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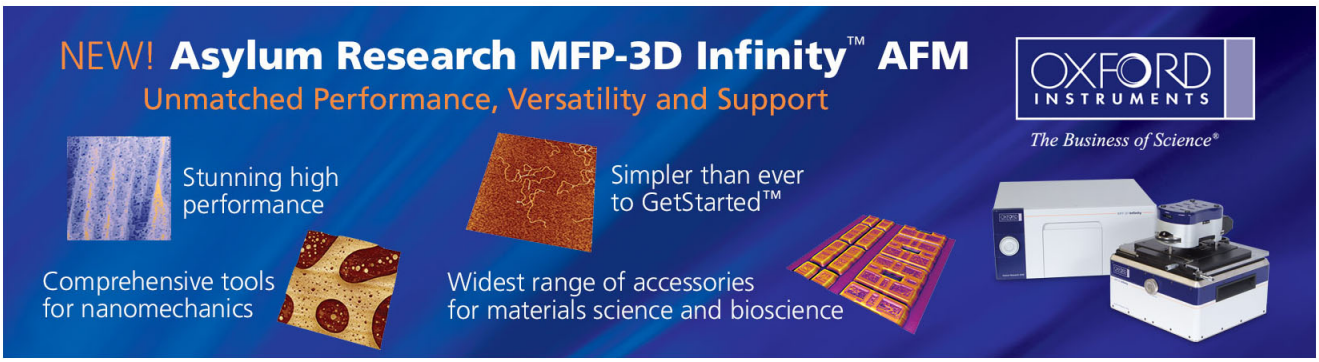

Mg acceptor level in AlN probed by deep ultraviolet photoluminescence

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Mg-doped AlN epilayers were grown by metalorganic chemical vapor deposition on sapphire substrates. Deep UV picosecond time-resolved photoluminescence (PL) spectroscopy has been employed to study the optical transitions in Mg-doped AlN epilayers. From PL emission spectra and the temperature dependence of the PL emission intensity, a binding energy of 0.51 eV for Mg acceptor in AlN was determined. Together with previous experimental results, the Mg acceptor activation energy in $Al_xGa_{1-x}N$ as a function of the Al content (x) was extrapolated for the entire AlN composition range. The average hole effective mass in AlN was also deduced to be about 2.7 m_0 from the experimental value of the Mg binding energy together with the use of the effective mass theory. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1594833]

With tremendous progress being made for III-nitrides research and development in terms of both fundamental understanding, as well as devices applications, AlN has become more critical for further understanding AlGaN alloys and for III-nitride device development. Recently, it has been demonstrated that the optical qualityof AlN epilayers grown on sapphire is comparable to that of GaN in terms of photoluminescence (PL) emission efficiency, especially at room temperature.[1] AlN epilayers with a free electron concentration of about 1×10^{17} cm^{-3} have also been achieved by Si doping.[2] Our group has recently achieved p-type conduction in Mg-doped $Al_xGa_{1-x}N$ epilayers for x up to $x=0.27$.[3] The resistivity of Mg-doped $Al_xGa_{1-x}N$, ρ, was found to increase with increasing x. The resistivity of Mg-doped AlN is, thus, expected to be very high. In this letter, we intend to address two related fundamental questions. The first question is whether or not one can achieve p-type conduction in AlN by Mg doping. The second question is what is the Mg acceptor energy level in AlN.

