Optical anisotropy in [0001]-oriented Al$_x$Ga$_{1-x}$N/AlN quantum wells ($x > 0.69$)

R. G. Banal, M. Funato,* and Y. Kawakami

Department of Electronic Science and Engineering, Kyoto University, Kyoto 615-8510, Japan

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The optical polarization in [0001]-oriented Al$_x$Ga$_{1-x}$N/AlN multiple quantum wells (QWs) in the deep-ultraviolet region ($x > 0.69$) was studied. Photoluminescence spectroscopy performed at 8.5 K revealed that the predominant polarization direction in QWs with a well width of $\sim 1.5$ nm switched from GaN-like $E \perp [0001]$ to AlN-like $E \parallel [0001]$ at an Al composition $x$ of $\sim 0.83$, where $E$ is the electric field vector of emitted light. This Al composition is much higher than the previously reported critical compositions for polarization switching phenomena. Furthermore, decreasing the well width from more than 10 to 1.5 nm promoted $E \parallel [0001]$ polarization. These results can be explained by the effect of strain and quantum confinement on the valence-band structures.

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Realizing deep-ultraviolet (DUV) semiconductor-based emitters will provide compact, nontoxic, and high-efficiency light sources for various applications, ranging from biological agent detection to next-generation data storage. AlN, though such devices primarily require Al$_x$Ga$_{1-x}$N-based quantum wells (QWs) with a high Al content, their fundamental optical properties remain controversial. For example, it has experimentally been demonstrated that surface emissions from [0001]-oriented Al$_{0.66}$Ga$_{0.34}$N/Al$_{0.75}$Ga$_{0.25}$N QWs (Refs. 3 and 4) and Al$_{0.11}$In$_{0.03}$Ga$_{0.86}$N/Al$_{0.2}$In$_{0.07}$Ga$_{0.73}$N QWs (Ref. 6) are quite weak because of the predominant optical polarization along the [0001] $c$ direction. In contrast, a theoretical study has predicted that valence-band engineering through the well width and/or in-plane compressive strain in $c$-oriented Al$_x$Ga$_{1-x}$N QWs may remarkably enhance the emission polarized perpendicular to the $c$ axis, which suggests that surface emitters can be fabricated by better-established growth on the $c$ plane.

Those discussions originate from the valence-band structure in AlN strikingly different from that in conventional GaN. In wurtzite AlN or GaN, the degeneracy of the $p$-like states at the $\Gamma$ point is lifted by both crystal-field splitting and spin-orbit splitting, resulting in three valence bands at the Brillouin zone center. Interestingly, AlN has a negative crystal-field splitting energy ($\Delta_{c,-} = -217$ meV), whereas GaN has a positive $\Delta_{c,+}$ of $11$ meV.13 These splittings lead to valence-band arrangements in the order of $\Gamma_7$, $\Gamma_6$, and $\Gamma_5$ from the top for AlN, and in the order of $\Gamma_9$, $\Gamma_7$, and $\Gamma_5$ for GaN. The topmost $\Gamma_5$ in AlN is the crystal-field split-off hole (CH) band governed by $p_z$-like state, and $\Gamma_5$ in GaN is the heavy hole (HH) band governed by $p_x$-like and $p_y$-like states. Here, orthogonal coordinates $x$ and $y$ are in the $c$ plane, while $z || c$. Therefore, the emission from high (low) Al-content Al$_x$Ga$_{1-x}$N is expected to be polarized along (perpendicular to) the $c$ axis. In fact, such a characteristic has been reported for Al$_x$Ga$_{1-x}$N thick layers; the polarization switches from $E \perp c$ to $E \parallel c$ at $x = 0.25$ as the Al composition increases, where $E$ is the electric field vector of emitted light.14

This result implies weak surface emission from $c$-oriented, Al-rich Al$_x$Ga$_{1-x}$N QWs, and there are several supporting experimental results as mentioned above.3,4,6 Then, one may feel that a promising way for strong surface emission from Al-rich Al$_x$Ga$_{1-x}$N QWs is the growth on non-$c$ planes such as (1100) and (1120), but the growth technology currently remains in its infancy. Herein, the optical polarization anisotropy in Al-rich Al$_x$Ga$_{1-x}$N/AlN ($x > 0.69$) multiple QWs (MQWs) grown on sapphire (0001) substrates is systematically investigated using photoluminescence (PL) spectroscopy. We demonstrate that the $E \parallel c$ polarization of the emission can be achieved up to $x \sim 0.80$, which is even higher than the theoretical prediction.7 We interpret this observation using a simple model.

