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Citation: Applied Physics Letters **80**, 1210 (2002); doi: 10.1063/1.1450038
View online: http://dx.doi.org/10.1063/1.1450038
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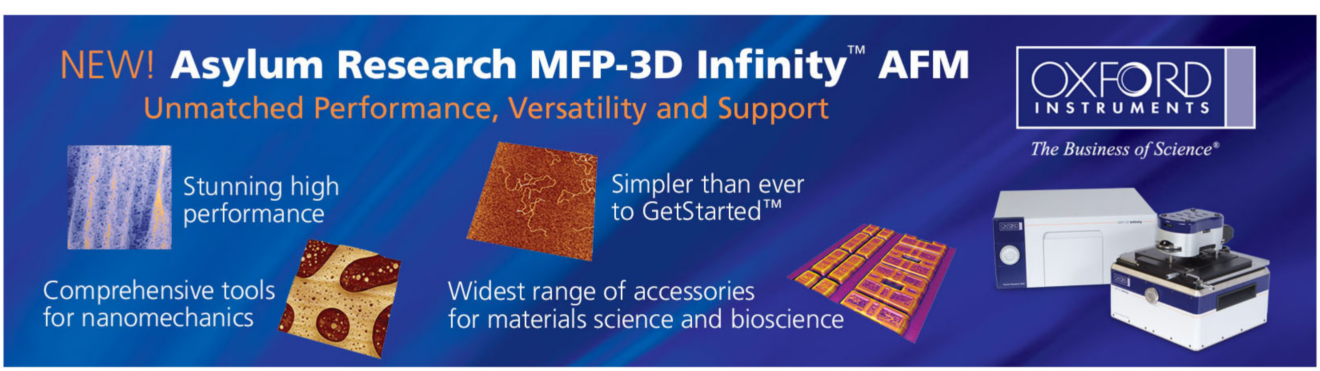

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Optical and electrical properties of Mg-doped *p*-type $Al_xGa_{1-x}N$

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(Received 18 September 2001; accepted for publication 6 December 2001)

Mg-doped $Al_xGa_{1-x}N$ epilayers with Al content up to 0.27 were grown on sapphire substrates by metalorganic chemical vapor deposition (MOCVD). *p*-type conduction in these alloys has been achieved, as confirmed by variable temperature Hall-effect measurements. Emission lines of band-to-impurity transitions of free electrons with neutral Mg acceptors as well as localized excitons have been observed in the *p*-type $Al_xGa_{1-x}N$ alloys. The Mg acceptor activation energies E_A were deduced from photoluminescence spectra and were found to increase with Al content and agreed very well with those obtained by Hall measurements. From the measured activation energy as a function of the Al content, E_A versus x the resistivity of $Al_xGa_{1-x}N$ alloys with high Al contents can be deduced. Our results thus indicated that alternative methods for acceptor activation in AlGaN alloys with high Al contents must be developed. Our results have also shown that PL measurements provide direct means of obtaining E_A, especially where this cannot be obtained accurately by electrical methods due to high resistance of Mg-doped $Al_xGa_{1-x}N$ alloys with high Al content.
© *2002 American Institute of Physics.* [DOI: 10.1063/1.1450038]

Group III–nitride semiconductors have been recognized as very important materials for optoelectronic devices such as light emitting diodes and laser diodes (LDs) for applications in the short wavelengths. *p*-type doping in GaN and AlGaN is considered to be the key to realizing nitride based ultraviolet (UV)/blue light emitters. In addition, highly conductive *p*-type films are necessary for improving the performances of LDs including reducing threshold voltages. Currently, there is a great need of solid-state UV emitters for chem-bio-agent detections as well as for general lighting. In such applications, *p*-type AlGaN alloys with relatively high Al content are indispensable. However, it is difficult to achieve high *p*-type conductivity in *p*-type $Al_xGa_{1-x}N$ alloys due to high activation energy of Mg dopants as well as reduced crystalline quality of the alloys.

