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Properties of $Al_xGa_{1-x}N$ layers grown by plasma-assisted molecular-beam epitaxy under Ga-rich conditions

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$Al_xGa_{1-x}N$ films were grown by plasma-assisted molecular-beam epitaxy on (0001) sapphire substrates under Ga-rich conditions. To control the $Al_xGa_{1-x}N$ composition over the entire range, the Al and Ga arrival rates were fixed while the nitrogen arrival rate was varied. We have found that the Al fraction increased with decreasing N flow due to preferentially favorable bonding of Al and N over Ga and N. Consequently, the growth rate decreased as the Al mole fraction increased. A photoluminescence quantum efficiency at 15 K was markedly higher for the $Al_xGa_{1-x}N$ layers grown under Ga-rich conditions (3%–48%) compared to the layers grown under N-rich conditions (1%–10%), indicating much reduced nonradiative recombination in samples grown under Ga-rich conditions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1506206]

Owing to its tunable gap, the $Al_xGa_{1-x}N$ alloy is of paramount interest for optoelectronic devices, as the flurry of activity during the past few years indicates.[1] The band gap of this material, which is direct, lies in a typical range of 3.42 ($x=0$) to 6.2 ($x=1$) at $T=300$ K.[2] Devices that employ $Al_xGa_{1-x}N$ layers include light-emitting diodes,[3] laser diodes,[4] UV photodetectors,[5,6] and heterojunction field-effect transistors.[6,7] In all of these devices, the $Al_xGa_{1-x}N$ alloy constitutes a pivotal component and determines such properties as carrier and light confinement, and sheet carrier density at heterointerfaces. With the recent advent of short-wavelength sources and detectors, AlGaN is increasingly taking the role of active emission and absorption medium as well. Though a number of these devices have been reported, there are still serious issues to be addressed. Among them is the deteriorating radiative recombination efficiency with increasing Al content[8] and control of the mole fraction. The influence of growth conditions on the aluminum mole fraction and the quality of the $Al_xGa_{1-x}N$ film were studied in detail in the case of metalorganic chemical-vapor deposition (MOCVD).[9,10] Molecular-beam-epitaxy (MBE) growth of $Al_xGa_{1-x}N$ on sapphire is less well understood, except for some regularities of the growth established for the MBE growth employing the electron cyclotron resonance–microwave plasma source of nitrogen.[11] In this letter, we report on the growth and properties of $Al_xGa_{1-x}N$ epilayers deposited on (0001) sapphire substrates by radio-frequency (rf) plasma-assisted MBE under Ga-rich conditions for a wide range of aluminum compositions (0.13–0.92). X-ray diffraction (XRD), and photoluminescence (PL) analyses were carried out to evaluate the properties of the $Al_xGa_{1-x}N$ under investigation.

The $Al_xGa_{1-x}N$ epilayers studied were grown on (0001) sapphire substrates by plasma-assisted MBE using conventional effusion cells for the metallic species and a rf plasma source for the nitrogen. In all samples, a nominal 50-nm-thick AlN buffer layer was deposited on sapphire at a substrate temperature of 850 °C. The substrate temperature was then lowered to 750 °C for the growth of $Al_xGa_{1-x}N$ layers. An overabundant Ga flux (two Ga sources) and moderate N pressure were kept to maintain N-limited (Ga-rich) growth conditions. The Al mole fraction in the alloy was controlled by fixing the Al and Ga source temperatures and varying the N flow. Variation of the nitrogen partial pressure in the MBE chamber in the range of 2.7×10^{-6}–9×10^{-6} Torr during growth provided $Al_xGa_{1-x}N$ with almost a complete range of *x*. A similar growth regime has been previously employed for growth of Ga- and N-rich $Al_xGa_{1-x}N$ by MOCVD (Ref. 10) and MBE,[12] although in other cases the attempts to control the Al mole fraction were undertaken by varying the Al cell temperature,[9,13] Ga cell temperature,[9] both Ga and Al fluxes with the fixed Al/Ga ratio,[9,11] and Al/Ga ratio with the fixed total flux.[14] For comparison, we have grown a few epilayers under nitrogen-rich conditions, where only one Ga source was used and the mole faction was changed by varying the Ga or Al flux or both, in an overabundant N flux.

The aluminum mole fraction *x* of the $Al_xGa_{1-x}N$ epilayers was evaluated from the peak separation between GaN and AlGaN peaks in the XRD curves, assuming that the variation of the lattice parameter *c* between GaN and AlN is proportional to the aluminum mole fraction (Vegard's law). Representative samples were cross checked with secondary ion mass spectroscopy and Rutherford back scattering, which resulted in good agreement with the XRD data.[15] Steady-state PL was excited with a third harmonic of the Ti–sapphire laser (245 nm), dispersed by a 1200 rules/mm grating in a 0.5 m monochromator and detected by a photomultiplier tube.

