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# $Al_xGa_{1-x}N$/GaN band offsets determined by deep-level emission

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We present studies of the compositional dependence of the optical properties of $Al_xGa_{1-x}N(0<x<0.22)$ alloys by modulation spectroscopy and photoluminescence. The yellow luminescence, which is well known in GaN and is generally assigned to shallow donor–deep acceptor pair recombination has also been observed in $Al_xGa_{1-x}N$. As aluminum concentration increases, the color of the band changes from yellow (2.2 eV) to blue (2.6 eV). The shift was less than that of the band gap. Together with previously published studies, it implies that the deep acceptor level is pinned to a common reference level to both materials, thus the deep level responsible for the yellow emission is used as a common reference level to determine the band alignment in $Al_xGa_{1-x}N$/GaN heterojunctions. Combining with the near-band-edge modulation spectra, the estimated ratio of conduction-to-valence band discontinuity is 65:35. Our results are close to the values obtained from PL measurements on $Al_{0.14}Ga_{0.86}N$/GaN quantum wells and those calculated by linear muffin-tin orbital method and linearized augmented plane wave method. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1383259]

## I. INTRODUCTION

GaN-based III–V nitride semiconductors are currently under intensive investigations for their scientific values and promising device applications. The wide band-gap nitrides have the capability of operating in the high-power, high-temperatures, and hostile environments due to their superior thermal and structural stability. High quality $Al_xGa_{1-x}N$ alloys are of special interest because they cover a wide range of spectral response ranging from ~3.4 eV (GaN) to ~6.2 eV (AlN), resulting to an energy variation of 2.8 eV. Thus this continuous alloy system can be fabricated to operate between visible and ultraviolet spectral ranges by simply modifying the aluminum composition.

Much effort had been made to study the fundamental band gaps,[1] bowing parameters,[2–4] and many other electro-optical properties of $Al_xGa_{1-x}N$.[5] Nevertheless, due to the technical difficulty, there are rare studies focusing on the band-gap offsets of this material system. The previously reported values of the band offset in $Al_xGa_{1-x}N$/GaN heterojunctions reveal large discrepancies.[6–12] The origin of the controversy can be attributed to the indirect nature of measurements and the detailed condition of interface preparation. However, the band-offset ratio is of tremendous significance for elucidating the carrier confinement mechanisms and for designing and optimizing optoelectronic devices based on $Al_xGa_{1-x}N$ alloys.

In this article, we report a study on the $Al_xGa_{1-x}N$/GaN band-gap offsets, which is based on the variations of the band gaps and yellow luminescence with alloy compositions. The yellow luminescence (YL) is a broad luminescence band and a universal feature in *n*-type GaN and GaN-based III–V nitride semiconductors, independently on the epitaxial techniques and sample substrates. Since it reduces the efficiency of optoelectronic devices made out of nitride materials, the mechanism responsible for YL has drawn much attention over recent years, and there have been many theoretical and experimental investigations aiming at clarifying its origin.[13–22] Neugebauer's theoretical study[13] on defect formation energies and the strong electron–phonon coupling of the YB[14] suggest that a deep acceptor state is involved in the recombination. Besides, investigations of detailed photoluminescence and optically detected magnetic resonance experiments revealed that the donor to deep defect transition took place in the recombination.[15] Furthermore it was found that the pressure dependence of the YL band is the same as that of the GaN band gap.[16] Thus it is generally accepted that the YL is due to shallow donor–deep acceptor pair recombination and is also responsible for the inherent *n*-type conductivity and the persistent photoconductivity effect (PPC) in GaN epilayers.[14] The microscopic origin of the deep level is still not clear. The first principle calculation made by Perlin *et al.*[17] and Neugebauer *et al.*[13] gave contradictory results. The former favored nitrogen vacancies and the latter proposed Ga vacancies, and both of them could have found their own experimental support.[14,18,19] At this stage, we cannot fully exclude the possibility that the microscopic nature of the deep acceptor may be different in samples grown by different methods and under different experimental conditions. In either case, it is reasonable to expect that the corresponding PL band in $Al_xGa_{1-x}N$ shares the same physical origin with that of GaN since shallow donors, nitrogen vacancies, and Ga vacancies also exist in $Al_xGa_{1-x}N$. Indeed such band also exists in $In_xGa_{1-x}N$ alloy systems.[23] Up to date, there are relatively fewer studies on the corresponding YL bands in nitride alloy systems. Thus we measured a series of $Al_xGa_{1-x}N$ samples grown on GaN with Al concen-

