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Growth and optical properties of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys

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In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys with different In and Al compositions were grown by metalorganic chemical vapor deposition. Optical properties of these quaternary alloys were studied by picosecond time-resolved photoluminescence. It was observed that the dominant optical transition at low temperatures in In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys was due to localized exciton recombinations, while the localization effects in In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys were combined from those of InGaN and AlGaN ternary alloys with comparable In and Al compositions. Our studies have revealed that In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys with lattice matched with GaN epilayers ($y \approx 4.8x$) have the highest optical quality. More importantly, we can achieve not only higher emission energies but also higher emission intensity (or quantum efficiency) in In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys than that of GaN. The quantum efficiency of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys was also enhanced significantly over AlGaN alloys with a comparable Al content. These results strongly suggested that In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys open an avenue for the fabrication of many optoelectronic devices such as high efficient light emitters and detectors, particularly in the ultraviolet region.

III nitrides including GaN epilayers, InGaN and AlGaN alloys, and InGaN/GaN and GaN/AlGaN multiple quantum wells (MQWs) have been intensively studied due to their many applications in ultraviolet (UV)/blue light emitters, solar-blind UV detectors, and high power/temperature electronics. It has been demonstrated that most nitride based devices must take advantage of MQWs and heterostructures such as GaN/AlGaN and InGaN/GaN as well as the tunability of the band gaps in the alloys from InN ($1.9$ eV) to GaN ($3.4$ eV) and to AlN ($6.2$ eV). Thus an important issue is still quantum well (QW) or heterostructure device structural perfection, which requires development of innovative approaches to synthesize high quality III-nitride QWs and heterostructures. Recently, In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys have been recognized to have the potential to overcome some shortfall of GaN epilayers and InGaN and AlGaN alloys. By varying In and Al compositions $x$ and $y$ in In$_x$Al$_y$Ga$_{1-x-y}$N, one can change the energy band gap while keep lattice matched with GaN. In addition to the key features of lattice match with GaN and the tunability in energy band gap, In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys also have the potential to provide a better thermal match to GaN, which could be an important advantage in epitaxial growth. The potential applications of InAlGaN quaternary alloys as InGaN/InAlGaN QW light emitters, GaN/InAlGaN heterojunction field-effect transistors, and UV detectors have been demonstrated recently.

It was observed previously that photoluminescence (PL) emission intensity or quantum efficiency (QE) of Al$_x$Ga$_{1-x}$N alloys decreases exponentially with an increase of Al content. QE of UV light emitters fabricated from Al$_x$Ga$_{1-x}$N alloys are thus expected to drop significantly as the emission energy extends into deeper UV region. This is one of the key problems for the fabrication of high-performance UV optoelectronic devices. In fact, in a recent proof-of-concept demonstration work, an output power of $13 \mu$W at $20$ mA was measured from an AlGaN/GaN MQW light emitting diode (LED) in the UV spectral region near $354$ nm. This output power is more than two orders of magnitude lower than a $3$ mW output power from blue LEDs fabricated from InGaN/GaN MQWs.

In this letter, we report the growth and optical properties of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys. A $0.5–1.0 \mu$m GaN epilayer was first deposited on the sapphire substrate with a $25$ nm low temperature GaN buffer layer, followed by the deposition of a $0.1 \mu$m In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloy epilayer by the low pressure metalorganic chemical vapor deposition (MOCVD). The growth temperature and pressure for the underneath GaN epilayer were $1050$ °C and $300$ Torr, respectively. For In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys, the growth temperature was $780$ °C and In and Al compositions were controlled by varying the flow rates of TMIn and TMAI. Picosecond time-resolved PL was employed to study the optical properties of these materials. Contents of In and Al were determined by different methods including x-ray diffraction (XRD), energy dispersive system, Rutherford backscattering, and PL measurements and were within $5\%$ variation. It was found that In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys with lattice matched with GaN epilayers ($y \approx 4.8x$) have the highest PL intensity as well as the narrowest XRD linewidth.

Table I lists the optimal growth parameters and emission properties of one of the In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys that are lattice matched with GaN together with those of In$_x$Ga$_{1-x}$N and Al$_x$Ga$_{1-x}$N alloys. Room temperature electron mobilities and concentrations have also been measured and listed in Table I as well.

