

Determination of energy-band offsets between GaN and AlN using excitonic luminescence transition in AlGa_xN alloys

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We report the determination of the energy-band offsets between GaN and AlN using the linewidth (full width at half maximum) of an extremely sharp excitonic luminescence transition in Al_xGa_{1-x}N alloy with $x=0.18$ at 10 K. Our sample was grown on *C*-plane sapphire substrate by metal-organic chemical-vapor deposition at 1050 °C. The observed value of the excitonic linewidth of 17 meV is the smallest ever reported in literature. On subtracting a typical value of the excitonic linewidth in high-quality GaN, namely, 4.0 meV, we obtain a value of 13.0 meV, which we attribute to compositional disorder. This value is considerably smaller than that calculated using a delocalized exciton model [S. M. Lee and K. K. Bajaj, *J. Appl. Phys.* **73**, 1788 (1993)]. The excitons are known to be strongly localized by defects and/or the potential fluctuations in this alloy system. We have simulated this localization assuming that the hole, being much more massive than the electron, is completely immobile, i.e., the hole mass is treated as infinite. Assuming that the excitonic line broadening is caused entirely by the potential fluctuations experienced by the conduction electron, the value of the conduction-band offset between GaN and AlN is determined to be about 57% of the total-band-gap discontinuity. Using our model we have calculated the variation of the excitonic linewidth as a function of Al composition in our samples with higher Al content larger than 18% and have compared it with the experimental data. We also compare our value of the conduction-band offset with those recently proposed by several other groups using different techniques. © 2006 American Institute of Physics. [DOI: 10.1063/1.2158492]

INTRODUCTION

During the past few years, an enormous amount of effort of the semiconductor research community has been devoted to the study of the structural, electronic, and optical properties of III–V nitrides, their alloys, and their heterostructures. The motivation for this effort has been provided by applications in a variety of electronic and optoelectronic devices, such as high-power field-effect transistors, light-emitting diodes, and laser diodes operating in the visible to ultraviolet range of the electromagnetic spectrum. These devices have been fabricated using metal-organic chemical-vapor deposition (MOCVD) and molecular-beam epitaxy (MBE) growth techniques, and their performance characteristics have been studied in considerable detail. A number of these devices are now commercially available. In addition, a large number of experimental and theoretical investigations have been carried out to gain a better understanding of the fundamental properties of these materials. Although we have obtained a wealth of information during the past few years, a full understand-

ing of the various mechanisms involved in the operation of these devices and of the fundamental properties of these material systems is still lacking.

Several groups have investigated the optical properties of an AlGa_xN alloy system using a variety of characterization techniques such as absorption, photoluminescence excitation (PLE), cathodoluminescence, and photoluminescence (PL) spectroscopies during the past few years. In particular, the variation of the linewidth, defined as the full width at half maximum (σ) of an excitonic transition at low temperatures, as a function of alloy composition in the AlGa_xN alloy system has been studied by several groups^{1–4} using PL spectroscopy. It is well known that such studies can provide useful information about the quality of the alloys.⁵ In their pioneering work, Steude *et al.*¹ studied the optical properties of coherently strained Al_xGa_{1-x}N alloys ($0 \leq x \leq 0.22$) grown on (0001)-oriented sapphire by MOCVD using a variety of characterization techniques such as absorption, transmission, reflection, cathodoluminescence, and PL at low temperatures. In particular, they have measured the variation of σ as a function of Al concentration (x) at 4 K and found, as expected, that it increases as a function of x .

Following this work, Coli *et al.*^{2,3} have reported a study

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of the variation of σ as a function of the Al concentration in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys using PL spectroscopy at 10 K. In their studies the value of x was varied from 0 to 0.7. Their samples were grown by low-pressure MOCVD on sapphire (0001) substrates. They found that the values of σ increased as a function of x , as expected, but are somewhat smaller than those measured by Steude *et al.*¹ In addition, the measured values of σ are close to those calculated by Lee and Bajaj,⁶ who assumed completely random alloys and delocalized excitons. Both Steude *et al.*¹ and Coli *et al.*,^{2,3} however, did not provide any information on the structural characteristics of their samples. Pendlebury *et al.*⁴ have also measured the variation of σ with Al concentration in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ using PL spectroscopy at 4 K. Their samples were grown by MOCVD on C-plane sapphire substrates and the Al concentration was varied from 0 to 0.5. Their values of σ are larger than those reported by Coli *et al.*^{2,3} and are comparable to those measured by Steude *et al.*¹ They also performed PLE measurements and measured the variation of Stokes's shift, i.e., the difference in energy between the peak positions in PLE and PL and find that it increases as a function of Al concentration, thus suggesting a strong localization of excitons in their samples. Recently, Cho *et al.*⁷ have investigated the optical properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers using a variety of characterization techniques such as PL, PLE, and time-resolved PLE. Their samples were grown by MOCVD on (0001)-oriented sapphire substrates and the value of the Al concentration was varied from 0 to 0.6. They measured the variation of the energy of the PL peak position as a function of temperature and observed a well-known "S-shaped" behavior (decrease-increase-decrease). In addition, the excitonic linewidth follows an "inverted S-shaped" behavior (increase-decrease-increase) as a function of temperature. These are well known signatures of emission due to localized excitons. Cho *et al.*⁷ also did not provide any information concerning the structural properties of their epilayers.