 

tration varies up to 22%. Aided by the results of the near-band-edge modulation spectra, we are able to determine the band offsets between GaN and $Al_xGa_{1-x}N$. About 65% and 35% of the band-gap difference is estimated to be accommodated in the conduction and the valence band, respectively. The results are close to the values obtained by PL measurements for $GaN/Al_{0.14}Ga_{0.86}N$ quantum wells[10] and those calculated by the linear muffin-tin orbital method[12] and linearized augmented plane wave method.[9]

## II. EXPERIMENT

The $Al_xGa_{1-x}N$ alloy samples were grown by metalorganic chemical vapor deposition (MOCVD) on (0001) sapphire substrates. There were thin low-temperature-grown GaN buffer layers first deposited on the substrates before the growth of 1.5-$\mu$m-thick epilayers. The aluminum mole fraction was controlled by the flow rates of trimethylgallium (TMG) and trimethyaluminum (TMAI). More description of the samples can be found elsewhere.[24] The photoluminescence (PL) measurement is an excellent tool to study defect-related physics in semiconductors. The PL measurements use a He–Cd laser working at 325 nm as the excitation source. The PL system has been described in detail in a previous report.[25] One of the characteristics of $Al_xGa_{1-x}N$ is its long-disputed band-gap bowing effect.[2–4] It is of crucial importance to accurately determine the band-gap transitions, thus we study the band-gap variation with aluminum concentration by means of modulation spectroscopy. Modulation spectroscopy has been proved to be a powerful technique for studying many physical properties of bulk/thin film semiconductors,[26] semiconductor microstructures,[27] surface/interface,[28] and actual device configurations.[29,30] The modulated signals possess derivative nature and thus are very appropriate for accurate determination of physical parameters. Contactless electroreflectance (CER), photoreflectance (PR), and piezoreflectance (PzR) are among the most widely used modulation techniques. The CER approach has a great advantage to study the wide band-gap nitride samples and does not require an ultraviolet laser as the pumping source and also avoids the PL background generated by the excitation source. Furthermore, it is a nondestructive measurement since there is not contact with the sample. Thus we adopt the CER to study the band-gap transitions. In our measurements, we use a conductive metal net that serves as an electrode. We do not use quartz with a transparent conductive coating indium tin oxide (ITO) on the surface, which has been commonly used because of the poor transmission property of ITO above photon energy exceeding 3.5 eV. There is a second electrode made up of a metal strip which is separated from the first electrode by a very thin layer of vacuum. The sample is placed between these two capacitor-like plates. Thus there is no direct contact with the front surface of the sample. An ac modulating voltage of 900 V peak to peak at 200 Hz was applied between the electrodes. A xenon lamp filtered by a monochromator provided the probe beam. The reflected light is collected and detected by a photomultiplier tube (PMT). The signal is finally recorded by a dual phase SR530 lock-in amplifier. An electro servo maintains the dc power of the PMT for protection. An Edward Cryodrive 1–5 closed-cycle refrigerator equipped with an Oxford ITC-4 thermocontroller was used for low-temperature measurements.