Figure 1 shows the PL emission spectra of GaN epilayer (No. 567), Al$_x$Ga$_{1-x}$N alloy (No. 347), In$_x$Ga$_{1-x}$N alloy (No. 693), and In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloy (No. 706) measured at $T = 10$ K. The arrows indicate the spectral peak positions. The integrated PL intensity, $I_{em}$, for each of the alloy samples is included in Table I. The lower emission peak at $3.487$ eV in the PL spectrum of InAlGaN quaternary alloy in Fig. 1(d) is due to the underneath GaN epilayer. The
emission spectrum of InGa1_x-yAl_yN quaternary alloys in Fig. 1(d) shows that we can achieve not only higher emission energies but also higher emission efficiency in InGa1_x-yAl_yN quaternary alloys than that of GaN. The physical origin of this enhanced QE in InAlGaN alloys is not yet clear. However, it is now well known that InGa1_x-yAl_yN alloys have higher QE than GaN epilayers. It is thus not surprising that the QE is enhanced after the incorporation of indium into AlGa1-x-yN.

PL spectra at different temperatures were also measured for InAlGaN, InGaN, and AlGaN alloys. Emission intensities in these samples all decrease with increasing temperature. The Arrhenius plots of PL intensity of InGaN, AlGaN, and InAlGaN alloys are shown in Fig. 2(a). The solid lines in Fig. 2(a) are the least squares fit of data with the equation

\[ I(T) = I_0 / [1 + C \exp(-E_0 / kT)] , \]

where \( E_0 \) is the activation energy and \( C \) is a fitting constant. The fitted values of \( E_0 \) are 16.3, 16.7, and 23.4 meV for InGaN, AlGaN, and InAlGaN alloys, respectively.

From Table I, it is interesting to note that the growth conditions as well as the emission properties of InGa1_x-yAl_yN are more closely related with InGa1-x-yN than AlGa1-x-yN. The growth temperature and pressure for the optimized InGa1_x-yAl_yN quaternary alloys \( T_g = 780°C \) and \( P = 300 \text{ Torr} \) are exactly the same as for InGa1-x-yN alloys. The relative integrated PL intensities of InGa1_x-yAl_yN quaternary alloys are 175 \( (T = 10 \text{ K}) \) and 2.58 \( (T = 300 \text{ K}) \). These values are comparable with the values of 185 \( (T = 10 \text{ K}) \) and 3.9 \( (T = 300 \text{ K}) \) for InGaN, but much larger than the values of 80 \( (T = 10 \text{ K}) \) and 0.72 \( (T = 300 \text{ K}) \) for AlGaN. It is thus concluded that InGa1_x-yAl_yN quaternary alloys are InGaN-like rather than AlGaN-like, although Al composition is almost a factor of 5 larger than In.

The dominant PL transitions in InGa1_x-yAl_yN quaternary alloys at low temperatures are also due to the localized exciton recombination, just as the cases in InGaN and AlGaN alloys. This fact is reflected in the characteristics of time-resolved PL as well as decay lifetimes. Decay lifetimes of PL emission at their spectral peak positions were also measured for InAlGaN, InGaN, and AlGaN alloys and Fig. 2(b) shows the PL decay profiles measured at their corre-

<table>
<thead>
<tr>
<th>Sample</th>
<th>InGa1_x-yAl_yN</th>
<th>AlGa1-x-yN</th>
<th>InAlGa1-x-yN</th>
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<tbody>
<tr>
<td>KSU 693</td>
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<td>1060</td>
<td>780</td>
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<tr>
<td>KSU 347</td>
<td>359</td>
<td>375</td>
<td>411</td>
</tr>
<tr>
<td>KSU 706</td>
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<td>215</td>
<td>236</td>
</tr>
<tr>
<td>In and Al contents</td>
<td>x ~ 2.6%</td>
<td>x ~ 13.6%</td>
<td>x ~ 2.6%, y ~ 12.4%</td>
</tr>
<tr>
<td>( n ) (10^{17} \text{ cm}^{-3})</td>
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<td>5.40</td>
<td>3.60</td>
</tr>
<tr>
<td>( E_p ) (eV)</td>
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<td>3.722</td>
<td>3.575</td>
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<tr>
<td>( I_{\text{em}} ) (a.u.)</td>
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<td>80</td>
<td>175</td>
</tr>
<tr>
<td>FWHM (meV)</td>
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<td>26</td>
<td>29</td>
</tr>
<tr>
<td>( E_{\text{activation}} ) (meV)</td>
<td>16.3</td>
<td>16.7</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Plotted in eV.

**FIG. 1.** PL spectra of GaN, AlGa1-x-yN, InGa1-x-yN, and InAlGa1-x-yN quaternary alloys measured at \( T = 10 \text{ K} \). The emission spectrum of InGa1-x-yAl_yN shows that we can achieve not only higher emission energies but also higher emission efficiency in InAlGa1-x-yN quaternary alloys than that of GaN. The emission efficiency of InGa1-x-yAl_yN is also higher than that of AlGa1-x-yN and is comparable to that of InGa1-x-N.