In this paper, we present results of structural and low-temperature PL measurements on an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ sample with Al concentration $x=0.18$. We use this information to calculate the values of the band offsets between GaN and AlN using a model where the holes are completely localized. We have used this model to calculate the variation of the excitonic linewidth as a function of Al concentration in our samples which have Al content larger than 18% and have compared it with the experimental data.

EXPERIMENTAL DETAILS

Our sample with 18% Al concentration was grown by MOCVD and consisted of a thin (10 nm) GaN nucleation layer grown on C-plane sapphire at 550 °C, a 1 μm -thick GaN layer grown on the nucleation layer at 1050 °C, and a 2000-Å-thick $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer also grown at 1050 °C. No cap layer was used in this sample. Several analytical and structural measurements were performed using Rutherford backscattering (RBS), x-ray diffraction (XRD), and transmission electron microscopy (TEM). All PL measurements were performed at 10 K using a single-photon counting detection system together with a microchannel-plate photomultiplier

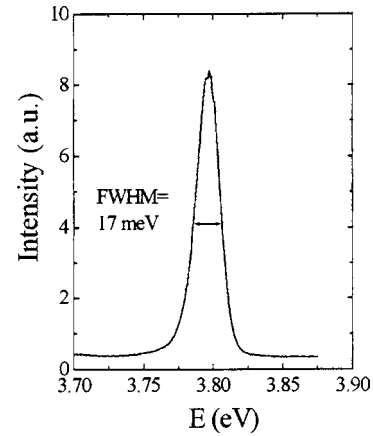


FIG. 1. PL spectrum of the $\text{Al}_{0.18}\text{Ga}_{0.82}\text{N}$ sample at 10 K.

tube, with the detection capability ranging from 185 to 800 nm and an overall resolution of 0.2 meV. The wavelength of the exciting radiation was 292 nm, and the PL signals were collected in reflecting mode at an incident angle of about 30°.

RESULTS AND DISCUSSION

The value of the Al concentration x in our sample was determined using Rutherford backscattering and x-ray-diffraction techniques. The latter measurement did not show any atomic ordering. This result was confirmed by examining the $[10\bar{1}0]$ zone-axis diffraction pattern (ZADP), where the $[0001]$ spot cannot arise due to double diffraction. Our TEM results indicate the presence of composition modulations along the $[0001]$ direction with a period of (1.1 ± 0.7) nm. In Fig. 1, we display the PL spectrum of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ for $x=0.18$ at 10 K.

During the past 20 years a number of groups⁵ have reported calculations of σ as a function of alloy composition in completely disordered semiconductor alloys. The results of these calculations, as well as their comparison with the experimental data in a number of III-V and II-VI alloys, have been reviewed recently.⁵ We will compare our measured value of σ with those calculated using the model of Lee and Bajaj.⁶ Using a quantum statistical approach, they obtained the following expression for σ :

$$\sigma = 0.41\sigma_0, \quad (1)$$

where

$$\sigma_0 = \frac{dE_g(x)}{dx} \left[\frac{8 \ln(2)x(1-x)V_c}{(4\pi/3)R_{\text{ex}}^3} \right]^{1/2}. \quad (2)$$

Here V_c is the volume of the primitive cell, $dE_g(x)/dx$ describes the variation of the energy of the band gap with alloy composition, $R_{\text{ex}} = \epsilon_0 \hbar^2 / \mu e^2$ is the Bohr radius, $\mu = (1/m_e + 1/m_h)^{-1}$ is the reduced mass, m_e and m_h are the electron and the hole mass, respectively, and ϵ_0 is the static dielectric constant. The values of m_e and ϵ_0 in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ used in our calculations are obtained from those of GaN and AlN (Ref. 2) by linear interpolation, namely,