A few studies have been reported on Mg-doped *p*-type $Al_xGa_{1-x}N$ with low Al content ($x \leqslant 0.15$).[1–4] It was found that the activation energies E_A of Mg acceptors in Mg-doped $Al_xGa_{1-x}N$, all determined by variable temperature Hall measurements, increased with the increase in Al content. Due to the increased Mg activation energy, it has been difficult to achieve *p*-type conductivity in $Al_xGa_{1-x}N$ with high Al content. In addition, no direct observation of band-to-impurity transition of free electrons with neutral Mg acceptors in *p*-type GaN or $Al_xGa_{1-x}N$ has so far been reported. Because these materials are of great importance in realizing nitride-based optoelectronic devices, studies that could provide better understanding and realization of highly conductive *p*-type GaN and $Al_xGa_{1-x}N$ are urgently needed.

In this letter, we report the growth and characterization of Mg-doped $Al_xGa_{1-x}N$ alloys. Electrical studies have revealed that we have achieved *p*-type conduction in $Al_xGa_{1-x}N$ for x up to 0.27. Photoluminescence (PL) emission lines due to band-to-impurity transitions of free electrons with neutral Mg acceptors in $Al_xGa_{1-x}N$ alloys have been observed, from which the values of E_A were deduced and were found to increase with an increase of Al content. These were found to match very well with those obtained by Hall measurements.

Mg-doped *p*-type $Al_xGa_{1-x}N$ epitaxial layers of 1 μm thickness were grown by metalorganic chemical vapor deposition on sapphire substrates with a 30 nm GaN buffer layers. The sources used were trimethylgallium (TMG), trimethylaluminum (TMAl) and ammonia. For Mg doping, biscyclopentadienyl-magnesium (Cp_2Mg) was transported into the growth chamber with ammonia during growth. Postgrowth annealing at 950 °C in nitrogen gas ambient for 8 s resulted in *p*-type conduction, verified by Hall measurements. The Al content was determined by energy dispersive x-ray measurements. Continuous wave (cw) PL spectra were measured using a Ti–sapphire laser spectroscopy system with an average output power of about 40 mW, photon energy of 4.66 eV, and a spectral resolution of about 0.2 meV. For time-resolved measurements, a streak camera detection system with time resolution of 2 ps was used. Details of the laser system setup are described elsewhere.[5]

Figure 1 is the room temperature PL spectra of the Mg-doped *p*-type $Al_xGa_{1-x}N$ for $x = 0.22$ after anneal of 950 °C for 8 s and shows two emission peaks at 3.2 and 3.62 eV. The emission peak at 3.2 eV is the main peak and in some of the samples studied, this was the only peak observed. The 3.2 eV transition has been well documented in Mg-doped *p*-type GaN, which is located at 2.95 eV.[6] A further anneal at 600 °C for 2 min in nitrogen gas resulted in the spectrum shown in Fig. 1(b) where the peak at 3.2 eV is now reduced significantly at room temperature. The peak at 3.62 eV is slightly redshifted to 3.60 eV but is now predominant, with about an order of increase in the emission intensity.

Figure 2 shows room temperature PL spectra of the Mg-doped *p*-type $Al_xGa_{1-x}N$ for $x = 0.22$, 0.25, and 0.27, following the two-step anneals described above. As can be seen,

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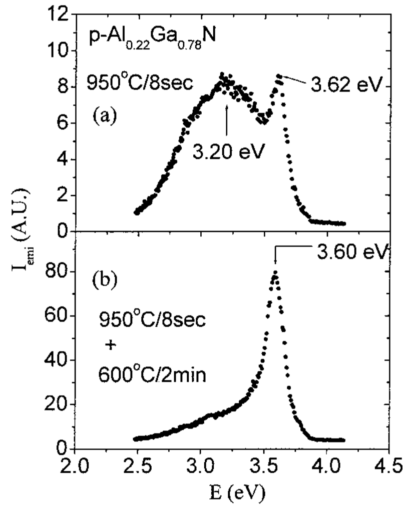

