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$Al_xGa_{1-x}N$ alloys with x up to 0.7 were grown by metalorganic chemical vapor deposition and their optical properties were investigated by deep UV time-resolved photoluminescence (PL) spectroscopy. Our results revealed that both the activation energy of the PL emission intensity and the PL decay lifetime exhibit sharp increases at x of around 0.4. The results can be understood in terms of the sharp increase of the impurity binding energy or the carrier/exciton localization energy around $x = 0.4$. A three orders of magnitude increase in resistivity of undoped AlGaN alloys at x of around 0.4 was also observed, which further corroborated the optical results. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1418255]

With recent rapid progress in III-nitride based devices, materials growth and fundamental understanding of the optical and electrical properties of Al-rich AlGaN alloys have become increasingly important. Al-rich $Al_xGa_{1-x}N$ alloys are both difficult to grow and to characterize due to having much wider energy band gaps than GaN. However, Al-rich AlGaN alloys are indispensable in deep UV light emitters as well as in high performance electronic devices.[1,2] GaN and AlN form alloys with direct band gaps, whose band gaps range from 3.4 to 6.2 eV, giving an energy gap difference ΔE_g of 2.8 eV. This is much larger than the typical value of a few tenths of eV in II–VI semiconductor alloys, in which a strong localization effect is known to exist.

In this letter, we report the growth and optical and electrical properties of $Al_xGa_{1-x}N$ alloys for x up to 0.7. Our results have revealed that the photoluminescence (PL) emission intensity decreases with an increase of the Al content. On the other hand, the activation energy of the impurity level or the carrier/exciton location energy in $Al_xGa_{1-x}N$ alloys was found to increase sharply at x of around 0.4. These results provide further information regarding both n- and p-type conductivity of $Al_xGa_{1-x}N$ with $x > 0.4$.

$Al_xGa_{1-x}N$ epilayers ($x < 0.7$) 1 μm thick were grown by metalorganic chemical vapor deposition (MOCVD) on sapphire (0001) substrates with 25 nm low temperature AlN nucleation layers. The growth temperature and pressure were 1060 °C and 80 Torr, respectively. Trimethylgallium (TMG) and trimethylaluminum (TMAl) were used as the metalorganic sources. In order to measure the time-resolved PL of Al-rich AlGaN alloys, a deep UV (195 nm) laser system was specifically designed to generate femtosecond (100 fs) tunable laser pulses with 10 mW average power and 76 MHz repetition rate. More detailed information about the deep UV laser system can be found in Ref. 3. A single photon counting detection system together with a microchannel plate (MCP) photomultiplier tube tube (PMT) and a streak camera with a detection capability ranging from 185 to 800 nm were used to record continuous wave (cw) and time-resolved PL spectra. The Al composition of the AlGaN alloys was determined

by the flow rates of TMG and TMAl as well as by an energy dispersive x-ray chemical microanalyzer (model 4060 Oxford) and from the PL peak positions by assuming the energy band gap E_g of AlGaN follows

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

with the bowing parameter $b = 0.98$ eV.[4] Values of 3.42 and 6.20 eV were used for the room temperature energy band gaps of GaN and AlN, respectively. The Al contents for selective samples were also determined by x-ray diffraction and secondary ion mass spectroscopy (performed by Charles Evans & Assoc.) measurements. All these methods provide consistent Al compositions with accuracy within ~0.02.

Low-temperature (10 K) cw PL spectra of $Al_xGa_{1-x}N$ alloys with $x = 0.3$, 0.5, and 0.7 are presented in Fig. 1. The PL peak position, E_p, the full width at half maximum (FWHM), as well as integrated intensity, S, are also indicated. Besides the shift of the peak position towards shorter wavelength with increasing Al content, one can also notice a considerable decrease in the PL intensity and an increase in the FWHM, which is caused by alloy broadening. The solid lines are the least-squares fits of data with two peaks of Gaussian distributions. With longitudinal optical (LO) pho-
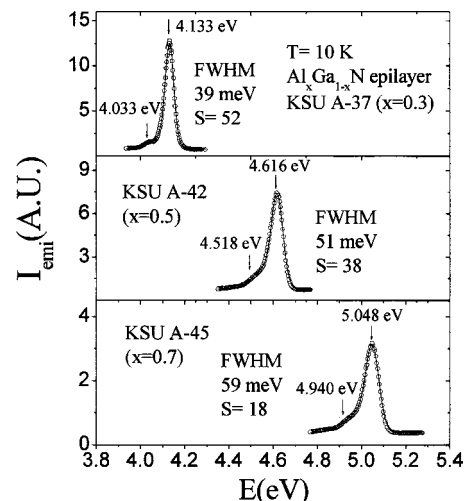

