs matrix, which can be observed in the XRD and TEM. Recently we have also successfully identified the range of the growth parameters for a reproducible and
uniform Te incorporation in amorphous GaN$_{1-x}$As$_x$ Te layers with $x$ close to 0.6 and a maximum Te concentration of $9 \times 10^{20}$ cm$^{-3}$ [81]. Te incorporation resulted in n-type doping with film resistivities below 10$\Omega$ cm, electron concentration in mid 10$^{19}$ cm$^{-3}$ and electron mobilities of $\sim$1 cm$^2$ V$^{-1}$ s$^{-1}$. The ability to control the electrical properties of these alloys that exhibit a wide bandgap range of 0.8–3.4 eV can lead to exciting applications in electronics and photovoltaics.

4. LT-MBE GaN$_{1-x}$Sb$_x$ HMAs

For photoelectrochemical water-splitting application, an ideal photocathode must meet three criteria: corrosion stability, a band gap between 1.8 and 2 eV to produce sufficient overpotential to drive the water-splitting reactions while still absorbing a significant fraction of the solar spectrum, and band edges straddling the hydrogen and oxygen redox potentials for spontaneous water splitting [82, 83]. Since the anion mismatch is even larger between Sb and N, BAC calculations on the electronic band structure of the GaN$_{1-x}$Sb$_x$ alloys predict that less than 6% of Sb is needed to achieve an alloy with a bandgap $\sim$2.2 eV with the CBM and the VBM still straddling the water redox potentials. Hence GaN$_{1-x}$Sb$_x$ HMAs could be suitable as photoelectrodes for photoelectrochemical water splitting applications [40]. Although GaSbN dilute nitride films have been studied in the last decade, there is little to nothing known about the growth of GaN$_{1-x}$Sb$_x$ alloys in the N-rich regime.

4.1. GaSb-rich dilute nitride HMA

It was recognized that addition of N to GaSb could potentially produce a direct bandgap material suitable for long-wave infrared detection [84–90]. By also alloying on the group III site with In, it could be possible to drastically reduce the bandgap while staying lattice matched to a GaSb substrate [86, 89–92]. Such large band gap bowing has also been explained using the BAC model taking into account the modification of the conduction band of GaSb by the localized N states [87, 88, 90]. Using Fourier transform IR absorption measurements on GaNSb HMAs with N content in the range of 0.2%–1.0%, Jefferson et al demonstrated that the anticrossing coupling parameter was 2.6 eV with the N state at 0.78 eV above the valence band of GaSb [88]. Buckle et al found that the apparent incorporation of N in GaSb was easily controlled with the substrate temperature and demonstrated incorporation up to 1.75% [93]. In the same way, Wang et al reported the incorporation of up to 1.4% N in GaSb and verified the reduction in bandgap using optical absorption and photoluminescence [84]. Unfortunately, the lower substrate temperature growth process also resulted in a dramatic degradation in the crystalline as well as electro-optical qualities of the films. The unintentional background p-type carrier concentration increased from low $10^{15}$ cm$^{-3}$ by
several orders of magnitude. At the same time, the minority carrier lifetime of GaSb, which is not competitive to begin with at ~35 ns, degraded to the femto-second range. The degradation of the optical quality of these dilute alloys were believed to arise from non-radiative centers. It was speculated that these non-radiative centers are due to the presence of N–As and N–N split interstitials [94]. A recent study by Nair et al correlating photoluminescence intensities with XRD and ion channeling measurements on GaInSbN quantum wells confirmed the presence of these non-radiative centers due to non-substitutional N, possibly in the form of N clusters and split interstitials [86].

Most of these early experiments relied on XRD for the determination of the concentration of N in the films. Based on the observation of textbook Pendelloesung fringes, the structural quality of the films was prematurely judged to be very high. The reduction of the bandgap with the x-ray derived N-concentration also indicated a well-behaved alloy system. Later, however, it became apparent that the total amount of N in all films produced in this way was the same within experimental errors. By examining the nitrogen content with chemical analysis methods that sample all atoms, irrespective of lattice position, such as secondary ion mass spectroscopy or Rutherford back scattering (RBS) it was determined that the substrate temperature only affected the group-V lattice site occupation of some of the nitrogen atoms. These atoms did reduce the bandgap following the BAC model, while the rest of the nitrogen was apparently optically inactive. These non-substitutional N were referred to as ‘dark nitrogen’ [95].

The origin of the ‘dark nitrogen’ was investigated using channeling nuclear reaction analysis and was consistent with interstitials or split interstitials defects [86]. This, however, relies on the assumption of a non-distorted homogeneous film. Using high-resolution TEM we have observed that the introduction of N in GaSb also produces an undulating layering that is not detected by XRD. The incorporation of small amounts of N in the GaSb lattice is still not completely understood, but may hint at a common issue with the alloy. The contradictory XRD and chemical analysis results are mirrored in a perplexing way on the opposite composition end, where it is the chemical concentration measurements that correlate with the bandgap shift while the XRD results are sometimes unaffected.

Research in this material system, however, became less active after the discovery that the bandgap of InAsSb is small enough to achieve an optical gap in the 8–12 μm range, and which can be grown with very high quality [96, 97]. Nevertheless, the dilute N GaSb(N) work revealed some intriguing growth and materials properties that may have general implications for alloying on GaN-rich end of the GaN$_{1-x}$Sb$_x$ composition spectrum.

4.2. GaN-rich GaN$_{1-x}$Sb$_x$ alloys

Although GaSbN dilute nitride films have been studied in the last decade there has been no report on the growth of GaN$_{1-x}$Sb$_x$ alloys in the N-rich regime. The alloys discussed in this paper were grown at the University of Nottingham (chamber 1) and the US Army Research Laboratory (chamber 2). Chamber 1 is a MOD-GEN II system with a HD-25 Oxford Applied Research RF activated plasma source to provide active nitrogen, and elemental Ga and Sb as group III and V sources. The surface reconstruction is monitored with RHEED. Prior to the growth of the GaN$_{1-x}$Sb$_x$ layers, the sapphire wafers were annealed at 700 °C for 20 min. After annealing, the substrate was cooled down to the growth temperature over a 20 min period under a reduced active nitrogen flux and growth was initiated by simultaneous opening of the Ga and N shutters. The Sb shutter was opened after a 1 min delay in order to avoid the deposition of any Sb on the sapphire surface before GaN growth. The growth time was kept constant at 2 h for all layers. Chamber 2 is a GEN II 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 chamber 2 produces significantly less atomic N; therefore growths are done at a much slower rate than used in chamber 1.