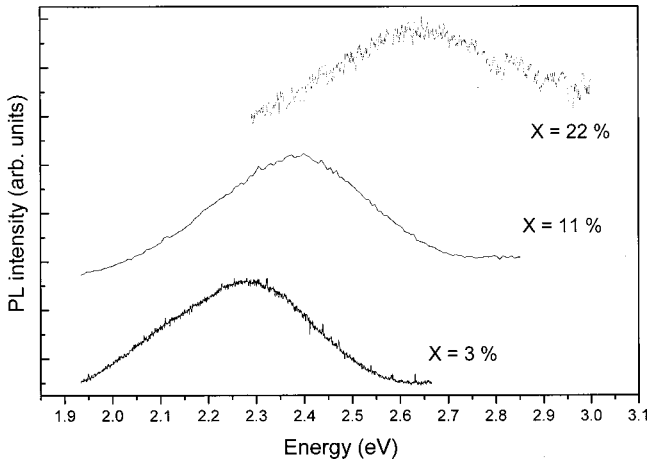


FIG. 1. Shift of the yellow band in $Al_xGa_{1-x}N$ alloys towards the blue with increasing Al mole fraction. The PL spectra were taken at temperature 12 K.

## III. RESULTS AND DISCUSSION

Figure 1 displays the PL spectra of the $Al_xGa_{1-x}N$ below the near-band-edge region at temperature 12 K. The broad and deep bands are considered to be the $Al_xGa_{1-x}N$ analog of the yellow band peaked around 2.2 eV in GaN. The YL is a common feature of *n*-type III nitrides and its physical mechanism is also believed to be the cause of *n*-type conductivity and the PPC effect.[31] So far, the general consensus is that the YL arises from the recombination involving a shallow donor and a deep acceptor. The deep acceptor could be a Ga or a nitrogen vacancy but it is irrelevant to our purpose here. As can be seen from Fig. 1, the peak energies of the bands are found to shift gradually to blue with increasing aluminum composition. Yet, in this report the bands are still referred to as the yellow band (YB). From Fig. 1, we obtain the change of the YB peak between GaN and $Al_xGa_{1-x}N$ follows

$$\Delta E_{\mathrm{YB}}(x) = 0.6x + 5.05x^2 \pm 0.03x. \tag{1}$$

It is important to assess the relative change of the band gap and the YL in the $Al_xGa_{1-x}N$ alloys. Yet there were contradictory studies on the band-gap bowing of $Al_xGa_{1-x}N$.[2–4] To enhance the reliability of the data, we utilized modulation measurement to study the band-gap variations. The CER spectra at temperature 12 K in the region of the direct band gap from the $Al_xGa_{1-x}N$ samples are displayed by the solid lines in Fig. 2. The energies of the corresponding transitions can be determined in the context of Aspnes' third derivative line shape method.[26] The functional form can be expressed in the following form:[32,33]

$$\Delta R/R = \mathrm{Re}\left[\sum_{j=1}^{n} C_j e^{i\Theta j}(h\upsilon - E_j + i\Gamma_j)^{-m}\right], \tag{2}$$

where $n$ is the total number of signal features, and $m$ has the values 5/2 for 3D critical points and 2 for excitons. $C_j$ and

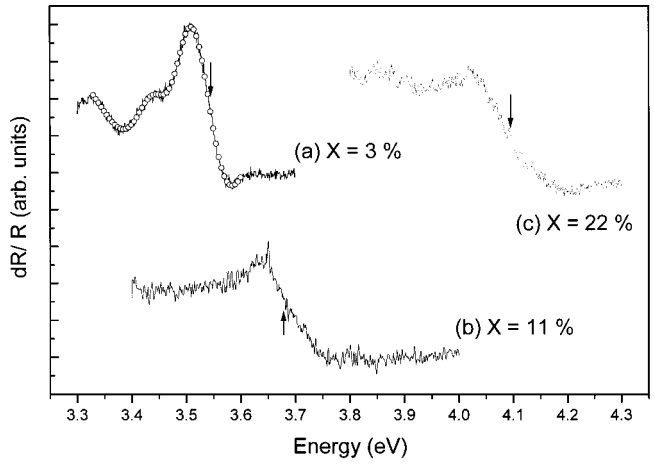


FIG. 2. CER spectra of (a) $X=3\%$, (b) $X=11\%$; (c) $X=22\%$ of $Al_XGa_{1-x}N$ alloys at temperature 12 K. The solid lines are the experimental results, and the dotted line is the fitting to Eq. (2).