In Fig. 1, the dependence of the Al mole fraction in $Al_xGa_{1-x}N$ epilayers grown under Ga-rich conditions at constant substrate temperature is shown versus the MBE chamber pressure determined by N flow. The Al mole fraction is about inversely proportional to the N flow, and the Al concentration increases rapidly when the pressure is lower than 4×10^{-6} Torr. This phenomenon can be explained by preferential formation of the AlN component in the $Al_xGa_{1-x}N$ alloy under Ga-rich growth conditions.[10,11] Indeed, since the

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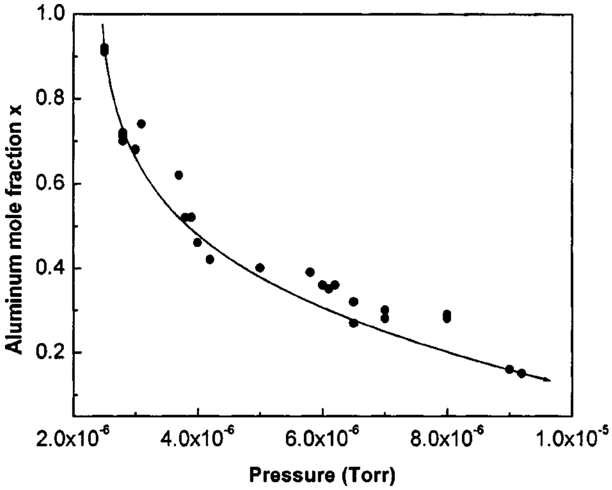

FIG. 1. Aluminum mole fraction x in $Al_xGa_{1-x}N$ alloys as a function of nitrogen plasma pressure under Ga-rich conditions. Temperature of the Al cell is 1005 °C. Temperature of the two Ga cells is 1125 °C.

Al–N bond is stronger than the Ga–N bond, it is reasonable to surmise that the available N would preferentially be used to form AlN. The remaining N would then form the GaN bonds for the alloy. Consequently, the N arrival rate would determine the mole fraction in the presence of an abundant amount of Ga on the surface in some range of substrate temperatures. As expected, under these conditions, the Al mole fraction in $Al_xGa_{1-x}N$ remained the same even with increasing temperature of the gallium sources.

Figure 2 shows the growth rate limited by both Al and N fluxes as a function of Al mole fraction in $Al_xGa_{1-x}N$. The growth rate decreases markedly with increasing x, approaching typical growth rates of GaN and AlN in metal-rich conditions when x approaches 0 and 1, respectively. With decreasing N flux, the growth rate decreased as expected for the Ga-rich conditions. Since Al preferentially bonds with N, a smaller amount of the remaining N is available for the GaN component of the alloy at low N flow, the GaN component is reduced thereby increasing the Al mole fraction and reducing the overall growth rate.

For a comparative analysis, albeit limited to a few mole

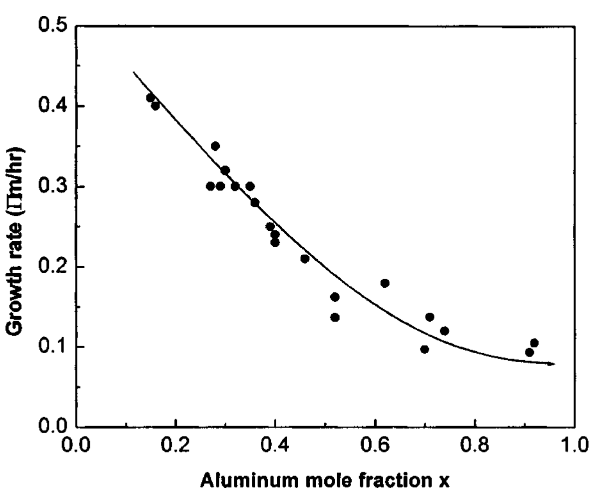

FIG. 2. Growth rate of $Al_xGa_{1-x}N$ alloys as a function of nitrogen plasma pressure under Ga-rich conditions. Temperatures of Al and Ga cells are the same as in Fig. 1.