FIG. 1. Room temperature (300 K) PL spectra of the Mg-doped p-type $Al_xGa_{1-x}N$ for $x=0.22$ (a) after anneal of 950 °C for 8 s and (b) after a second anneal at 600 °C for 2 min.

the emission intensities of these spectra decrease with increase in x, a phenomenon we observed previously,[7] which is related to reduction in crystalline quality with increasing x. The emission peaks are observed at 3.615, 3.667, and 3.682 eV for $x=0.22$, 0.25, and 0.27, respectively, which are greater than the band edge transition of 3.42 eV for GaN. We assign these emission lines to the band-to-impurity transitions for the recombination of free electrons with neutral Mg acceptors in $Al_xGa_{1-x}N$. With the origin of these peaks thus assigned, the activation energy $E_A(x)$ of the ionized Mg impurity in $Al_xGa_{1-x}N$ can be deduced simply by the difference between the energy gap $E_g(x)$ and the observed band-to-impurity emission peak $E(e^-,A^0)$. $E_g(x)$ can be estimated from the expression

$$E_g(x)=(1-x)E_{g,\mathrm{GaN}}+xE_{g,\mathrm{AlN}}-bx(1-x), \tag{1}$$

and $E_A(x)=E_g(x)-E(e^-,A^0)$. In the above expression, we use widely accepted value of the energy gap for GaN, $E_{g,\mathrm{GaN}}=3.42$ eV, for AlN, $E_{g,\mathrm{AlN}}=6.20$ eV, and of the bowing parameter $b=0.90$.[8] With these, E_A values of 0.262,

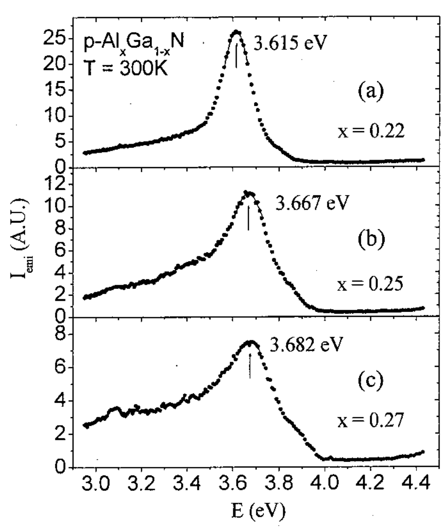

FIG. 2. Room temperature (300 K) cw PL spectra from Mg-doped p-type $Al_xGa_{1-x}N$ for (a) $x=0.22$, (b) $x=0.25$, and (c) $x=0.27$.

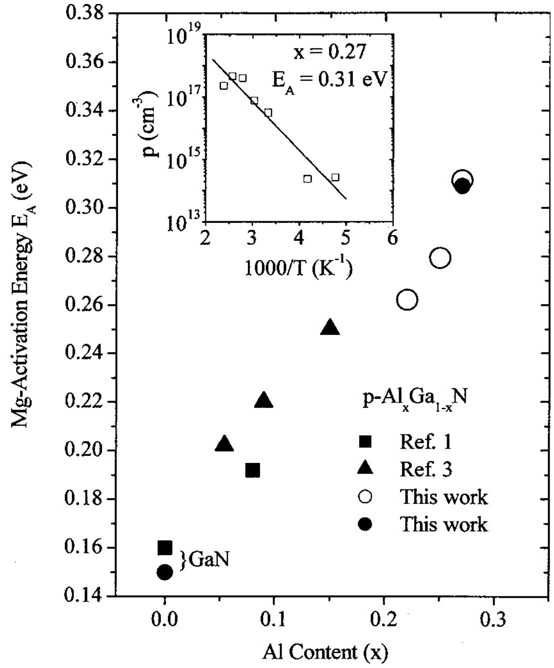

FIG. 3. Activation energies of Mg acceptors in Mg-doped p-type $Al_xGa_{1-x}N$ as a function of Al content x. Closed squares and triangles are data from Refs. 1 and 3, respectively, while closed circles are data from this work, all obtained by Hall measurements. Open circles indicate data obtained by PL measurements from this work. The inset shows measured temperature dependence of Hall concentration p in the Mg-doped p-type $Al_{0.27}Ga_{0.73}N$ sample from which $E_A=0.310$ eV was obtained.