$\Theta_j$ are the amplitude and the phase of the $j$th resonance, respectively. $E_j$ is the transition energy and $\Gamma_j$ stands for the broadening parameter of the modulated signal. This is demonstrated in Fig. 2(a). The open circles on the CER spectrum from $Al_{0.03}Ga_{0.97}N$ epilayer are the least-square fits to Eq. (2). Because the aluminum concentration is low, the band gap of $Al_{0.03}Ga_{0.97}N$ epilayer shifts only a little. Thus in interpretating the spectrum, we must incorporate the contribution from the GaN buffer layer. From previously published CER study of GaN,[33,34] we know that the fundamental absorption edge in wurtize GaN has three excitonic transitions related to the $\Gamma_9^V-\Gamma_7^C,\Gamma_7^V$ (upper-band)-$\Gamma_7^C$ and $\Gamma_7^V$ (lower band)-$\Gamma_7^C$. Two of them are too close to be resolved, and the other is separated from them by about 65 meV at 300 K. Here, we adopt two features to characterize the contribution from GaN that is separated by about 50 meV, which is in reasonable agreement with that reported by other group.[34] As shown in Figs. 2(a)–2(c), the transition energies shift from 3.54 eV for $x=3\%$ to 4.09 eV for $x=22\%$, which are indicated by the arrows.

From Fig. 2, we obtain that the change in band gap between GaN and $Al_xGa_{1-x}N$ is given by

$$\Delta E_G(x)=1.05x+7.62x^2\pm 0.02x. \tag{3}$$

This result is consistent with the previous report.[24,34] Obviously, the slope of $\Delta E_G(x)$ is steeper than that of $\Delta E_{\mathrm{YB}}(x)$. Since the shallow donor level is expected to be pinned to the conduction band edge, this result shows that the deep acceptor level is not pinned to the valence band and strongly supports the fact that the deep acceptor level is pinned to a common reference level to both materials. Recently, Manz *et al.*[23] studied the YL bands of $In_xGa_{1-x}N$ and had found the same conclusion.

This is shown in Fig. 3. Under this configuration, the peak shift of the YB with $x$ equals the band offset $\Delta E_C(x)$. The band-gap offset thus can be evaluated by

$$\Delta E_G(x)=\Delta E_C(x)+\Delta E_V(x)=\Delta E_{\mathrm{YB}}(x)+\Delta E_V(x), \tag{4}$$

and

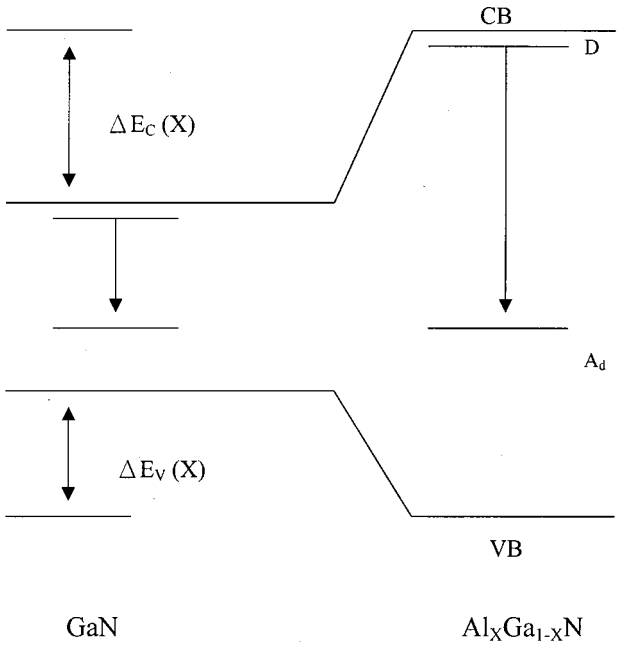


FIG. 3. Schematic diagram shows the band configuration of the yellow luminescence in AlGaN. The deep acceptor level $A_d$ is assumed to be held fixed to a common level.