4.2.1. Sb incorporation. Previously, we found that growth of GaN$_{1-x}$As$_x$, with x > 0.02 under Ga-rich growth conditions and at relatively high temperatures of ~600 °C results in phase separation into N-rich and As-rich phases [39]. Since Sb and N are even more mismatched in size and electronegativity than As and N, we expect that the incorporation of Sb in the N sublattice will be even more challenging. In order to incorporate substantial amounts of Sb into GaN we grew N-rich dilute Sb samples on (0001) sapphire substrates by PA MBE in chamber 1 at thermocouple temperatures ranging from 80° to 600 °C, significantly below the normal MBE GaN growth temperature of ~800 °C.

The initial experiments included two series of Ga-rich (Ga BEP ~ 2.2 × 10$^{-4}$ Torr) and N-rich (Ga BEP ~ 1.6 × 10$^{-7}$ Torr) growth conditions grown in chamber 1 at an extremely low temperature of 80 °C under fixed Ga and N overpressures, but different Sb overpressures. A constant N flux (total N BEP) ~1.5 × 10$^{-5}$ Torr with RF power 200 W) was maintained for these series. In both series, there was a monotonic increase in Sb content with increasing Sb overpressure, as shown in figure 8, where the composition is plotted as a function of the Sb/N BEP ratio. The Ga-rich samples were grown at 0.27 μm hr$^{-1}$ and the N rich samples were grown at 0.23 μm hr$^{-1}$.

It is known that the group III growth rate affects the group V compositions in group III–V alloys with mixed group constituents. For instance, for other fixed conditions, the Sb incorporation into GaAsSb and InAsSb [98] increases by a non-negligible amount at the expense of As as the cation flux increases. The interaction between Sb and N in relation to the Ga flux in our case is not yet known. For samples with lower Sb composition (<25%), the relationship between the Sb/N BEP ratio and the Sb composition appears to be linear and unaffected by the change in Ga flux. For Sb compositions above 35% it appears that the Ga-rich sample incorporates...
more Sb as a function of the BEP ratio. This is intuitive since the Sb should want to stick to the Ga-terminated surface, especially in a group V-deficient environment. We also noticed in prior InAsSb and GaAsSb experiments that for slow growth rates, it took a much larger change in the group V flux ratio to effect a significant change in the composition [98]. If the GaNSb HMASs could be grown faster, it would likely require a much smaller change in the Sb/Asux ratio to increase the Sb composition.

The incorporation of the Sb as a function of growth temperature was also explored in the temperature range of 80°C–600°C under Ga-rich and N-rich growth environments in chamber 1. Figure 9 shows the Sb content in GaN_{1−x}Sbx films as a function of growth temperature $T_g$ under both N-rich (Ga BEP $\sim 1.6 \times 10^{-7}$ T, Sb $\sim 9 \times 10^{-7}$ T) and Ga-rich (Ga BEP $\sim 2.2 \times 10^{-7}$ T, Sb BEP $\sim 3 \times 10^{-8}$ T) conditions. We note that at constant Sb BEP, the Sb content is rather insensitive to the growth temperature over the large temperature range 60°C $< T_g <$ 400°C. This is particularly true for films grown under the Ga-rich condition. Note that the samples grown under N-rich conditions have a 3 times higher Sb BEP, that results in 3 times higher Sb content in the films. These results can be contrasted with the growth of GaN_{1−x}Asx HMASs that, as also shown in figure 9, exhibits a stronger effect of temperature on the As content for $T_g <$ 400°C. At $T_g > 500°C$ the decrease in Sb content with increasing $T_g$ is even more pronounced when the films were grown under Ga-rich conditions. For example, at $T_g \sim 600°C$, only $\sim$0.04% of Sb was incorporated.

GaN_{1−x}Sbx alloys were also grown in chamber #2 under N-rich conditions. A moderately low substrate temperature in the range of 325°C–550°C were used in this case. The growth rates were 0.09 μm hr$^{-1}$ on sapphire, which is considerably slower than the growth rates used in chamber #1. The Sb mole fraction ($x$) as a function of Sb/As flux ratio at a growth temperature of 325°C is plotted in figure 10. Note that since the samples were grown in two different chambers, and the flux ratios shown in figures 8 and 9 are BEP ratios and the ratios in figure 10 are flux ratios, a direct quantitative comparison cannot be made between these figures.

Typically, to first order, the Sb concentration can be described by $[\text{Sb}] = \frac{\Phi_{\text{Sb}}}{\Phi_\text{N}}$ where $\Phi_{\text{Sb}}$ and $\Phi_\text{N}$ refer to the Sb and N flux, respectively. The interaction parameter, $\Omega$ describes the deviation from ideal incorporation. A parameter of $\Omega = 1$ describes incorporation with no interactions between the constituent atoms, where the concentration of the alloys is simply proportional to the impinging fluxes. While that is typically the case for group III–V alloys with mixed group III constituents under normal growth conditions, it is not the case for alloys with mixed group V constituents, particularly for alloys grown outside of ‘normal’ temperature ranges. This has been discussed at length in a prior report on the growth of InAsSb in chamber 2 [98]. The dotted lines in figure 10(a) shows the ‘ideal’ case of Sb/N ratio versus Sb incorporation when $\Omega = 1$. For low Sb/N flux ratios of up to 0.2 (inset of figure 10(a)), the incorporation is well-behaved and can be described by an interaction parameter of $\Omega \sim 0.62$ (gray solid line). However, for higher Sb/N ratios it appears that the Sb composition dramatically levels off at about 18% at this growth temperature. We had been able to grow across the composition spectrum at 80°C, so 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 general, group V incorporation is influenced by the substrate temperature in group III–V alloys with mixed group V constituents. We saw this effect in InAsSb, which showed that the Sb incorporation decreased with increasing substrate
temperatures [99]. Similarly, over a substrate temperature range of 325 °C–600 °C, the Sb incorporation decreases for fixed Sb/N conditions, as shown in figure 10(b). Note that for a low Sb/N flux ratio (0.1) the Sb mole fraction decreases linearly with increasing \( T_s \). For the higher Sb/N ratios, however, there is a marked decrease in Sb incorporation for temperatures above 475 °C. This is consistent with the results obtained on samples grown in chamber #1 as shown in figure 9.