After growing $\sim 600$-nm-thick high-quality AlN by modified migration-enhanced epitaxy (MEE) (Ref. 15) on sapphire (0001) substrates at $1200$ °C, Al$_x$Ga$_{1-x}$N/AlN MQWs were also fabricated by modified MEE and this time, additional trimethylgallium (TMG) was supplied together with trimethylaluminum (TMA). In addition to controlling the thickness of the barrier and well layers on a per-growth-cycle basis (AlN barriers: 21 cycles and Al$_x$Ga$_{1-x}$N wells: 1–12 cycles), this method enabled an atomically flat surface to be maintained. The AlN barrier was $13.5$ nm thick, and the number of QWs was ten. To increase Ga incorporation into the QWs, the growth temperature was decreased in the range of $1200$ and $1060$ °C, while maintaining the flow rates of TMG and TMA.

The QW parameters, such as the Al composition, well widths, and barrier widths, were derived from the satellite peaks observed in the X-ray diffraction (XRD) measurements. Reciprocal space mapping by XRD was also performed to confirm the coherent growth of the Al$_x$Ga$_{1-x}$N/AlN QWs with respect to AlN underlying layers. The optical measurements were carried out at 8.5 K. The excitation source was a pulsed ArF excimer laser ($\lambda = 193$ nm, $\tau = 4$ ns, $25$ Hz, and $10$ MW/cm$^2$), which was incident at the surface normal of the samples. PL was collected from the sample edge by one collimating lens and another lens focusing upon the entrance of a $30$ cm monochromator (resolution: $0.1$ nm). This configuration allowed the polarization PL properties of $E \parallel c$ and $E \perp c$ to be directly assessed using a polarizer inserted between the lenses. The detection was ensured by a liquid-N$_2$-cooled CCD camera.

To discuss the Al composition dependence of the polarization properties, Fig. 1 shows the PL spectra of a series of
that the topmost valence bands of the MQWs change from the predominant polarization switched from QWs, as the Al composition decreased from 0.91 to 0.69, respectively, suggesting a strong surface emission even with compositions: 0.91, 0.82, and 0.69.

This quantity signifies a strong polarization along the c direction, which is consistent with earlier reports and verifies the current experimental setup. For Al$_{1-x}$Ga$_x$N/AIN QWs, as the Al composition decreased from 0.91 to 0.69, the predominant polarization switched from $E_{\|c}$ to $E_{\bot c}$ at $x \sim 0.82$. The polarization degrees ($\rho$) were evaluated to be $0.24$, $0.03$, and $0.07$ for $x=0.91$, $0.82$, and $0.69$, respectively, suggesting a strong surface emission even with $x=0.82$. In fact, we performed surface emission measurements at 8.5 K for the same series of the QWs and found that the PL intensities of the QWs with $x=0.82$ and 0.69 increased by factors of 8 and 15, respectively, compared to that of the QW with $x=0.91$.

The observed polarization switching phenomena suggest that the topmost valence bands of the MQWs change from $\Gamma_7$ similar to that in AlN to $\Gamma_0$ like that in GaN at $x \sim 0.82$. This Al composition of 0.82 is much higher compared to previous reports, and the mechanism is discussed below. Here, it should be noted that, because the PL measurements were performed at 8.5 K, majority of photogenerated holes populated the topmost valence band, which dominated the polarization properties observed in this study. The second valence band may influence the PL only when it closely approaches the topmost band. A small peak shift of $\sim 15$ meV detectable for the QW with $x=0.82$ (see Fig. 1) may be due to this effect.

Then the well width dependence of the polarization properties was assessed using Al$_{0.82}$Ga$_{0.18}$N/AIN MQWs, and the results are shown in Fig. 2. The polarization degrees gradually increased as the QW thickness decreased and were $0.17$, $-0.12$, and 0.03 for QWs with well thicknesses of 13, 8.0, and 1.3 nm, respectively. The emissions from QWs thicker than 8.0 nm showed $E_{\|c}$ polarization, whereas that of the 1.3-nm-thick QW showed $E_{\bot c}$ polarization, indicating that quantum confinement affects the valence-band order and, consequently, promotes $E_{\bot c}$ polarization.

In order to comprehensively understand the polarization properties of Al$_{1-x}$Ga$_x$N/AIN QWs, QWs were then fabricated with various Al compositions and well widths. Figure 3 summarizes the results. As expected, a higher (lower) Al composition resulted in the $E_{\|c}$ ($E_{\bot c}$) polarization. For QWs thinner than $\sim 3$ nm, the critical Al composition for the polarization switch was $\sim 0.80$ and was independent of the well width. On the other hand, for QWs thinner than $\sim 3$ nm, the critical composition shifted toward a higher Al composition, which can be attributed to the quantum confinement effect.