FIG. 1. Low-temperature (10 K) cw PL spectra of $Al_xGa_{1-x}N$ alloys with $x = 0.3$, 0.5, and 0.7.
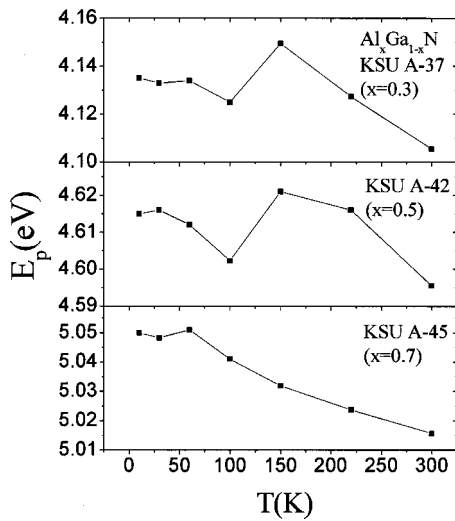
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FIG. 2. Temperature variations of the main PL emission peak positions, E_p, of $Al_xGa_{1-x}N$ alloys with $x=0.3$, 0.5, and 0.7.

FIG. 4. Activation energy E_0 as a function of Al composition x. A dramatic increase of E_0 is evident at $x \sim 0.4$.

non energies around 112 and 92 meV for AlN and GaN, respectively,[5] the low energy shoulders in Fig. 1 are assigned to LO phonon replicas of the main emission peak.

Figure 2 shows temperature variations of the main emission peak positions (E_p) of $Al_xGa_{1-x}N$ alloys with $x=0.3$, 0.5, and 0.7, where values of E_p were determined by fitting the PL spectra near the emission peaks by Gaussian functions. The E_p versus temperature plots shown in Fig. 2 for $x=0.3$ and 0.5 clearly depict the S-shape behavior, similar to in the case for AlGaN alloys with low Al content ($x < 0.35$).[6,7] The S-shape behavior has been explained in terms of the effects of localized states induced by alloy fluctuations in AlGaN alloys. The systematic behavior exhibited by the data of Fig. 2 for $x=0.3$ and 0.5 may be understood in terms of the impurity bound or localized exciton transition in the tail states due to alloy fluctuation. Similar behavior has been reported previously for the temperature-dependent PL emission energy shift in InGaN/GaN multiple quantum wells[8] and in pseudomorphic AlGaN/GaN heterostructures.[9] However, the E_p versus temperature behavior for the $x=0.7$ AlGaN

alloy is quite different than that of $x=0.3$ and 0.5. For $x=0.7$, the fluctuation is so large that the S shape is less pronounced or it has disappeared.

Figure 3 shows Arrhenius plots of the PL emission intensity of $Al_xGa_{1-x}N$ alloys with $x=0.3$, 0.5, and 0.7. The solid lines are the least-squares fit of data with

$$I_{emi}(T)=I_0/[1+C\exp(-E_0/kT)], \qquad (2)$$

where E_0 is the activation energy of the PL emission intensity. The fitted activation energy E_0 is indicated in Fig. 3. Figure 4 shows a plot of the Al composition (x) dependence of the activation energy, E_0, obtained for the set of three samples together with AlGaN alloys of low Al content.[7] The most intriguing result is that E_0 has a sharp increase at $x \sim 0.4$. For $x > 0.5$, E_0 is as large as 90 meV, much larger than the thermal energy at room temperature (25 meV).

There are many important consequences for large E_0 for x greater than 0.4. Larger E_0 implies larger impurity binding energies or carrier/exciton localization energies, which will make the conductivity of these materials very low, a fact that is well known for Al-rich AlGaN alloys.[10] It has been suggested that the binding energies of impurities in $Al_xGa_{1-x}N$ increase with x, and cause low conductivities for undoped Al-rich AlGaN alloys.[10] We have measured the conductivity of a set of undoped AlGaN alloys with x between 0.3 and 0.5 and the results are summarized in Table I. As shown in Table I, the resistivity increases by about three orders of magnitude when the Al content is increased from 0.3 to 0.4. It becomes a highly resistive material at x of around 0.5 for undoped $Al_xGa_{1-x}N$ alloys. The results shown in Table I further corroborate the optical data presented in Fig. 4.
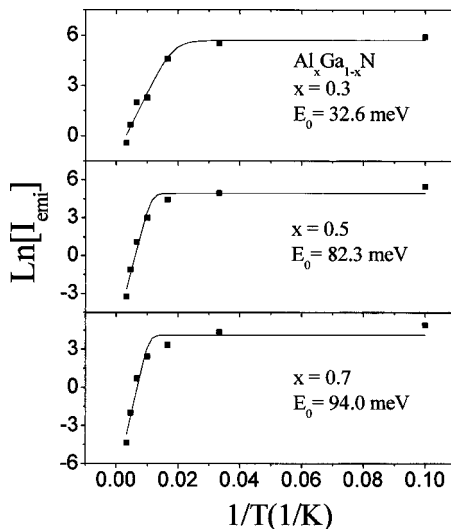