4.2.2. Film structure. The effect of Sb flux on the incorporation of Sb in GaN\textsubscript{1−x}Sb\textsubscript{x} is best illustrated in one sample grown in chamber #2 with fixed substrate temperature of 325 °C, and fixed N and Ga fluxes, but varying Sb flux by gradually opening the Sb valve by equal sized steps. The Ga and N BEP were 5.18 \( \times \) 10\textsuperscript{8} and 1.48 \( \times \) 10\textsuperscript{5} Torr, respectively, nominal conditions for N-rich growth. The Sb-flux as a function of valve position was calibrated before growth by opening the valve in steps. The structure and composition was examined \textit{ex situ} with cross-sectional TEM and RBS depth profiling. Figure 11 correlate the structural characteristics and chemical profile with the Sb BEP. The high resolution TEM cross section of the initial growth region without Sb (figure 11(c)) shows the typical columnar polycrystalline structure of GaN and low Sb-content GaN\textsubscript{1−x}Sb\textsubscript{x}. The growth planes are rotated within the plane, but are mostly aligned with the substrate. At the position where the RHEED intensity began to drop, the atomic depth profile shows that the GaN\textsubscript{1−x}Sb\textsubscript{x} alloy contained \( \sim \)5% Sb. After this point we see some interruption in the columnar pattern and slightly less preference to align with the substrate, as shown in figure 11(d). The material is still completely polycrystalline. At the point where the Sb is 9%, most of the remaining columnar structure is lost, although most of the growth orientation preference is still evident. There is still a continuous decrease in RHEED intensity at this point. At 2570 s, where the RHEED intensity became constant, there is a complete loss of any orientation preference, and there are no long-range slip planes, so all dislocations coming from the interface with the substrate have annihilated. The Sb composition at this point is around 15%. The composition at the end of the growth was 22%. Even at this high Sb composition, the material was a poly-amorphous mix, with small crystallites present (figure 11(e)). We still did not see evidence of Sb clusters, or any Sb accumulated at the surface.

This study enables us to track growth conditions and estimate which Sb/Ga ratio is needed to obtain a single film with a specific Sb composition. We also know what morphology can be expected at that composition.

As observed in figure 9 for samples grown in chamber #1, alloys grown at relatively high temperature of \( \sim \)600 °C can only incorporate 0.04%–1% Sb, similar to results shown in figure 10 for alloys grown in chamber #2. XRD and ion channeling results showed that these dilute alloys grown at \( \sim \)600 °C still have good crystallinity. For example, as shown in figure 12, samples with 0.04% Sb showed a minimum channeling yield \( \sim \)0.18 as compared to \( \sim \)0.04 for GaN films grown under similar conditions. A much more rapid dechannelling rate is also observed in the sample with 0.04% Sb, indicating that the material has a much higher density of extended defects as compare to the undoped sample. This suggests that even very small amount of Sb atoms strongly disrupt the crystallinity of the GaN lattice.

The microstructure of dilute GaN\textsubscript{1−x}Sb\textsubscript{x} alloys grown at relatively high temperature of 600 °C are further studied by high resolution cross sectional TEM measurements. Figure 13 shows the microstructures of the two films shown in figure 12. For the undoped GaN film, we observe a regular columnar structure, similar to that shown in figure 11. The high resolution image shows that this undoped layer has good crystallinity with a higher density of defects close to the GaN/sapphire interface. In contrast, the film grown with only
0.04% of Sb shows a non-columnar structure with high dislocation density. This is in good agreement with the ion channeling results shown in figure 12.

It has been previously discussed in section 3.2 that due to the strong ionic nature of GaN, a c-axis oriented polycrystalline hexagonal GaN phase dominates even at the lowest growth temperature of 80 °C [39, 41, 70, 71, 100]. As shown in figures 9 and 10, at this low growth temperature, more Sb can be incorporated in the GaN_{1−x}Sb_x film as the Sb flux increases. XRD measurements (figure 14(a)) showed that at the growth...
temperature of 80 °C the samples become less crystalline with increasing Sb content and eventually become entirely amorphous with $>\sim 5\%$ of Sb. Figure 14(b) shows (0002) diffraction peaks of GaN$_{1-x}$Sb$_x$ samples grown at different substrate temperatures with similar Ga and Sb BEP and with Sb content of $\sim$4%–5.5%. At this Sb content, films grown below 100 °C are entirely amorphous. At $T_g \sim 135 \degree$ C the film becomes partially crystalline as evidenced by the weak and broad (0002) diffraction peak. This diffraction peak is most likely coming from small crystalline grains within the amorphous matrix. At higher growth temperatures the (0002) peak intensity increases, indicating that a larger fraction of the film is crystalline with larger grain sizes. At the even higher growth temperature of 470 °C, the (0002) diffraction peak becomes strong, suggesting growth of a fully crystalline film that is preferentially oriented to the growth direction of the substrate. However at a higher Sb content of $\sim$7%, the films remain amorphous even for a growth temperature as high as
285 °C. Phase separation occurs at the high growth temperature of 470 °C when the Sb content increases to \( x > 0.06 \) with a clearly visible (210) zinc blende GaSb peak at \( 2\theta \sim 32.6° \) as shown in the top scan of figure 14(b).

Cross sectional TEM images and SAD patterns for samples grown at (a) 80 °C (b) 195 °C and (c) 470 °C with similar Ga and Sb fluxes and with Sb content in the range of 4%–6% are shown in figure 15. At the low growth temperature of 80 °C, the sample with 6.2% Sb appears to be entirely amorphous. The columnar structure that was observed in the sample with lower Sb content is completely absent in this film. The diffuse rings in the SAD pattern shown in figure 15(a) confirm that the film is primarily amorphous, in good agreement with the XRD results. The microstructure of the film with 6.2% Sb grown at 195 °C shown in figure 15(b) reveals that the film has both crystalline grains of ~5 nm size and amorphous regions. SAD patterns also show crystalline diffraction rings indicating polycrystalline grains as well as an amorphous ring. These results are consistent with the XRD pattern of the sample showing only a weak (0002) GaN\(_{1-x}\)Sb\(_x\) diffraction peak. At the high growth temperature of 470 °C, both the TEM image and the SAD pattern indicate a polycrystalline film (figure 15(c)). From the thickness measured by cross-sectional TEM and the areal density from RBS, we calculated the density of the amorphous GaN\(_{1-x}\)Sb\(_x\) film with ~6% Sb to be ~84% of the corresponding crystalline phase.

4.2.3. Effect of growth stoichiometry. Sb incorporation and the overall III:V (\([\text{Ga}]/([\text{Sb}]+[\text{N}])\)) ratio depends quite strongly on the Ga flux during growth, particularly at low growth temperature. Figure 16 shows the Ga flux dependence on the Sb concentration in mole % and the III/V atomic ratio, \([\text{Ga}]/([\text{Sb}]+[\text{N}])\) of GaN\(_{1-x}\)Sb\(_x\) films grown at substrate temperature of 80 °C at a fixed Sb BEP of \(3.2 \times 10^{-8}\) Torr in chamber #1. As is seen in figure 16, increasing Ga flux at a fixed Sb flux results in decreased Sb incorporation and a corresponding increase in the III/V ratio of the film. Under these growth conditions, stoichiometric III/V material with Sb mole fractions of \( x \sim 0.05 \) can be obtained with a Ga flux of ~2 \( \times 10^{-7}\) Torr.