The observed results are closely related to the valence-

FIG. 1. (Color online) Polarization PL spectra of c-oriented AlN (inset) and Al$_x$Ga$_{1-x}$N ($\sim 1.5$ nm)/AIN MQWs with different Al compositions: 0.91, 0.82, and 0.69.

FIG. 2. (Color online) Polarization PL spectra of c-oriented Al$_{0.82}$Ga$_{0.18}$N/AIN MQWs with different well widths: 1.3, 8.0, and 1.3 nm.

FIG. 3. (Color online) Plot of polarization direction of the emission from Al$_x$Ga$_{1-x}$N/AIN QWs as functions of Al composition and well width.
band order as the nature of each band determines the polarization property. Therefore, the valence-band order must be discussed. Figure 4 schematically depicts the band structures for (a) unstrained AlxGa1−xN, (b) strained AlxGa1−xN on unstrained AlN, and (c) AlxGa1−xN/AlN QWs near the Γ point. CB and LH denote the conduction band and light hole band, respectively.

\[ E(\Gamma_7) - E(\Gamma_9) = -\frac{\Delta'}{2} + \left[ \frac{(\Delta' + \delta)^2}{2} - \frac{2}{3} \Delta' \delta \right], \]

where \( \Delta' = \Delta_{so} + [D_3-D_1(C_{33}/C_{11})]e_{z} \), \( \delta \) is the spin-orbit splitting energy, \( D_1 \) is the deformation potential, \( C_i \) is the elastic stiffness constant, and \( e_z \) is the strain tensor element along the c direction.\(^\text{16}\) For AlN, \( E(\Gamma_7) - E(\Gamma_9) > 0 \) is satisfied due to the negative \( \Delta_{so} \), and the resultant polarization is \( E||c \), whereas for GaN, \( E(\Gamma_7) - E(\Gamma_9) < 0 \) and \( E \perp c \). For AlxGa1−xN, \( E(\Gamma_7) - E(\Gamma_9) \) can be zero at a certain \( x \) (the critical Al composition), where the polarization switch occurs. As seen from Eq. (1), the condition of \( E(\Gamma_7) - E(\Gamma_9) = 0 \) corresponds to \( \Delta' = 0 \), and thus, the critical Al composition can be extracted assuming a linear relationship between the AlN and GaN parameters. Theoretical calculations\(^\text{9,10}\) and a recent experiment\(^\text{11}\) indicate that \( \Delta_{so} \) in AlN is around \( \pm 220 \) meV. Therefore, \( -0.217 \) meV (Ref. 9) was used here, while the remaining parameters were from Ref. 13.

In unstrained AlxGa1−xN, the critical Al composition was estimated to be 0.044 from the condition of \( \Delta' = 0 \). For strained AlxGa1−xN on unstrained AlN, the condition of \( \Delta' = 0 \) provided \( x = 0.60 \). This increase in the critical Al composition can be qualitatively understood by considering the effect of strain on each valence band. The in-plane compressive strain in AlxGa1−xN pushes the \( |X \pm iY\rangle \)-related bands (Γ9 and lower Γ7) upward, but it is tensile strain along the growth direction which pushes the \( |Z\rangle \)-related band (upper Γ7) downward, as schematically illustrated in Figs. 4(a) and 4(b). Consequently, the energy separation between the topmost Γ7 and Γ9 decreased, and then a larger Al composition was necessary for the polarization switch. It should be noted that 1-μm-thick AlxGa1−xN on sapphire (0001) experimentally showed the polarization switch at \( x = 0.25 \),\(^\text{14}\) implying the presence of residual compressive strain.

An additional factor that can affect the valence-band structure is quantum confinement. Because the hole effective mass at the topmost Γ7 in AlN is much lighter than that at Γ9 (0.26m0 vs. 3.57m0),\(^\text{13}\) the energy of this Γ7 is drastically lowered by quantum confinement. As drawn in Figs. 4(b) and 4(c), stronger confinement eventually causes the crossover between Γ7 and Γ9. In order to quantify the quantum confinement effect on the valence-band order, we numerically calculated the quantized level for the upper Γ7 and Γ9 in AlxGa1−xN/AlN single QWs using a simple one-dimensional Schrödinger equation. The strain-dependent effective mass was assumed at Γ7.\(^\text{16}\) Figure 5 is the contour plot of the calculated energy difference of \( E(\Gamma_7^QW) - E(\Gamma_9^QW) \) in the unit of electron volts. Red/gray dotted thick line is the \( E(\Gamma_7^QW) - E(\Gamma_9^QW) = 0 \) line for flat-band QWs without a polarization field, while (black) thick and thin lines are for QWs with polarization fields. The assumed spontaneous polarization was \( -0.040 \) C/m².