The 1-μm-thick Mg-doped AlN epilayers were grown by metalorganic chemical vapor deposition (MOCVD) on sapphire (0001) substrates with low temperature AlN nucleation layers. Trimethylaluminum (TMAl) and NH_3 were used as Al and N sources. For Mg doping, bis-cyclopentadienylmagnesium (Cp_2Mg) was transported into the growth chamber during growth. Atomic force microscopy measurements revealed a smooth surface morphology with a rms of about 1 nm across a 2 μm$\times$2 μm scanning area for Mg doped AlN, which is comparable to that (1.1 nm) of an undoped AlN epilayer.[4] Hall-effect measurements were attempted to measure the conductivity of Mg-doped AlN epilayers. However, all as-grown Mg-doped layers were highly resistive. Moreover, subsequent postgrowth annealing of Mg-doped AlN in nitrogen gas ambient did not result in p-type conduction. Secondary ion mass spectroscopy measurements (performed by Charles Evans) revealed that Mg-dopant concentration was about 7×10^{18} cm^{-3} in Mg-doped AlN epilayer. The deep UV picosecond time-resolved laser spectroscopy system used here consists of a frequency quadrupled 100 fs Ti:sapphire laser with an excitation photon energy set around 6.28 eV (with a 76 MHz repetition rate and a 3 mW average power), a monochromator (1.3 m), and a streak camera with a detection capability ranging from 185 to 800 nm and a time resolution of 2 ps.[5]

Figure 1 shows PL spectra measured at different temperatures for Mg-doped AlN epilayers. The low temperature (10 K) spectrum of an undoped AlN epilayer is also included for comparison. The band edge transition at 6.06 eV is the dominant transition in undoped AlN epilayers, which is at a slightly higher energy position than previously reported.[1,6] This is probably due to the fact that the magnitude of the strain varies slightly from sample to sample, similar to the case in GaN. Mg-doped AlN exhibits two dominant emission lines at 4.70 and 5.54 eV at 10 K, which are absent in undoped AlN and are thus attributed to Mg impurity related transitions. The spectral peak positions of these emission lines suggest that they are either band-to-impurity or donor-acceptor pair (DAP) transitions. However, the slow component of the recombination lifetimes of both emission lines measured at 10 K are about 1 μs (not shown), which precludes the possibility for the band-to-impurity type transitions which are known to have a recombination lifetime in the order of 1 ns.[7]

Figure 2(a) shows the Arrhenius plot of the PL intensity of the 5.54 eV emission line in Mg-doped AlN in the temperature region $T<150$ K. The solid lines are the least squares fit of data with equation

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

where E_0 is the activation energy of the PL emission intensity. The fitted activation energies $E_0=60$ meV for the 5.54 eV emission line again suggests that the 5.54 eV emission line is a DAP transition involving a Mg acceptor and a shallow donor (with an ionization energy of 60 meV). The ionization energy of substitutional shallow donors in AlN was predicted to be about 60 meV by the effective mass theory with an electron effective mass of $m^*=0.33\ m_0$.[8,9] It is also very close to the ionization energy of 86 meV measured for Si donor impurities in AlN.[2] The monotonic decrease of the 5.54 eV emission intensity with increasing temperature shown in Fig. 2(a) is due to the thermal dissociation of the shallow donors involved. By neglecting the Coulomb inter-

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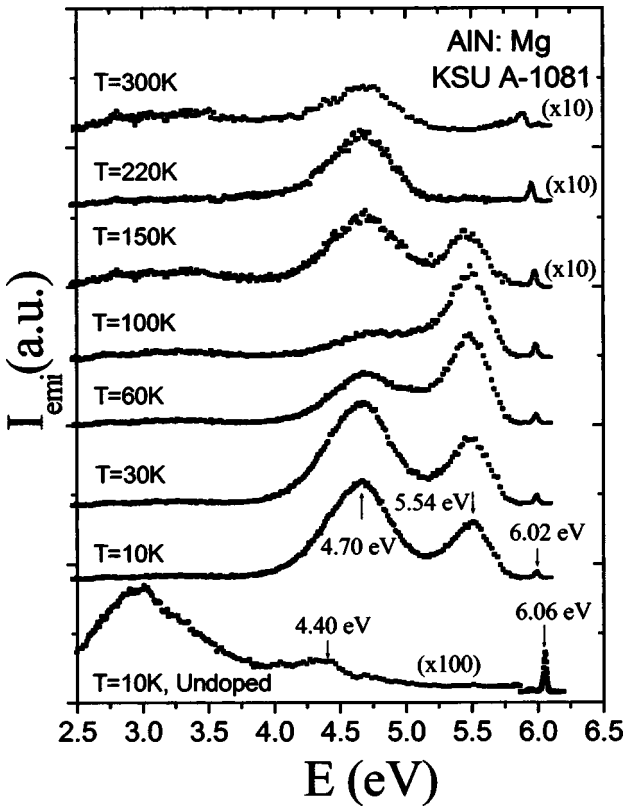