Figures 17(a) and (b) show the Sb incorporation and III/V ratio for GaN\(_{1-x}\)Sb\(_x\) films grown at a substrate temperature of 80 °C with increasing Sb BEP under N-rich (Ga BEP ~ 1.6 \( \times 10^{-7}\) Torr) and Ga-rich (Ga BEP ~ 2.2 \( \times 10^{-7}\) Torr) conditions, respectively. Note that at the low growth temperature
Fig. 17. Concentrations of Sb in mole % together with the III/V atomic ratio, [Ga]/[(Sb)+[N]) of the films grown at substrate temperature of 80 °C (a) with increasing Sb flux for N-rich (Ga BEP ~ 1.6 × 10^{-7} T), and (b) Ga-rich (Ga BEP ~ 2.2 × 10^{-7} T) conditions. Reprinted with permission from [70]. Copyright 2014 AIP Publishing LLC.

$T_g$ ~ 80 °C the incorporation of Sb increases linearly with Sb BEP independent of the Ga BEP. Under the Ga-rich growth condition, GaN_{1−x}Sb_{x} films with III/V ratio of unity can be obtained with Sb BEP up to 8 × 10^{-8} Torr with up to 10 mole % Sb. However, under N-rich growth condition, stoichiometric films can be obtained only for Sb BEP ~ 2 × 10^{-8} Torr, giving rise to ~4 mole % of Sb in the film. This suggests that Ga-rich growth conditions are required to incorporate high concentrations of Sb into GaN_{1−x}Sb_{x} while still maintaining a good film stoichiometry. However, for low Sb flux, a Ga-rich growth may also favor the incorporation of Ga antisites GaN. Such GaN antisites may introduce deep levels within the gap as previously discussed in the LT-GaN materials.

4.3. Electronic properties

As discussed in section 2, electronic band structures of HMAs can be described by the anticrossing interactions between impurity localized states and the extended states of the host matrix. For GaN_{1−x}Sb_{x} HMAs, the approximate location of the Sb level in GaN can be deduced from its known position at 1.0 eV below the VBM of GaAs [44]. Considering that the valence band edge offset between GaAs and GaN equals 2 eV, this places the Sb level at about 1 eV above the VBM of GaN. We utilize the GaN_{1−x}Sb_{x} samples with dilute Sb impurity grown at 600 °C to better locate the position of the Sb level in GaN.

Room temperature cathodoluminescence (CL) measurements on Sb doped GaN samples with dilute amount of Sb (<1%) grown at 600 °C showed a broad luminescence at 2.0–2.5 eV with peak intensity at ~2.2 eV [101]. We note that only the band edge luminescence of ~3.4 eV is observed for the sample grown at similar conditions but without Sb. This suggests that the broad CL peak can be attributed to incorporation of the Sb. Wu et al. [29] have shown that the composition dependence of the bandgap in GaNAs alloys can be explained by the BAC model with the localized As level $E_{\text{As}}$ ~ 0.62 eV above the VBM of GaN. Photoluminescence measurements on As doped GaN by Foxon et al. showed a broad luminescence from 2.23 to 2.9 eV with peak intensity at ~2.65 eV [73]. Considering a likely ~0.1 eV Stokes shift in the PL peak, this places the $E_{\text{As}}$ ~ 0.65 eV, in good agreement with the value obtained by Wu et al. Since the electronegativity difference between Sb and N is larger than between As and N, it is expected that Sb-derived localized levels lie higher above the valence band edge than that the As levels. Again, assuming the Stokes shift of 0.1 eV places the Sb level at $E_{\text{Sb}}$ ~ 1.1 eV above the VBM of GaN. This is in a good agreement with the value extrapolated from the position of the Sb level at 0.9 eV below the VBM in GaAs [44]. However, it is important to note that the CL peak at 2.2 eV coincides with the commonly observed ‘yellow’ luminescence in GaN that has been attributed to native defects or defect complexes. Since incorporation of Sb affects the crystalline quality of the films it is therefore possible that Sb levels and native defects contribute to the observed CL.

4.3.1. Optical absorption. The absorption coefficient $\alpha$ of GaN_{1−x}Sb_{x} films was measured using transmission and reflection measurements. Figure 18(a) shows $\alpha$ for GaN_{1−x}Sb_{x} films with increasing Sb content grown in chamber #1 at 80 °C under N-rich growth conditions. The absorption coefficient for a sample with $x = 0.062$ grown under Ga-rich sample is also shown. A monotonic increase of the sub-bandgap optical absorption starting with photon energies of less than 2 eV is observed with increasing Sb content. This absorption can be attributed to optical
transitions from the Sb-derived band \(E_v\) to the conduction band. It is very weak at low Sb concentrations but starts to dominate when the Sb content reaches a few mole %. Note that although the film becomes amorphous for \(x > 0.07\), the optical absorption shows a well-developed, relatively sharp absorption edge. In contrast, a GaN\(_{1-x}\)Sb\(_x\) film grown under Ga-rich conditions (Ga BEP > 2.2 \times 10^{-7} T) exhibits a strong absorption at energy as low as 1 eV. This is believed to originate from GaN related defect band, consistent with our investigation on the optical properties of LT-GaN [71].

Figure 18(b) shows the absorption coefficient of a series of GaN\(_{1-x}\)Sb\(_x\) films grown in chamber \#2 at a higher temperature of 325 °C by growing a multilayer structure with a number of alternating layers of GaN and GaSb. An intermixing of the layers produced alloys with thicknesses of 150–300 nm and Sb compositions up to \(x = 0.42\). Using this technique we were able to grow GaN\(_{1-x}\)Sb\(_x\) HMAs with \(x\) up to \(\sim 0.4\) at higher temperature without phase separation. The average composition of the alloys was controlled by the GaN to GaSb layer thickness ratio. Figure 18(b) shows that even for the sample with no Sb, the absorption spectra does not have a sharp onset. This is consistent with our previous studies of LT-GaN under Ga-rich conditions [71]. Since the thin films are grown in chamber \#2 are under slightly Ga-rich conditions, we associate the absorption tail with similar type of GaN related defects as seen in the absorption spectra for the GaN\(_{1-x}\)Sb\(_x\) films grown by LT-MBE under Ga-rich conditions in [71]. However, in contrast to the earlier studied Ga-rich samples, as the Sb fraction is increased the absorption coefficient increases and the sub-band gap absorption edge shifts to lower energies and becomes more dominant at higher Sb contents. This behavior was similar to N-rich grown samples shown in figure 18(a), despite the very different growth methods.