$$\frac{m_e(x)}{m_0} = 0.22(1-x) + 0.33x \quad (3a)$$

and

$$\epsilon_0(x) = 9.7(1-x) + 6.3x. \quad (3b)$$

The values of the hole masses associated with the topmost valence bands in GaN and AlN are not reliably known. A number of attempts, however, to determine the value of the average hole mass of the topmost valence band in GaN have been made and are reviewed by Vurgaftman *et al.*⁸ and by Vurgaftman and Meyer.⁹ These values range from $0.3m_0$ to $2.2m_0$. They suggest a value of $1.0m_0$, based on the analysis of the available experimental data. There is practically no experimental information available about the hole mass of the topmost valence band of AlN. In addition, in AlN the crystal-field splitting is negative and thus the topmost valence band has a different symmetry than that in GaN. In view of these uncertainties, we use a value of $1.0m_0$ for the hole mass in our sample which has a low (18%) Al concentration. As the value of the reduced mass is primarily determined by the mass of lighter particle, namely, the electron, this assumption about the hole mass should not introduce any significant error. The volume is $V_c(x) = a_0^3(x)/\sqrt{2}$ where $a_0(x) = 3.16(1-x) + 3.112x$ Å is the lattice constant in the basal plane. The variation of the energy of the band gap $E_g(x)$ with the Al concentration is given as

$$E_g(x) = (1-x)E_g(\text{GaN}) + xE_g(\text{AlN}) - b(1-x)x, \quad (4)$$

where b is the bowing parameter and the values of the energy gaps at 10 K are $E_g(\text{GaN}) = 3.504$ eV and $E_g(\text{AlN}) = 6.285$ eV. The value of the bowing parameter b we used in our calculation is taken to be 0.6 eV.²

As shown in Fig. 1, the line shape of the excitonic transition is almost Gaussian with the value of σ of 17.0 meV. In order to consider only the effect of the compositional alloy disorder on σ we subtract from 17.0 meV the constant value of the inhomogeneous broadening $\sigma(\text{GaN})$, namely, 4.0 meV, a typical value found in many high-quality samples grown on sapphire substrates in our MOCVD reactor. The value of σ of 13.0 meV thus obtained is the lowest value of the excitonic linewidth ever reported in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ with $x = 0.18$. The value of σ calculated for this sample using the formalism of Lee and Bajaj⁶ is 16.5 meV, larger than 13.0 meV. The observed value of the linewidth in our sample is also considerably smaller than the best reported value in literature.² Any deviation from the perfectly random distribution of cations in our sample will only enhance the value of σ . It should be pointed out that the measured value of σ in our sample also contains contributions from other mechanisms such as those due to the presence of random electric fields which arise from the significant additional incorporation of ionized impurities due to the presence of Al.

As mentioned earlier, the emission in AlGaIn alloys at low temperatures is primarily due to highly localized excitons. Such is also the case in a number of other semiconductor alloys such as InGaP,¹⁰ GaAsN,¹¹ InGaAsN,¹² and GaAsSbN.¹³ The microscopic nature of excitonic localization by potential fluctuations and/or defects in alloys is not

known. To simulate the exciton localization, Zeman *et al.*¹⁰ assumed complete localization of the hole (namely, the hole mass was treated as infinite) in InGaP layers lattice matched to GaAs and explained their data on the variation of the diamagnetic shift of the localized excitons with magnetic field at low temperatures. A similar assumption has also been made recently by Senger *et al.*^{13,14} to explain their PL data on the variation of the diamagnetic shift of the localized excitons with magnetic field in GaAsSb/GaAs and GaAsSbN/GaAs quantum well structures, respectively, at low temperatures. It seems that the assumption that the holes are completely localized best describes the situation of excitons localized by potential fluctuations and/or defects in the above-mentioned alloys. We believe that such is also the case in AlGaIn alloys. If we assume that the holes due to their much larger masses are completely localized, namely, we treat the hole mass as infinite then only the electrons experience the fluctuating potential of the conduction band. The hole clearly does not experience any potential fluctuations. Substituting this value of the hole mass and replacing dE_g/dx by dE_c/dx we find that for $\sigma = 13.0$ meV, the value of the conduction-band discontinuity is such that $dE_c/dx = 0.57(dE_g/dx)$.

Recently, Foxon *et al.*¹⁵ have studied the behavior of the yellow and blue emissions in GaN and $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ epilayers. The yellow emission is assumed to be due to the recombination of a shallow donor with a deep acceptor due to Ga vacancy, and the blue emission is due to the recombination of a deep donor (presumably As antisite) with a shallow acceptor. Using the fact that the positions of deep levels in semiconductors against common vacuum reference level do not change with alloy composition, they determined the value of the conduction-band offset of 0.55 of the band-gap discontinuity. Helman *et al.*¹⁶ have studied the intersubband transitions due to conduction electrons in GaN/AlN quantum wells and have found that a conduction-band offset of 0.64 best explains their data. These two values of the conduction-band offsets are quite close to the value we calculated.