$$\Delta E_V(x)=\Delta E_G(x)-\Delta E_{\mathrm{YB}}(x). \tag{5}$$

The situation resembles the model proposed by Langer and Heinrich,[35] in which the deep level acts as a common reference level to determine the band alignment and similar models were applied to the cases of DX centers in III–V phosphides[36] and YL bands in $In_xGa_{1-x}N$/GaN systems.[23] Now we are in the position to derive the band discontinuities. The band offsets $\Delta E_C(x)$ and $\Delta E_V(x)$ for the $Al_xGa_{1-x}N$ on GaN are given by

$$\Delta E_C(x)=\Delta E_{\mathrm{YB}}(x)=0.6X+5.05X^2\pm 0.03X, \tag{6}$$

and

$$\Delta E_V(x)=\Delta E_G(x)-\Delta E_C(x)=0.45X+2.57X^2\pm 0.05X. \tag{7}$$

From these results, we obtained that the ratio of conduction-to-valence band discontinuity is about 65:35.

It is worth noting that there exist several early attempts at determining AlGaN/GaN band discontinuity by different approaches. A ratio of 50:50 was reported very early by an analysis of cathodoluminescence from AlN/GaN (0001) superlattices.[6] The layer thicknesses were generally thinner then 10 nm and the structures were thus strained but the fitting of the authors was somewhat problematic because of their neglect of the influence of the strain that has been known nowadays to have a considerable influence on the band structure. Besides they treated the band offset as a single parameter in the fitting but neglect the fact that in such a highly strained system, band offset will generally depend on the layer thickness. Previous x-ray photoelectron spectroscopy (XPS) attempts did not yield consistent and satisfying results. The ratio reported by Martin *et al.*[7] was 75:25 while by Waldrop *et al.*[8] was 52:48 for the strain-free layers. The huge discrepancy of 0.56 eV of the valence band dis-

continuity by the same approach may come from the uncertainty in determining $E_{\mathrm{Ga}\ 3d}^{\mathrm{GaN}}-E_{v}^{\mathrm{GaN}}$ in their fitting. The actual reason for this is still in debate.[9] The conduction to valence band discontinuity ratios obtained by PL measurements for $GaN/Al_{0.14}Ga_{0.86}N$ quantum wells is 60:40.[10] By using transition metal impurity level as a common reference level, the obtained ratio is 82:18,[11] but this result is less comparable with almost all reported values. On the theoretical side, Albanesi *et al.*[12] calculated the band offset using linear muffin-tin orbital (LMTO) method to be 70:30. Based on linearized augmented plane wave (LAPW) method, Wei *et al.*[9] calculated the ratio to be 71:29. Our results are thus close to the value obtained by using PL measurements and to the theoretical calculations by LMTO and LAPW methods. It should be noted that apart from the inconsistent XPS measurements our experimental result is the closest to the two theoretical results.[9,12]

## IV. CONCLUSION

In summary, we have studied near-band-edge transition and the yellow luminescence of $Al_xGa_{1-x}N$ epilayers by the CER and the PL measurements at 12 K. The CER measurements are more appropriate and straightforward than photoluminescence and transmission measurements to determine the band gap of alloys. On the other hand, the PL measurements may be more practical to study the deep and broad yellow band recombination because the transition occurs over a large energy range resulting in complicated modulation spectra. We have demonstrated that by comparing the CER and the PL spectra, the band offsets for $Al_xGa_{1-x}N(x<0.22)$ grown on GaN may be estimated. We obtained the average values of about 65% and 35% of the band-gap difference is accommodated in the conduction band and the valence band, respectively. The obtained result is close to the values measured by PL measurement and calculated by LMTO and LAPW methods. We compared our results with previously published ones and agreements and discrepancies are discussed. The present result is the closest to the theoretical predictions except the inconsistent XPS data.

## ACKNOWLEDGMENT

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