FIG. 1. PL spectra measured at different temperatures for Mg-doped AlN epilayers. The low temperature (10 K) spectrum of an undoped AlN epilayer is also included for comparison.

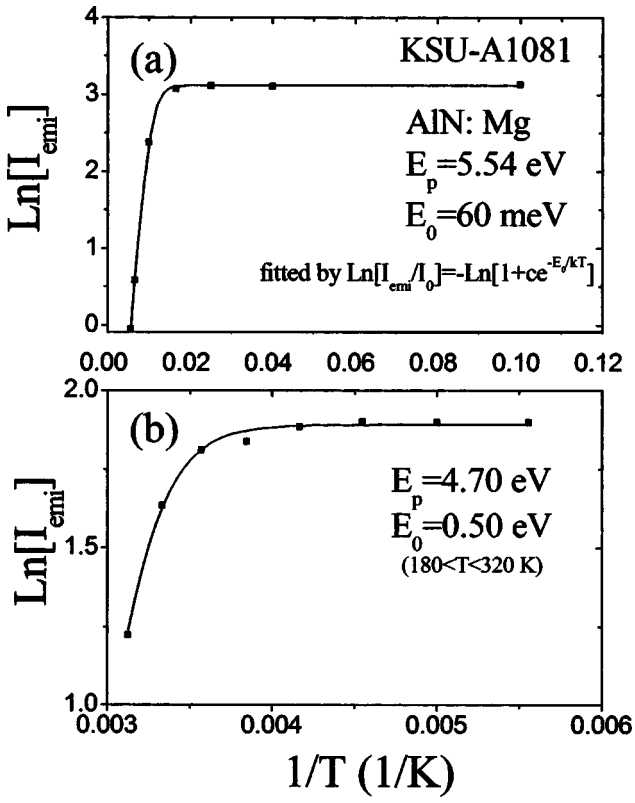

FIG. 2. The Arrhenius plots $[\ln(I_{emi})$ vs $1/T]$ for two emission lines in Mg-doped AlN: (a) 4.70 eV at $T<150$ K and (b) 5.54 eV at $T>150$ K. The solid lines are the least squares fits of data with Eq. (1). The fitted activation energies (E_0) are indicated in the figure.

action between the ionized donors and acceptors $(-e^2/\varepsilon r$ with r being the distance between the ionized donor and acceptor and ε being the static dielectric constant), a value of $E_A=0.52$ eV for the Mg acceptor binding energy in AlN is deduced from $E_A \approx E_g - 5.54\,\text{eV} - 0.06\,\text{eV}$ with $E_g = 6.12$ eV at 10 K.[6]

We assign the 4.70 eV emission line to a DAP transition involving a deep level donor and Mg acceptor. Due to the competing recombination channel at 5.54 eV at low temperatures, the thermal activation process of the 4.70 eV emission line is more complicated than that of the 5.54 eV line. However, the Mg impurity level E_A can also be obtained simply from the Arrhenius plot of the 4.70 eV PL intensity for $T>150$ K, above which the 5.54 eV emission line is no longer present. Based on the PL spectral peak position of the 4.70 eV line, we can conclude that the energy level of the donor involved is deeper than that of the Mg impurities. Thus, the thermal activation behavior shown in Fig. 2(b) is a direct measure of the activation of Mg impurities. A value of $E_0 = 0.50$ eV is obtained from Fig. 2(b) for the 4.70 eV emission line, which corroborates quite well with the Mg acceptor binding energy of 0.52 eV deduced from Fig. 2(a). Therefore, the Mg acceptor level in AlN is about 0.51 (± 0.01) eV above the valence band. Again by neglecting the Coulomb interaction between the ionized donors and acceptors, the binding energy of the deep level donor (E_D) involved in the 4.70 eV transition can be calculated from $E_D \approx E_g - 4.70\,\text{eV} - 0.5\,\text{eV} \approx 0.90$ eV.