0.279, and 0.311 eV corresponding to Al contents 0.22, 0.25, and 0.27, respectively, are obtained. It is expected that different choices of the bowing parameter b would result in variations in the E_A values. However, because the Mg acceptor level in AlGaN alloys is quite deep, the uncertainties in E_A values due to different choices of b are not very significant. For example, the above optically determined E_A values from Eq. (1) will be reduced by about 17–20 meV if the bowing parameter $b=1$ is used. The values of E_A we obtained in the above manner are plotted as a function of Al content x in Fig. 3, together with those reported previously,[1,3] all obtained by means of variable temperature Hall measurements. Also shown in this figure are data points for p-GaN and for p-$Al_{0.27}Ga_{0.73}N$ where we determined E_A by variable temperature Hall measurements (0.15 and 0.309 eV, respectively). The measured temperature dependence of Hall concentration (p) in the Mg-doped p-type $Al_{0.27}Ga_{0.73}N$ sample is shown in the inset of Fig. 3, from which a value $E_A=0.310$ eV was obtained. Since the hole concentrations in AlGaN alloys are relatively low and impurity band formation is not likely, our results of E_A deduced from the PL spectra match quite well with those obtained by Hall measurements, which further corroborates our assignment that the observed transitions between 3.62 and 3.68 eV in Fig. 2 are band-to-impurity transitions of free electrons to the neutral Mg acceptors. The increase of E_A with increase in band gap energy for the III–nitrides has been reported previously in other studies[1,3,9] and is predicted by the effective mass theory.[10–12] As a comparison with our results, the value of E_A estimated from the effective mass theory for $x=0.25$ for example, is between 0.263 and 0.294 eV, which agrees well with the measured value of 0.279 eV.

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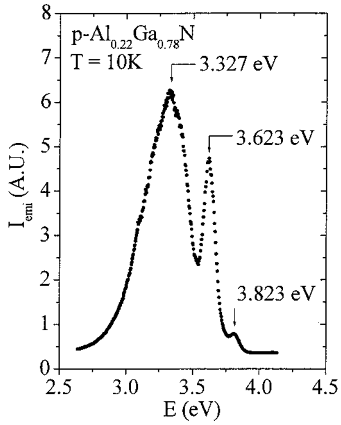

FIG. 4. Low temperature (10 K) cw PL spectrum of Mg-doped p-type $Al_xGa_{1-x}N$ with $x=0.22$.

Figure 4 shows low temperature (10 K) PL spectrum of one of the samples with $x=0.22$, where three emission peaks at 3.327, 3.623, and 3.823 eV were resolved. The peaks observed at 3.327 and 3.623 eV are the same transitions as those observed at 3.20 and 3.62 eV at 300 K [Fig. 1(a)]. The peak at 3.823 eV is believed to be due to the recombination of localized excitons, with the peak energy E_p given by

$$E_p = E_g - E_{bx} - E_{\mathrm{loc}}, \tag{2}$$

where E_g is the energy gap as defined in Eq. (1), E_{bx} is the excitonic binding energy, and E_{loc} is the localization energy of the localized exciton. For $x=0.22$, the value $E_g=3.877$ eV is obtained from Eq. (1). With estimated values of $E_{bx}=25$ meV and $E_{\mathrm{loc}}=30$ meV,[7] a value of $E_p=3.822$ eV is obtained for $x=0.22$, which matches very well with the observed emission peak (3.823 eV) in this spectrum, supporting our assignment of localized exciton for this emission line.