### 4.3.2. Electronic band structure

The electronic band structures of the GaN\(_{1-x}\)Sb\(_x\) were calculated using the modified BAC model described in section 2.2. As mentioned previously, the simplest way to extend the BAC model was to compositionally weight the BAC results obtained in the dilute limits to the whole composition range [29, 35, 36, 102]. This approach was successful in predicting overall trends but significantly overestimated the band gap reductions for alloys with mid-range compositions. The main deficiencies of the model were that it ignored the composition dependence of the coupling parameter and assumed that BAC interactions fully determine the shifts of the conduction and the valence band edges. To correct for the deficiencies we adopt here a hybrid model by using the VCA on the valence and conduction matrix band edges as well as on the potential of the anion lattice site [46]. Hence the coupling parameters for GaN\(_{1-x}\)Sb\(_x\) are not constant but vary with composition. This allows the BAC interactions to be treated as perturbations. The detail of this modified BAC model has been presented in section 2.2.

At the same time we note that using the conventional method of linearly fitting \(\alpha^2\) as a function of photon energy to obtain the band gap cannot be applied at low Sb levels because of the complex, composition-dependent valence band structure. Since the optical absorption coefficient is proportional to the joint optical density of states and the dipole matrix element between initial and final states, six optical transitions from three valence to two conduction sub-bands have to be taken into account. We consider optical transitions
from three valence bands to the conduction band: the Sb derived impurity band ($E^i(k)$), Si spin–orbit split band ($E^{SO}(k)$) and the GaN matrix-like band ($E^C(k)$). Also, to account for broadening in the bands inherent to the BAC model and arising from localized composition fluctuations, we convolve the energy dependent joint optical density of states with a Gaussian function at each $k$ value. The fitting procedure used here is similar to that used by Mayer et al to evaluate the absorption coefficient in ZnO$_{1-x}$Se$_x$ HMA alloys [35]. For example, the optical absorption coefficient associated with transitions from the higher valence band $E^i(k)$ to the lower conduction band $E^C(k)$ is proportional to the corresponding joint density of states and can be written as:

$$g^i(h\omega) = \frac{1}{4\pi\sqrt{\pi}} \int \frac{\sin \left( \frac{\theta_V}{2} \right)^2 \sin \left( \frac{\theta_C}{2} \right)^2}{\Delta_c + \Delta_V} \exp \left[ -\frac{h\omega - \left( E^C(k) - E^i(k) \right)}{\Delta_c + \Delta_V} \right] k^2 dk,$$

(8)

where $\Delta_c$ and $\Delta_V$ are the broadening parameters of $E^C(k)$ and $E^i(k)$, respectively. In addition we have assumed that there is no optical coupling between extended and localized states, so that the optical absorption is proportional to the delocalized part of the wavefunction of a given sub-band. This effect is accounted for by the first two factors under the integral in the above equation

$$\theta_V = \tan^{-1} \left( \frac{C_Sb(x)\chi^2}{E(k) - E_{Sh}} \right) \quad \text{and} \quad \theta_C = \tan^{-1} \left( \frac{C_N(x)\chi^2}{E(k) - E_{Sh}} \right).$$

(9)

where $C_{Sb}(x)$ and $C_N(x)$ are the composition dependent coupling parameters of the localized Sb level ($E_{Sh}$) with the valence band and N level ($E_{N}$) with the conduction band, respectively for GaN$_{1-x}$Sb$_x$. The expression for the total absorption coefficient includes the six transitions described above, with each transition $i$ weighted by its degeneracy factor $g_i$ as $\sum_i g_i \alpha_i g(h\omega)$, where $\alpha_i$ is a scaling constant obtained by fitting the experimental absorption spectrum.

Figure 19(a) shows the band structure of a GaN$_{0.82}$Sb$_{0.18}$ alloy calculated using our modified BAC model. Here $E_{Sh}$ is at 1.2 eV above the VBE of GaN, $E_{N}$ at 0.45 eV above the CBE of GaSb; a coupling parameter of 2.7 eV for the N localized level with the conduction band of GaSb and 2.5 eV for the Sb level with the valence band of GaN were used [70, 88]. Since the p-like states of elemental Sb have a relatively large spin–orbit splitting energy of 0.75 eV [103, 104] the optical transitions from this band is considered as well. The band gap energy for the alloys are defined for the lowest transition energy between the $E^i(k)$ and the $E^C(k)$ bands. Figure 19(b) shows the total absorption coefficient for the GaN$_{0.82}$Sb$_{0.18}$ thin film along with the six different contributions as calculated from equation (8).

The total calculated absorption coefficients for samples with different composition using the above approach are also shown as dashed lines in figure 18(b). Fitting the experimental data yields the coupling parameter of 2.5 eV for the Sb level with the GaN valence band states with broadening parameters varying from 0.01 to 0.5 eV. The obtained band gap energies for these samples, both from chamber #1 and #2 are shown in figure 20. Band gap values from GaSb-rich GaSbSb from [88] are also included in the plot along with the composition dependence of the band gap predicted by the original BAC model, i.e. with composition independent coupling parameters as presented in [70]. Positions of the CBE and VBE predicted by the two models are shown in the inset of figure 20. As can be seen in the figure, the modified model provides a much better fit to the experimentally determined gaps and predicts a smaller downward shift of the CBE as a function of Sb content.

Figure 20 shows that the calculated bandgap dependence on composition is in very good agreement with the experimental values, especially for Sb contents <30%. For samples with Sb content >30%, the calculated values are consistently smaller than the experimental values. This can be attributed to the fact that RBS measures the total Sb concentration that may be higher than the actual amount of Sb substituting the N site and contributing to the modification of the band structure of the alloy. This difference is expected to be more severe for high Sb contents. It should also be noted that the strong decrease in the bandgap of dilute Sb alloys is associated with a large, discontinued upward shift of the VBM from the VBE of GaN to $E_{C}^i$ subband originating from the localized Sb levels in GaN$_{1-x}$Sb$_x$. As is seen in the inset of figure 20 the large drop of the absorption edge energy (from 3.4 to ~2.3 eV) is already observed for films with only a small amount of Sb (~3%).
from Jefferson et al gap energies for GaSb-rich alloys with up to 1% of N were taken signifi- cantly reduced to $0.2$. This corresponds to a band gap of about 1.3 eV. This allows for large flexibility in selecting the alloy composition most suitable for PEC application.