**FIG. 2.** (a) The Arrhenius plots of PL intensities of InAlGa1-x-yN quaternary alloys. (b) PL decay profile of InAlGa1-x-yN quaternary alloys.
Figure 3. Time-resolved PL spectra as well as emission energy dependence of decay lifetime measured at 10 K for (a) In$_{0.4}$Ga$_{0.6}$N alloys, (b) Al$_{0.45}$Ga$_{0.55}$N alloys, and (c) In$_{0.4}$Al$_{0.6}$Ga$_{1-x-y}$N quaternary alloys.

The measured decay lifetimes at 10 K for In$_x$Ga$_{1-x}$N, Al$_y$Ga$_{1-y}$N, and In$_x$Al$_y$Ga$_{1-x-y}$N alloys are listed in Table I.

In Fig. 3 is the plot of time-resolved PL spectra as well as emission energy dependence of decay lifetime measured at 10 K for In$_x$Ga$_{1-x}$N, Al$_y$Ga$_{1-y}$N, and In$_x$Al$_y$Ga$_{1-x-y}$N alloys. The behavior of emission energy dependence of decay lifetime is very similar among these three alloys. While In$_x$Ga$_{1-x}$N has the longest decay lifetimes, the decay lifetime decreases with an increase of emission energy at above their corresponding spectral peak positions. This is a well-known character of localized excitons and is due to the transfer of excitons from higher to lower energy sites within the tail states caused by alloy fluctuations.

The increased decay lifetime as well as activation energy in quaternary alloys points to an enhanced localization effects in In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys compared with In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N ternary alloys. The measured PL decay lifetime for In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys at $T=10$ K, from Table I, is 0.49 ns, while that for In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N are 0.28 and 0.35 ns, respectively. It is interesting that the measured decay lifetime of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys at $T=10$ K, $\tau_{\text{InAlGaN}}$, is correlated with those of In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N alloys, $\tau_{\text{InGaN}}$ and $\tau_{\text{AlGaN}}$ respectively, with the relation $\tau_{\text{InAlGaN}}=0.49 \text{ ns}=(\tau_{\text{InGaN}}^{-2}+\tau_{\text{AlGaN}}^{-2})^{-1/2}=(0.28^2+0.35^2)^{1/2}=0.45 \text{ ns}$. This fact provides some hint that localization effects in In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys are the summation of those in In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N alloys with comparable In and Al compositions. Further evidence to support this speculation is that the relation between the activation energies, $E_0$, in In$_x$Al$_y$Ga$_{1-x-y}$N and In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N as shown in Table I is the same as the decay lifetimes, i.e., $E_{0,\text{InAlGaN}}=23.4$ meV vs. $(E_{0,\text{InGaN}}^2+E_{0,\text{AlGaN}}^2)^{1/2}=(16.3^2+16.7^2)^{1/2}=23.3$ meV.

The important implication here is that not only In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys can provide lattice match with GaN, but also the emission intensity of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys is also much higher than that of AlGaN with a comparable Al composition. The enhanced emission intensity or QE have been observed recently in unstrained In$_x$Ga$_y$In$_{1-x-y}$N QWs and was attributed to the reduction of dislocation density as well as of the piezoelectric field. Our results show that besides the advantages of reducing dislocation density and/or piezoelectric field in lattice-matched In$_x$Ga$_y$In$_{1-x-y}$N and GaN/In$_x$Ga$_y$In$_{1-x-y}$N QWs, emission intensity or QE of In$_x$Ga$_y$In$_{1-x-y}$N is also higher than that of AlGaN with a comparable Al composition. This makes the In$_x$Ga$_y$In$_{1-x-y}$N quaternary alloys a better choice for many UV optoelectronic applications over AlGaN. It is expected that detrimental effects due to lattice mismatch between the barrier and well materials, such as layer cracking, piezoelectric field, and high dislocation density will be significantly reduced in devices based on quaternary alloys compared with those utilizing ternary alloys. This is very important for UV emitter applications, where either AlGaN or In$_x$Al$_y$Ga$_{1-x-y}$N will be used as active layers.

In summary, In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys have been grown by MOCVD on sapphire substrates. Optical properties of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys have been studied by picosecond time-resolved PL spectroscopy and compared with those of GaN epilayers as well as In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N alloys. By controlling In and Al compositions in In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys, we can achieve not only lattice match with GaN but also higher emission energies as well as higher emission efficiencies in the UV region in In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys than that in GaN epilayers. In addition, PL emission intensity or quantum efficiency of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys is enhanced over Al$_y$Ga$_{1-y}$N alloys with similar Al contents and is comparable to that of In$_x$Ga$_{1-x}$N alloys with similar In composition. It is also demonstrated that the physical properties of In$_x$Al$_y$Ga$_{1-x-y}$N quaternary alloys are more closely related with In$_x$Ga$_{1-x}$N than Al$_y$Ga$_{1-y}$N including growth conditions and material properties.

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