![Figure 4](image-url)  
**FIG. 4.** (Color online) Schematic of band structures for (a) unstrained AlxGa1−xN, (b) strained AlxGa1−xN on unstrained AlN, and (c) AlxGa1−xN/AlN QWs near the Γ point. CB and LH denote the conduction band and light hole band, respectively.

![Figure 5](image-url)  
**FIG. 5.** (Color online) Contour plot of the calculated energy difference of \( E(\Gamma_7^QW) - E(\Gamma_9^QW) \) in the unit of electron volts. Red/gray dotted thick line is the \( E(\Gamma_7^QW) - E(\Gamma_9^QW) = 0 \) line for flat-band QWs without a polarization field, while (black) thick and thin lines are for QWs with polarization fields. The assumed spontaneous polarization was \( -0.040 \) C/m².
ment and should promote the mechanism shown in Fig. 4(c). Because the reported spontaneous polarization in AlN spans a fairly broad range from $-0.12$ to $-0.036\ \text{C/m}^2$, we treated this as a fitting parameter. Consequently, a value of $-0.040\ \text{C/m}^2$ provided a good agreement between the experiment (Fig. 3) and calculation as indicated by (black) thick and thin lines in Fig. 5. Further decreasing the spontaneous polarization to the well-accepted $-0.090\ \text{C/m}^2$ (Ref. 13) pushed the zero line up to $x \sim 0.85$. Therefore, as has occasionally been reported, the spontaneous polarization in AlN is considered to be approximately $-0.040\ \text{C/m}^2$, with which the internal electric field in $\text{Al}_{0.80}\text{Ga}_{0.20}\text{N}/\text{AlN}$ QWs, for example, was estimated to be $-1.1\ \text{MV/cm}$, taking both spontaneous and piezoelectric polarizations into account. The internal electric field shifted the critical Al composition that satisfies $E(\Gamma_{7}^{\text{sym}}) - E(\Gamma_{9}^{\text{sym}}) = 0$ toward higher Al compositions, and the shift was more remarkable for thicker QWs. These findings can be interpreted as follows. For thin wells, the well width dominates the quantum confinement effect, and the internal electric field barely affects the critical Al composition. For thick wells, quantum confinement due to the well width becomes weak, whereas that due to the triangular potential well formed by the internal electric field remains. Thus, the critical Al composition for thinner QWs is determined by the internal electric field, independent of the well width.

Finally, we examined the reported optical polarization properties in $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$-based QWs. The $c$-oriented $\text{Al}_{0.66}\text{Ga}_{0.34}\text{N}/\text{Al}_{0.76}\text{Ga}_{0.24}\text{N}$ QWs on $\text{Al}_{0.80}\text{Ga}_{0.20}\text{N}$ (0.6 $\mu$m)/AlN (1.5 $\mu$m) templates showed $E || c$ polarization.\textsuperscript{3,4} The well thickness was 5 or 10 nm. Although at first glance, the result seems to disagree with Fig. 5, it can be explained by (i) weak quantum confinement due to the relatively thick well width, (ii) weak quantum confinement due to the $\text{Al}_{0.76}\text{Ga}_{0.24}\text{N}$ barrier layer, and (iii) the weak internal electric field in the well due to the compensation with that in the $\text{Al}_{0.76}\text{Ga}_{0.24}\text{N}$ barrier layer; all of which may contribute to the promotion of $E || c$ polarization. Although the strain state seems complicated due to the presence of the 0.6-$\mu$m-thick $\text{Al}_{0.86}\text{Ga}_{0.14}\text{N}$ layer, our simple model predicted $E(\Gamma_{7}^{\text{sym}}) - E(\Gamma_{9}^{\text{sym}}) \sim 0$ for an $\text{Al}_{0.66}\text{Ga}_{0.34}\text{N}/\text{Al}_{0.76}\text{Ga}_{0.24}\text{N}$ QW coherently grown on AlN. This is the most extreme condition, and if the underlying $\text{Al}_{0.86}\text{Ga}_{0.14}\text{N}$ layer is (partially) relaxed, $E || c$ polarization is promoted; thus, there is a tolerable agreement between our model and the reported polarization.

In summary, we investigated the polarization properties of $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$/AlN QWs. The emission with the polarization along $E \perp c$ is observed up to $x \sim 0.82$, particularly for thinner QWs. This large Al composition for the polarization switch between $E \perp c$ and $E || c$ is attributed to the in-plane compressive strain and the quantum confinement due to narrow wells and/or internal electric fields. The present results indicate that the appropriately designed $c$-oriented $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ QWs can produce a surface emission even in the DUV spectral range, and may be a key in reconciling good crystalline qualities and emission properties.

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