As can be seen from the inset of figure 20, the modified BAC model predicts that for GaN$_{1-x}$Sb$_x$ HMAs the band edges still straddle the redox potential for a composition $x$ up to 0.2. This corresponds to a band gap of about 1.3 eV. This allows for large flexibility in selecting the alloy composition most suitable for PEC application.

However, for photoelectrode applications, controllable electrical properties of the GaN based HMAs are desired. For GaN$_{1-x}$As$_x$ alloys, we have demonstrated that both $n$ and $p$-type doping of the material with Te and Mg, respectively, can be achieved. Given the similarity of the two alloy systems, the bipolar doping of GaN$_{1-x}$Sb$_x$ is expected to be achievable. However, a detailed study on the doping behavior of GaN$_{1-x}$Sb$_x$ has not been carried out to date.

As we have described in this review the growth parameter space for the incorporation of As or Sb in GaN is very large. As or Sb do not incorporate substitutionally under the high-temperature growth conditions that have been found to produce high quality GaN. We must therefore find other growth regimes that will enable incorporation while also producing material with optical and electrical properties that will enable functioning devices. The optical properties in particular seem challenging.

It is of course not obvious that any growth conditions achievable with MBE will result in substitutional incorporation of the larger group V atoms in GaN. Thus the systematic exploration of the parameter space is likely to be very time consuming even with the ramping experiments that we have introduced. It is therefore interesting to consider numerical growth incorporation modeling that would allow very rapid variations of growth conditions over wide ranges. With the existing volume of experimental growth conditions and results it should be possible to adjust a model to describe those and gain confidence in its predictive capabilities.

5. Potential applications

The direct conversion of sunlight into hydrogen by PEC water-splitting is one of the simplest methods to convert solar energy into a storable fuel. The practical realization of this technology depends critically on the availability of a suitable electrode material that combines acceptable solar response and efficiency and sufficient service lifetime for energy payback. For efficient hydrogen production by PEC water splitting, an ideal photoelectrode must meet three basic criteria: corrosion stability, a band gap small enough to absorb a significant fraction of the solar spectrum, and band edges straddling the hydrogen and oxygen redox potentials located, respectively at $\sim 4.5$ and $5.7$ eV below the vacuum level [82, 83]. To date, no known material satisfies all these requirements. Several oxides, most notably TiO$_2$, have shown good corrosion stability under operation, but have low efficiencies due to their wide band gaps [83, 105, 106]. III–V and II–VI semiconductors, such as GaInP$_2$ [107], have shown high water-splitting efficiencies but these materials have poor corrosion resistance and showed performance degradation and/or short lifetimes.

GaN is a mechanically hard and corrosion resistant semiconductor with CBE and VBE straddling the redox potential and hence can be a good candidate as photoelectrodes for PEC applications. However, the band gap of GaN is too large and therefore can only absorb the UV part of the solar spectrum. For GaN to be useful for PEC, its bandgap has to be significantly reduced to $< 2$ eV. In addition, because of the very low location of the VBE at almost 2 eV below the water oxidation potential the required band gap reduction has to be realized by an upward shift of the valence band rather than a downward shift of the CBE. As is seen in figure 20 this goal can achieved by incorporation of Sb into GaN as it provides a method to engineer not only the band gap but also the band offsets. Specifically incorporation of even small amounts of Sb results in large upward shift of the VBE. This offers the potential of using GaN$_{1-x}$Sb$_x$ as a semiconductor for PEC water dissociation.

Figure 20. Fitted bandgap energies for the GaN$_{1-x}$Sb$_x$ films. Band gap energies for GaSb-rich alloys with up to 1% of N were taken from Jefferson et al [88]. The band gap energy over the whole composition range was calculated using our modified BAC model (dashed red line) and compared to the band gap calculated using the old model in [2] (black dashed line). The inset shows the VBE and CBE over the whole composition range using both our modified BAC model (solid line) and the old BAC model (dashed line). The redox levels for pH = 2 are indicated as dotted lines. Reprinted with permission from [46]. Copyright 2015 AIP Publishing LLC.

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References

[1] Cardona M 1963 Optical properties of the silver and cuprous halides Phys. Rev. 129 69–78

[2] Van Vechten J A and Bergstresser T K 1970 Electronic structures of semiconductor alloys Phys. Rev. B 1 3351–8

[3] Richardson D 1971 The composition dependence of energy bands in mixed semiconductor systems with zincblende structures J. Phys. C: Solid State Physics 4 1289–91

[4] Schulz S, Caro M A, Lay-Theng T, Parbrook P J, Martin R W and O’Reilly E P 2013 Composition-dependent band gap and band-edge bowing in AlInN: a combined theoretical and experimental study Appl. Phys. Exp. 6 121001

[5] Walukiewicz W, Shan W, Yu K M, Ager J W III, Haller E E, Mistlowski J, Seong M J, Aluwadh H and Ramdas A K 2000 Interaction of localized electronic states with the conduction band: band anticrossing in II–VI semiconductor ternaries Phys. Rev. Lett. 85 1552–5

[6] Walukiewicz W, Alberi K, Wu J, Shan W, Yu K M and Ager J W III 2008 Physics of Dilute III–V Nitride Semiconductors and Material Systems: Physics and Technology ed Ayse Erol (Berlin: Springer) ch 3

[7] Wu J, Shan W and Walukiewicz W 2002 Band anticrossing in highly mismatched III–V semiconductor alloys Semicond. Sci. Technol. 17 860–9

[8] Weyers M, Sato M and Ando H 1992 Red shift of photoluminescence and absorption in dilute GaAsN alloy lasers Japan. J. Appl. Phys. 31 L853–5

[9] Baillargeon N, Cheng K Y, Hofler G F, Pearah P J and Hsieh K C 1992 Luminescence quenching and the formation of GaP1–xN x in GaP with increasing nitrogen content Appl. Phys. Lett. 60 2540–2

[10] Shan W, Walukiewicz W, Ager J W III, Haller E E, Geisz J F, Friedman D J, Olson J M and Kurtz S R 1999 Band anticrossing in GaN:As alloys Phys. Rev. Lett. 82 1221–4

[11] Uesugi K, Marooka N and Suemune I 1999 Reexamination of N composition dependence of coherently grown GaNAs band gap energy with high-resolution x-ray diffraction mapping measurements Appl. Phys. Lett. 74 1254–6

[12] Buyanova I and Weinim Chen (ed) 2004 Physics and Applications of Dilute Nitrides (New York: Taylor and Francis)

[13] Erol A (ed) 2008 Physics of Dilute III–V Nitride Semiconductors and Material Systems: Physics and Technology (Berlin: Springer)