Recently, Vurgaftman and Meyer⁹ have briefly reviewed the results of various calculations of the energy-band offsets between GaN and AlN. Satta *et al.*¹⁷ have pointed out that the energy-band offsets for GaN/AlN and AlN/GaN are different. From a detailed treatment of the strain-induced asymmetry at the (0001) polar heterojunctions Bernardini and Fiorentini¹⁸ have obtained 2.55 eV (93%) and 1.9 eV (69%) for the values of the conduction-band offsets for AlN/GaN and GaN/AlN interfaces, respectively. Vurgaftman and Meyer⁹ have also briefly reviewed the results of various measurements of the conduction-band offsets between GaN and AlN and found that these values range from 95% to 50% of the total-band discontinuity. Such an enormous disparity among the values of the conduction-band offset is ascribed to differences in effects of strain inhomogeneity, defects, and stoichiometry among the samples used by various groups. The consensus is, however, that the value of the conduction-band offset is larger than the valence-band offset. Clearly more work needs to be done before one can have confidence in the values of the band offsets in this materials system. It should be pointed out that our value of the conduction-band

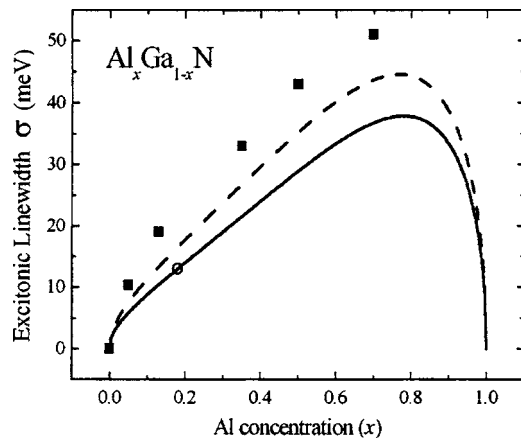


FIG. 2. Variation of the excitonic linewidth (σ) as a function of Al concentration (x). The solid and dashed curves are calculated using localized and free exciton models, respectively. The solid squares are the experimental data given in Ref. 3. The open circle denotes the value for the current sample.

offset is the upper limit as the value of σ (13.0 meV) may contain contributions from mechanisms other than compositional potential fluctuations.

As mentioned earlier, Coli *et al.*^{2,3} have measured the variation of σ as a function of Al concentrations in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ at 10 K. They found that their measured values of σ agree well with those calculated using the formalism of Lee and Bajaj⁶ that assumes completely random alloys and delocalized excitons. We have now strong evidence that excitons are localized in AlGaN alloys.⁷ We have therefore calculated the variation of σ as a function of Al concentration in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ using our model of the localized excitons as described above. We display our results (solid line) in Fig. 2 along with the results of a delocalized exciton model (dashed line) and the experimental data (solid squares) of Coli *et al.*³ We find that the values of σ obtained using the localized exciton model are considerably smaller than those calculated using the delocalized model and the experimental values. This is not surprising. It is well known that the growth of AlGaN alloys with higher values of Al concentration always leads to additional incorporation of impurities and defects, larger strain inhomogeneities, and possibly more clustering. The effects of these imperfections on the value of σ are not included in our calculations. The difference between our calculated values of σ using a localized exciton model and the experimental values is suggested to be due to the effects of these imperfections.

It should be pointed out that our approach to determine the values of the energy-band offsets does not involve the use of interfaces between GaN and AlN. Thus, our values are free from the uncertainties introduced by the presence of strain inhomogeneities, defects, and clustering at the interfaces. It is therefore more meaningful to compare our values of the energy-band offsets with those determined by Foxon *et al.*¹⁵ using radiative recombination between different centers in bulk AlGaN. Even though energy-band offsets are defined when two different semiconductors are brought in contact, the values determined by using bulk properties may

be closer to their intrinsic values. As mentioned earlier our sample exhibits composition modulation along the direction of growth and is of high structural quality. There may be similar composition modulations in the plane perpendicular to the growth direction as well. It is reasonable to assume that these composition modulations play an important role in completely localizing the hole at low temperatures.

CONCLUSION

We have measured the value of the linewidth of an excitonic transition in an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy with $x=0.18$ using PL spectroscopy at 10 K. Our sample was grown on (0001)-oriented sapphire substrate by MOCVD at 1050 °C. The value of the observed excitonic linewidth (13.0 meV) in this sample is the lowest ever reported in literature. It is significantly smaller than the value calculated using the delocalized exciton model of Lee and Bajaj and is the lowest value reported in the literature. The excitons are known to be strongly localized in this alloy system, and we have simulated this localization by assuming that the hole, being much more massive than the electron, is completely immobilized. In other words we treat its mass as infinite. Considering now that the excitonic linewidth is entirely caused by the potential fluctuations experienced by the electron, the value of the conduction-band discontinuity is determined to be 57% of the energy-band-gap difference. This value is similar to those recently found in GaN/AlN structures by some other groups.

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