Based on the results shown in Figs. 1 and 2, we have constructed the energy diagram for the impurity levels in AlN, as shown in Fig. 3. The upper limit of Mg^0 level in AlN is estimated to be about 0.97 eV if we assume that the Mg^0 level is lined up within the band gaps of GaN and AlN near the interface of a AlN/GaN heterojunction,[10,11] as illustrated in Fig. 3. The conduction band offset parameter is assumed to be 70% for the GaN/AlN heterostructure and E_A is 0.17 eV for Mg acceptors in GaN.[3,12–14] The lower limit of the Mg^0 energy level in AlN is determined by the effective mass theory with values scattered between 0.42 and 0.80 eV, as indicated by the shaded region in Fig. 3, due to the uncertainty in the hole effective mass in AlN.[15,16] Our experimental value of $E_A=0.51$ eV is close to the lower limit values obtained by the effective mass theory. By using the experimentally determined value of $E_A=0.51$ eV and the low frequency dielectric constant of $\varepsilon=8.5$,[16,17] an average hole effective mass m_h^* of about $2.7m_0$ in AlN is estimated, which agrees well with several previous calculations.[9,18,19] The value of m_h^* in GaN is determined to be about 0.46 m_0 by using $m_h^{\parallel}=2.03\ m_0$ and $m_h^{\perp}=0.33\ m_0$.[20] The larger m_h^* in AlN suggests a smaller hole mobility in AlN than in GaN.

The determination of the Mg acceptor ionization energy in AlN together with previous experimental results enables us to complete the plot of the activation energy of Mg acceptor in Mg-doped $Al_xGa_{1-x}N$ as a function of the Al content x. The final result is presented in Fig. 4, in which the dotted line is the linear extrapolation of data from Ref. 3. The solid line is guide to the eyes by including the value in Mg-doped AlN obtained here.

With the value of Mg acceptor ionization energy being determined for AlN, we are able to address the issue regarding the possibility of achieving p-type AlN with Mg doping. As a consequence of the large value of $E_A=0.51$ eV, only a

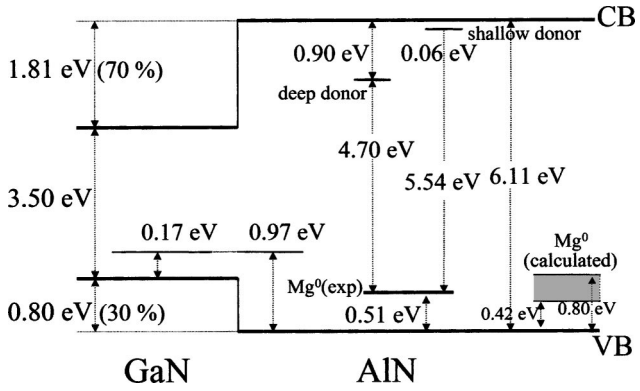

FIG. 3. Energy diagram showing the impurity levels, including Mg acceptor level, in AlN. The upper limit of Mg acceptor level in AlN is estimated to be about 0.97 eV by lining up its energy levels within the band gaps of GaN and AlN near the interface of an AlN/GaN heterojunction. The shaded region shows E_A predicted by the effective mass theory.