[14] Kondow M, Kitatani T, Nakatsuka S, Larson M C, Nakahara K, Yawaza Y, Okai M and Uomi K 1997 GaN:As: a novel material for long-wavelength semiconductor lasers IEEE J. Sel. Topics in Quantum Electron. 3 719–30

[15] Kondow M, Kitatani T, Larson M C, Nakahara K, Uomi K and Inoue H 1998 GaN:As for long-wavelength laser diodes J. Crystal Growth 188 255–9

[16] Friedman D J, Geisz J F, Kurtz S R, Myers D and Olson J M 1998 1 eV solar cells with GaN:As active layer J. Crystal Growth 195 409–15

[17] Kurtz S R, Allerman A A, Jones E D, Gee J M, Banas J J and Hammons B E 1999 InGaAsN solar cells with 1.0 eV band gap, lattice matched to GaAs Appl. Phys. Lett. 74 729–31

[18] López N, Reichertz L A, Yu K M, Campman K and Walukiewicz W 2011 Engineering the electronic band structure for multiband solar cells Phys. Rev. Lett. 106 028701

[19] Ahsan N, Miyashita N, Islam M M, Yu K M, Walukiewicz W and Okada Y 2012 Appl. Phys. Lett. 100 172111

[20] López N, Yu K M, Tanaka T and Walukiewicz W 2016 Multicolor electroluminescence from intermediate band solar cell structures Adv. Energy Mater. 6 1501820

[21] Bi W G and Tu C W 1996 N incorporation in InP and band gap bowing in InNP J. Appl. Phys. 80 1934–6

[22] Yu K M, Walukiewicz W, Shan W, Yu K M, Ager J W III, Haller E E, Xie H P and Tu C W 2001 Synthesis of InN, GaN, InP, and thin films by N ion implantation Appl. Phys. Lett. 78 1077–9

[23] Shan W, Walukiewicz W, Yu K M, Ager J W III, Haller E E, Xie H P and Tu C W 2000 Nature of the fundamental bandgap in GaNP1–x alloys Appl. Phys. Lett. 76 3251–3

[24] Li W, Héroux J B and Wang W I 2003 InGaAsSbN: a dilute nitride compound for midinfrared optoelectronic devices J. Appl. Phys. 94 4248–50

[25] Harmand J C, Uemura T, Uemura Y, Iijima J, Bando Y, Teshima Y, Gemma K, Hasegawa K, Tanaka T, Kusaba S, Mochinaga T, Saito K, Guo Q, Iyer S, Wu L, Li J, Potoczny S, Matney K and Kent P R C 2007 Effects of N incorporation on the structural and photoluminescence characteristics of GaSb:Sn/GaSb single quantum wells J. Appl. Phys. 101 113508

[26] Francoeur S, Seong M J, Miascarenhas A, Tixier S, Adamcyk M and Tiedje T 2003 Band gap of GaAs1–xSb x quantum wells for 0 < x < 3.6% Appl. Phys. Lett. 82 3874–6

[27] Huang W, Oe K, Feng G and Yoshimoto M 2005 Molecular-beam epitaxy and characteristics of GaNAs1–xSb x alloys J. Appl. Phys. 98 053505

[28] Wu J, Walukiewicz W, Yu K M, Denlinger J D, Shan W, Ager J W III, Kimura A, Tang H F and Kuech T F 2004 Valence band hybridization in N-rich GaN1–xAs x alloys Phys. Rev. B 70 115214

[29] Shu W, Walukiewicz W, Ager J W III, Yu K M, Wu J, Haller E E, Nabetani Y, Mukawa T, Ito Y and Matsumoto T 2003 Effect of oxygen on the electronic band structure in ZnO:Se1–x alloys Appl. Phys. Lett. 83 299–301

[30] Yu K M, Walukiewicz W, Wu J, Shan W, Beeman J W, Scarpulla M A, Dubon O D and Becla P 2003 Diluted II–VI oxide semiconductors with multiple band gaps Phys. Rev. Lett. 91 246203-4

[31] Yu K M, Walukiewicz W, Wu J, Shan W, Beeman J W, Scarpulla M A, Dubon O D and Becla P 2004 Synthesis and optical properties of II–V VI highly mismatched alloys J. Appl. Phys. 95 6232–8

[32] Tanaka T, Kusaba S, Mochinhaga T, Saito K, Guo Q, Nishio M, Yu K M and Walukiewicz W 2012 Molecular beam epitaxial growth and optical properties of highly mismatched ZnTe1–xO x alloys Appl. Phys. Lett. 100 011905

[33] Tanaka T, Nagao Y, Mochinaga T, Saito K, Guo Q, Nishio M, Yu K M and Walukiewicz W 2013 Molecular beam epitaxial growth of ZnCdTeO epilayers for intermediate band solar cells J. Cryst. Growth 378 259–62

[34] Mayer M A, Speaks D T M, Yu K M, Mao S S, Haller E E and Walukiewicz W 2010 Band structure engineering of ZnO1–xSe x alloys Appl. Phys. Lett. 97 022104

[35] Ting M, dos Reis R, Jaquez M, Dubon D O, Mao S S, Yu K M and Walukiewicz W 2015 Tunability of electronic band structures in ZnO:Te-rich highly mismatched ZnO1–xTe x alloys Appl. Phys. Lett. 106 092101

[36] Kent P R, Belloiche L and Zunger A 2002 Pseudopotential theory of dilute III–V nitrides Semicond. Sci. Technol. 17 851–9
Walukiewicz W 2009 Molecular beam epitaxy of crystalline and amorphous GaN layers with high As content J. Cryst. Growth 311 3417–22

[77] Yu K M, Novikov S V, Broesler R, Liliental-Weber Z, Levander A X, Dubon O D, Wu J, Walukiewicz W and Foxon C T 2010 Low gap amorphous GaN\textsubscript{1-x}As\textsubscript{x} alloys grown on glass substrate Appl. Phys. Lett. 97 101906

[78] Levander A X, Yu K M, Novikov S V, Liliental-Weber Z, Foxon C T, Dubon O D, Wu J and Walukiewicz W 2013 Local structure of amorphous GaN\textsubscript{1-x}As\textsubscript{x} semiconductor alloys across the composition range J. Appl. Phys. 113 243505

[79] Levander A X, Liliental-Weber Z, Broesler R, Hawridge M E, Novikov S V, Foxon C T, Dubon O D, Wu J, Walukiewicz W and Yu K M 2011 Thermal stability of amorphous alloys Appl. Phys. Lett. 98 161902