FIG. 3. Arrhenius plots of the PL intensity for AlGaN alloys with $x=0.3$, 0.5, and 0.7. The solid lines are the least-squares fit of data with Eq. (2). The fitted activation energy, E_0, is also indicated.
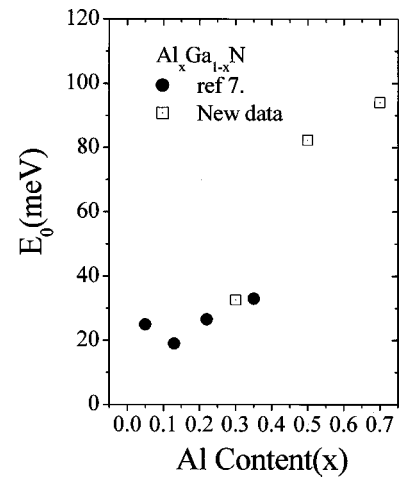
TABLE I. Resistivity of undoped $Al_xGa_{1-x}N$ alloys with x varying from 0.3 to 0.5.

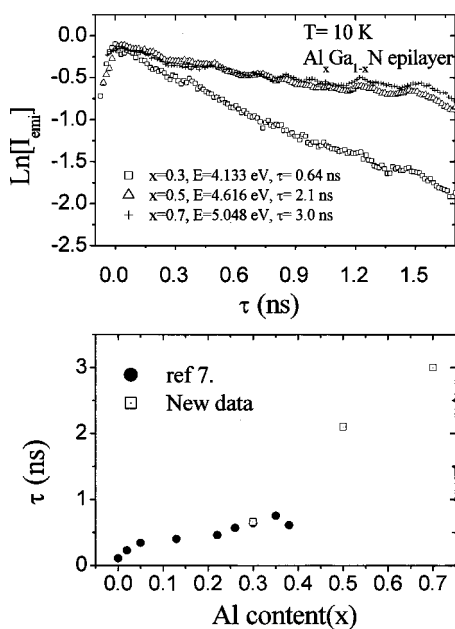| Al content, x	Resistivity ρ (Ω cm)
0.3	0.18
0.35	2.1
0.4	190
0.45	374
0.5	$> 10^5$

FIG. 5. Temporal responses for the PL emissions from $Al_xGa_{1-x}N$ alloys with $x = 0.3$, 0.5, and 0.7 measured at 10 K and their emission peak positions. (b) The Al content dependence of the measured decay lifetime ($T = 10$ K) of $Al_xGa_{1-x}N$ alloys. A similar trend for results shown in (a) and in Fig. 4 is evident.

Time-resolved PL spectra were measured at 10 K. Figure 5(a) shows the temporal responses of the PL emissions from AlGaN alloys (with $x = 0.3$, 0.5, and 0.7) measured at their respective spectral peak positions. It clearly shows an increase in the decay lifetime with increasing Al content. Figure 5(b) shows a plot of the decay lifetimes of these three samples together with those of low Al content AlGaN alloys obtained previously.[7] Quite convincingly, the decay lifetime shows exactly the same trend as that of the activation energy

of the PL emission intensity shown in Fig. 4. The PL decay lifetime is expected to increase with the impurity binding energy as well as with the carrier/exciton localization energy.[7,11]

In summary, we have investigated the optical and electrical properties of $Al_xGa_{1-x}N$ alloys for x up to 0.7. Our results strongly suggest either a deepening of the impurity level or a sharp increase of the localization energy in high Al content AlGaN alloys is responsible for the various behaviors reported here. These include sharp increases of the PL emission intensity activation energy, of the PL decay lifetime, and of the resistivity for undoped $Al_xGa_{1-x}N$ alloys at x of around 0.4.

[1] S. Nakamura and G. Fassl, *The Blue Laser Diode* (Springer, New York, 1997).
[2] K. B. Nam, J. Li, H. Kim, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **78**, 3690 (2001).
[3] http://www.phys.ksu.edu/area/GaNgroup
[4] M. R. H. Khan, Y. Koide, H. Itoh, N. Sawaki, and I. Akasaki, Solid State Commun. **60**, 509 (1986).
[5] *Semiconductors—Basic Data*, 2nd revised ed., edited by O. Madelung (Springer, Berlin, 1996).
[6] Y. H. Cho, G. H. Gainer, J. B. Lam, J. J. Song, W. Yang, and W. Jhe, Phys. Rev. B **61**, 7203 (2000).
[7] H. S. Kim, R. A. Mair, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **76**, 1252 (2000).
[8] Y.-H. Cho, G. H. Gainer, A. J. Fischer, J. J. Song, S. Keller, U. K. Mishra, and S. P. DenBaars, Appl. Phys. Lett. **73**, 1370 (1998).
[9] G. Steude, B. K. Meyer, A. Göldner, A. Hoffmann, F. Bertram, J. Christen, H. Amano, and I. Akasaki, Appl. Phys. Lett. **74**, 2456 (1999).
[10] M. D. Bremser, *Gallium Nitride and Related Semiconductors*, edited by J. H. Edgar, S. Strite, I. Akssaki, H. Amano, and C. Wetzel (Institute of Electrical Engineers, London, 1999), p. 147.
[11] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, M. Asif Khan, and C. J. Sun, Appl. Phys. Lett. **67**, 1653 (1995).