very small fraction ($e^{-E_A/kT}=e^{-0.51/0.025}=10^{-9}$) of the Mg dopants can contribute free holes for conduction at room temperature in Mg-doped AlN. This prevents the determination of any free hole concentrations by conventional measurements (such as Hall effect and capacitance–voltage). Based on the values of the Mg acceptor activation energies in $Al_xGa_{1-x}N$ shown in Fig. 4, we estimate the hole concentration (p) and resistivity (ρ) of Mg-doped $Al_xGa_{1-x}N$ as functions of the Al content x, for a Mg dopant concentration (N_A) of 10^{20} cm^{-3} and a hole mobility (μ_h) of 10 cm^2/V s. The resistivity of Mg-doped AlN, $\rho=(p\mu_h e)^{-1}$, is estimated to be as high as $\rho=3$ MΩ cm for a free hole concentration of $p=2\times10^{11}$ cm^{-3} and a mobility of $\mu_h=10$ cm^2/V s, which implies that it is extremely difficult to achieve p-type AlN by Mg doping. It is also interesting to point out that the binding energy of Mg acceptor (0.51 eV) is comparable to that of C acceptor (0.50 eV) in C-doped AlN.[21] It was reported previously that low resistive AlN epilayers could be achieved by C doping with a C fraction as high as 14% of AlN.[22,23] However, we believe that C can no longer be treated as dopants in that case because such high C concentrations should instead form AlCN alloys.

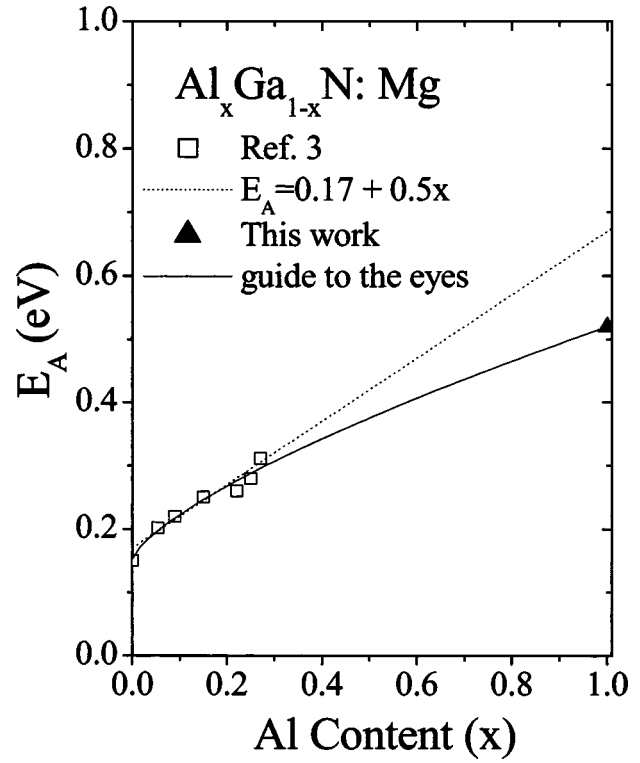

FIG. 4. Mg acceptor activation energy in Mg-doped $Al_xGa_{1-x}N$ as a function of the Al content (x). Closed squares are data from Ref. 3 and references therein, while the filled triangle is the data for AlN of this work. The dotted line is the linear extrapolation of data from Ref. 3 to $x=1$ and the solid line is a guide to the eyes.

In summary, we have investigated MOCVD growth and optical properties of Mg-doped AlN epilayers. Two emission lines at 4.70 and 5.54 eV were observed at 10 K, which were assigned to DAP transitions involving Mg acceptor and two different donors with different energy levels. These assignments have been confirmed by the time-resolved measurements at 10 K and the temperature dependence of the PL intensities. The binding energy of the Mg acceptor was obtained to be 0.51 eV. As a consequence of the large acceptor binding energy of $E_A=0.51$ eV, only a very small fraction ($\sim10^{-9}$) of Mg dopants can be activated at room temperature in Mg-doped AlN. The average hole effective mass (m_h^*) in AlN was deduced to be about 2.7 m_0 from the experimental value of E_A together with the use of the effective mass theory. The larger m_h^* in AlN also points to a smaller hole mobility in AlN than in GaN.

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