[80] Levander A X, Novikov S V, Liliental-Weber Z, dos Reis R, Dubon O D, Wu J, Foxon C T, Yu K M and Walukiewicz W 2011 Doping of GaN\textsubscript{1-x}As\textsubscript{x} with high As content J. Appl. Phys. 110 093702

[81] Novikov S V, Ting M, Yu K M, Sarney W L, Martin R W, Svensson S P, Walukiewicz W and Foxon C T 2014 Tellurium n-type doping of highly mismatched amorphous GaN\textsubscript{1-x}As\textsubscript{x} alloys in plasma-assisted molecular beam epitaxy J. Cryst. Growth 404 9–13

[82] Bak T, Nowotny J, Rekas M and Sorrell C C 2002 Photo-electrochemical hydrogen generation from water using solar energy, materials-related aspects Int. J. Hydrog. Energy 27 991–1022

[83] Sorrell C C, Sugihara S and Nowotny J (ed) 2005 Materials for Energy Conversion Devices (Cambridge, England: Woodhead Publishing Limited) ISBN-10:1 55753 932 1

[84] Wang D, Svensson S P, Shterengas L, Belenky G, Kim C S, Vurgaftman I and Meyer J R 2009 Band edge optical transitions in dilute-nitride GaN\textsubscript{x}Sb\textsubscript{1-x} J. Appl. Phys. 105 014904

[85] Svensson S P, Donetsky D, Wang D, Hier H, Crown F J and Belenky G 2011 Growth of type II strained layer superlattices, bulk InAs and GaSb materials for minority lifetime characterization J. Cryst. Growth 334 103–7

[86] Nair H P, Crook A M, Yu K M and Bank S R 2012 Structural and optical studies of nitrogen incorporation into GaSb-based GaN\textsubscript{x}Sb quantum wells Appl. Phys. Lett. 100 21103

[87] Veal T D et al 2005 Band gap reduction in GaN\textsubscript{x}Sb alloys due to the anion mismatch Appl. Phys. Lett. 87 132101

[88] Jefferson P H, Veal T D, Piper L F J, Bennett B R, McConville C F, Murdin B N, Buckle L, Smith G W and Ashley T 2006 Band anticrossing in GaN\textsubscript{x}Sb\textsubscript{1-x} Appl. Phys. Lett. 89 119121

[89] Belabbes A, Ferhat M and Zaoui A 2006 Giant and composition-dependent optical band gap bowing in dilute GaSb\textsubscript{1-x}N\textsubscript{x} alloys Appl. Phys. Lett. 88 152109

[90] Ashwin M J, Walker D, Thomas P A, Jones T S and Veal T D 2013 N incorporation in GaN\textsubscript{x}Sb\textsubscript{1-x} and lattice matching to GaSb J. Appl. Phys. 113 033502

[91] Sarney W L and Svensson S P 2009 Materials study of the competing group V element incorporation process in dilute-nitride films MRS Proc. 1202 1202–405

[92] Sarney W L, Svensson S P, Hier H, Donetsky D, Wang D, Shterengas L, Suchalkin S and Belenky G 2011 New approaches to direct bandgap III–V materials for LWIR detector applications AIP Conf. Proc. 1416 59–61

[93] Buckle L, Bennett B R, Jollands S, Veal T D, Wilson N R, Murdin B N, McConville C F and Ashley T 2005 Growth of dilute GaN\textsubscript{x}Sb by plasma-assisted MBE J. Cryst. Growth 278 188–92

[94] Jin Y, Jock R M, Cheng H, Ye Y, Mirtarov A M, Wang Y, Kurdak C, Merz J L and Goldman R S 2009 Influence of N interstitials on the electronic properties of GaAsN alloys Appl. Phys. Lett. 95 062109

[95] Sarney W L and Svensson S P 2013 Discrepancies in the nature of nitrogen incorporation in dilute-nitride GaSbN and GaAsN films J. Vac. Sci. Technol. B 31 051206

[96] Sarney W L, Svensson S P, Hier H, Kipshidze G, Donetsky D, Wang D, Shterengas L and Belenky G 2012 Structural and luminescence properties of bulk InAsSb J. Vac. Sci. Technol. B 30 02B109

[97] Lin Y, Wang D, Donetsky D, Shterengas L, Kipshidze G, Belenky G, Svensson S P, Sarney W L and Hier H S 2013 Conduction- and valence-band energies in bulk InAsSb and type II InAsSb/InAs strained-layer superlattices J. Electron. Mater. 42 918–26

[98] Sarney W L and Svensson S P 2015 The flux dependent Sb-incorporation during molecular beam epitaxy of InAsSb J. Vac. Sci. Technol. B 33 060604

[99] Sarney W L, Svensson S P, Anderson E M, Lundquist A M, Pearson C and Millunchick J M 2014 The influence of growth temperature on Sb incorporation in InAsSb, and the temperature-dependent impact of Bi surfactants J. Cryst. Growth 406 8–11

[100] Sarney W L, Svensson S P, Novikov S V, Yu K M, Walukiewicz W and Foxon C T 2013 GaN\textsubscript{x}Sb\textsubscript{1-x} highly mismatched alloys grown by low temperature molecular beam epitaxy under Ga-rich conditions J. Cryst. Growth 383 95–9

[101] Shaw M et al 2014 Composition and optical properties of dilute-Sb GaN\textsubscript{x}Sb\textsubscript{1-x} alloys grown by MBE J. Phys. D: Appl. Phys. 47 465102

[102] Zhao C-Z, Li N-N, Wei T, Wang S-S and Lu K-Q 2014 Bandgap evolution of GaN\textsubscript{x}Sb\textsubscript{1-x} in the whole composition range Appl. Phys. A 115 927–30

[103] Cardona M, Christensen N E and Fasol G 1988 Relativistic band structure and spin–orbit splitting of zinc-blende-type semiconductors Phys. Rev. B 38 1806–27

[104] Peralta J E, Heyd J, Scuseria G E and Martin R L 2006 Spin–orbit splittings and energy band gaps calculated with the Heyd–Scuseria–Emzerhof screened hybrid functional Phys. Rev. B 74 073101

[105] Ghosh A K and Muruska H P 1977 Photoelectrolysis of water in sunlight with sensitized semiconductor electrodes J. Electrochem. Soc. 124 1516–22

[106] Akikusa J and Khan S 1997 Photoreponse and AC impedance characterization of n-TiO\textsubscript{2} films during hydrogen and oxygen evolution reactions in an electrochemical cell Int. J. Hydrogen Energy 22 875–82

[107] Khaselev O and Turner J 1998 A monolithic photovoltaic-photocell electrochemical device for hydrogen production via water splitting Science 280 425–7