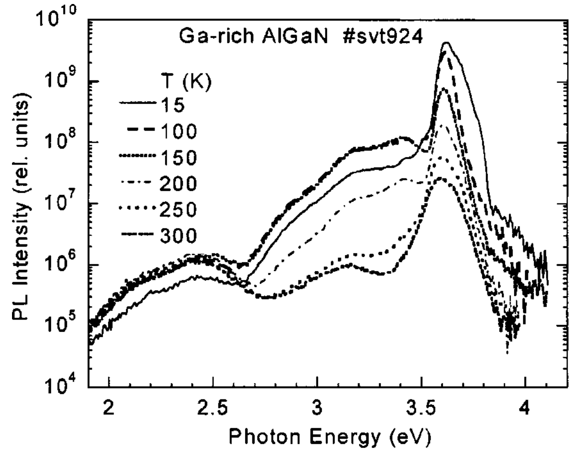

FIG. 3. PL spectra of the representative $Al_xGa_{1-x}N$ layer with $x=0.13$ grown under Ga-rich conditions.

fractions, we studied the properties of $Al_xGa_{1-x}N$ epilayers grown under nitrogen-rich conditions as well. The Al composition in this regime was controlled by varying the Ga source temperature with a constant Al flux for practical reasons. In this regime the Al mole fraction in $Al_xGa_{1-x}N$ remained the same with increasing the N pressure, since it is determined by Al and Ga fluxes at a given substrate temperature. The N flow rate beyond a certain point, which is determined by what is sufficient to satisfy bonds with the available Al and Ga species, does not seem to have a notable effect on the surface kinetics to cause a change in the mole fraction under the conditions employed here.

An example of temperature-dependent PL spectra of the $Al_xGa_{1-x}N$ layer grown under Ga-rich conditions with an Al mole fraction of 0.13 is shown in Fig. 3. PL spectra of all the $Al_xGa_{1-x}N$ layers grown under Ga-rich conditions indicated relatively broad near-band-edge emission peaks and defect-related bands in the green and blue regions at low temperatures. Interestingly, the width of the main peak decreased with increasing temperature due to fast quenching of its high-energy side: the full width at half maximum decreased from 93 to 63 meV in the temperature range between 15 and 100 K for the sample depicted in Fig. 3. This phenomenon can be explained by the existence of compositional fluctuations in $Al_xGa_{1-x}N$. Indeed, the narrowing of the emission peak with temperature due to quenching of its high-energy side can be attributed to thermal release of free carriers from the shallower short-range wells and their percolation into the deeper ones caused by local compositional fluctuations.[16]

PL intensity for the samples grown under Ga-rich conditions generally quenched at higher sample temperatures, as compared to the N-rich samples. The quenching behavior of PL from Ga- and N-rich $Al_xGa_{1-x}N$ for two samples with similar Al composition is compared in Fig. 4. The quantum efficiency of PL at 15 K was markedly higher for the $Al_xGa_{1-x}N$ layers grown under Ga-rich conditions (3%–48%) compared to the layers grown under N-rich conditions (1%–10%). These values, in turn, are much higher than the radiative efficiencies obtained by us for a large set of GaN layers (Ga polarity) grown in similar conditions: 0.01%–0.3% for Ga-rich and 0.1%–2% for N-rich GaN. Such improvement of radiative efficiency in $Al_xGa_{1-x}N$, especially under the Ga-rich conditions, point to a reduced density of

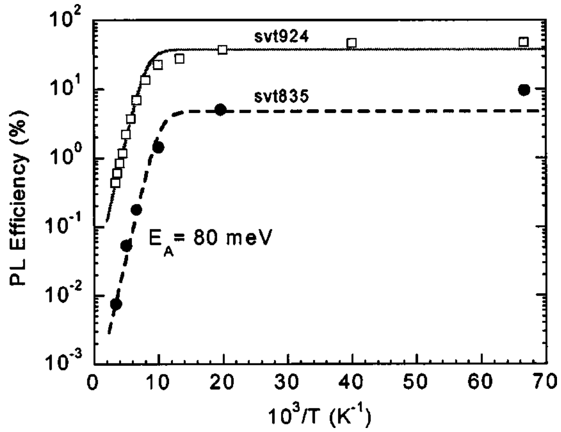

FIG. 4. Temperature dependences of PL quantum efficiency for the $Al_xGa_{1-x}N$ layers grown under Ga-rich (sample svt924) and N-rich (sample svt835) conditions.

dislocations, although carrier confinement cannot be excluded.

In conclusion, we demonstrated that the aluminum mole fraction can be well controlled over the entire alloy composition range by nitrogen flow rate in MBE growth of $Al_xGa_{1-x}N$ alloys under Ga-rich conditions. PL measurements reveal very high radiative efficiency in $Al_xGa_{1-x}N$ grown by this method. Compared to a few $Al_xGa_{1-x}N$ samples grown under N-rich conditions and a large number of GaN layers grown in different conditions, the nonradiative recombination is markedly reduced in $Al_xGa_{1-x}N$ films grown under Ga-rich conditions.

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