The dynamics of the optical transitions in the Mg-doped p-type $Al_xGa_{1-x}N$ was investigated by measuring the PL temporal response of one sample with $x=0.22$ at 10 K. The data for the transient measurements at emission peaks 3.327 and 3.623 eV are shown in Fig. 5. The decay at 3.327 eV can be fitted quite well with a single exponential giving a lifetime of 2.8 ns, while that at 3.623 eV can be fitted with two exponentials, with lifetimes of 0.18 and 1.5 ns. The difference in the decay dynamics of these two peaks is an indication that the origin of the 3.327 eV line is different from that of the 3.623 eV line. The orders of the measured decay lifetimes of the 3.623 eV line are consistent with the assigned optical transitions described above.

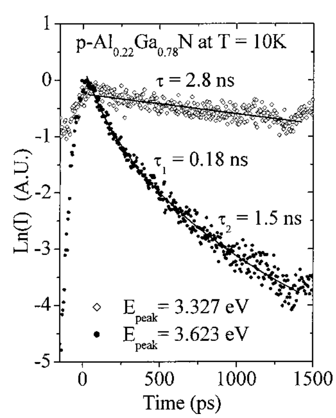

FIG. 5. Temporal response of the PL emissions from Mg-doped p-type $Al_{0.22}Ga_{0.78}N$ at 3.327 and 3.623 eV. The decay at 3.327 eV can be fitted with a single exponential giving a lifetime of 2.8 ns, while that at 3.623 eV can be fitted with two exponentials, with lifetimes of 0.18 and 1.5 ns. Continuous lines are fittings to the data points.

From the measured E_A versus x in Mg-doped p-type $Al_xGa_{1-x}N$, the resistivity versus x can be estimated as follows:

$$\begin{aligned}\rho(Al_xGa_{1-x}N) &= \rho_0 \exp(E_A/kT)\\ &= \rho_0 \exp\{[E_A(\mathrm{GaN})+\Delta E_A]/kT\}\\ &= \rho(\mathrm{GaN})\{\exp(\Delta E_A]/kT)\},\end{aligned} \tag{3}$$

where $\Delta E_A = E_A(Al_xGa_{1-x}N) - E_A(\mathrm{GaN})$ and our best p-type GaN has typical resistivity, ρ(GaN), of about 1.0 Ω cm. From Eq. (3), the resistivity of $Al_xGa_{1-x}N$ alloys with higher values of x can be deduced. For example, if the trend in Fig. 3 holds for higher x, at Al content $x=0.45$, the activation energy E_A is estimated to be 0.4 eV and the estimated resistivity should be as high as 2.2×10^4 Ω cm. Our results thus indicate that alternative methods for acceptor activation in AlGaN alloys with high Al contents have to be developed. The exponential increase of the resistivity with ΔE_A implies that the Hall measurements can no longer be used to measure the activation energy of $Al_xGa_{1-x}N$ alloys with high Al contents where resistivity becomes very high. However, with the observation of band-to-impurity transition, the PL method would be the alternative method for the determination of Mg acceptor activation energy.

In summary, we have obtained p-type conductivity in Mg-doped $Al_xGa_{1-x}N$ for x up to 0.27. The PL spectra show band-to-impurity transitions of free electrons with neutral Mg acceptors in the $Al_xGa_{1-x}N$. The values of activation energy E_A of the ionized Mg impurity in $Al_xGa_{1-x}N$ deduced from these spectra match quite well with those obtained from Hall measurements and increase with an increase of Al content, as predicted by the effective mass theory.

The authors wish to acknowledge support by grants from DARPA, ARO, ONR, BMDO, NSF (Grant Nos. DMR-9902431 and INT-9729582), and DOE (Grant No. 96ER45604/A000).

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