

Beryllium acceptor binding energy in AlN

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The acceptor binding energy of an alternative dopant, Be, in AlN epilayers has been probed by time-resolved photoluminescence (PL) spectroscopy. The binding energy of excitons bound to Be acceptors in AlN is determined to be about 33 meV, which implies that the Be acceptor binding energy in AlN is about 0.33 eV in accordance with Haynes' rule. The measured PL decay lifetimes of the acceptor-bound exciton transitions in Be- and Mg-doped AlN (93 and 119 ps, respectively) also indicate that the binding energy of Be acceptor is smaller than that of the most common acceptor dopant in AlN, namely, Mg. The smaller activation energy of Be in AlN has the potential to partly address the critical *p*-type doping issue in AlN- and Al-rich AlGa_xN by increasing the room temperature free hole concentration by $\sim 10^3$ compared to the case of Mg doping. © 2008 American Institute of Physics. [DOI: 10.1063/1.2996977]

Light sources such as light emitting diodes and laser diodes, and detectors operating in ultraviolet (UV) and deep UV (DUV) spectral region are of technological importance for ultrahigh-density optical data storage/readout and high resolution photolithography in micro- and nanofabrication technologies by extending the optical diffraction limit. Environmental science would also benefit from such sources and sensors in detecting minute hazardous particles, sterilization, and air/water purification. With a wide and direct band gap of ~ 6.1 eV and complete solubility with GaN (band gap ~ 3.4 eV) in the entire alloy composition range, AlN has emerged as an important semiconducting material for the fabrication of chip scale integratable DUV light sources and detectors.

In the past, AlN was considered to be an excellent insulator. But in recent years, with the advances in thin film growth techniques, the optical quality of undoped AlN epilayers has been demonstrated to be comparable to that of GaN.¹⁻³ Optoelectronic DUV devices require conductive *p*- and *n*-type AlN- and Al-rich AlGa_xN alloys. AlN epilayers with *n*-type conductivity with a reasonable free electron concentration (9.5×10^{16} to 7.4×10^{17} cm⁻³) have been obtained by Si doping by several groups,⁴⁻⁶ but the situation is quite challenging for *p*-type doping. Mg is the most commonly used *p*-type dopant in nitrides. Our group has previously achieved *p*-type conduction at room temperature in Mg-doped Al_xGa_{1-x}N for *x* up to 0.27.⁷ The resistivity of Mg-doped AlGa_xN is found to increase with Al content and becomes extremely high in Mg-doped AlN (~ 1 Ω cm in GaN to $>10^7$ Ω cm in AlN at 300 K) due to increased activation energy of Mg (~ 160 meV in GaN versus 510 meV in AlN)⁷⁻⁹ along with lower formation energy of donorlike native defects that act as hole compensating centers.¹⁰ We have also investigated Zn doping in AlN and experimentally confirmed that Zn is a deeper acceptor than Mg.¹¹ *p*-type conduction in Mg-doped Al_{0.70}Ga_{0.30}N and pure AlN was observable only at elevated temperatures (>700 K).^{12,13} Even

though there are a few reports on active devices based on pure AlN,¹⁴⁻¹⁶ the attainment of AlN with a controllable and reproducible room temperature *p*-type conductivity is still far from reality and it is a subject of intense research interest in the nitride community.

With Mg doping limited by saturation, assuming a maximum attainable doping concentration of $\sim 10^{20}$ cm⁻³, a maximum achievable free hole concentration (*p*) at room temperature in AlN would only be $\sim 10^{12}$ cm⁻³ [$p = N_A e^{-E_0/K_B T}$, where N_A is the doping concentration and E_0 (~ 0.51 eV) is the Mg activation energy], which may be further reduced by compensation. A previous calculation using effective mass theory has predicted that Be occupying Al site (Be_{Al}) in AlN acts as an acceptor with an activation energy of 0.26–0.47 eV.¹⁷ A more recent calculation also suggested a lower activation energy of Be_{Al} (~ 0.34 eV) than Mg_{Al}.¹⁸ The smaller activation energy of Be in AlN has the potential to partly address the *p*-type doping issue by increasing the room temperature free hole concentration. To date, no experimental results have been reported for the determination of the binding energy (BE) of Be acceptor in AlN. In this work, we report on the metal organic chemical vapor deposition (MOCVD) growth of Be-doped AlN and probing Be acceptor BE in AlN by time-resolved photoluminescence (PL).

The 0.5 μm thick Be-doped AlN epilayers were grown by low pressure MOCVD on (0001) *c*-plane oriented AlN/sapphire templates. The growth temperature and pressure were 1150 °C and 60 torr, respectively. A DUV time-resolved PL system was employed to investigate the energetic position and recombination lifetime of the acceptor-bound exciton transition (*I*₁) in Be-doped AlN. The PL system consists of a frequency quadrupled 100 fs Ti: sapphire laser with a 76 MHz repetition rate and excitation photon energy set around 6.30 eV. The PL signal was dispersed by a 1.3 m monochromator and detected by a streak camera.¹⁹

In Fig. 1, we plot the continuous-wave PL spectra of Be-doped AlN epilayers measured at 10 K in (a) a broad spectral range from 2 to 6.2 eV and in (b) a narrower spec-

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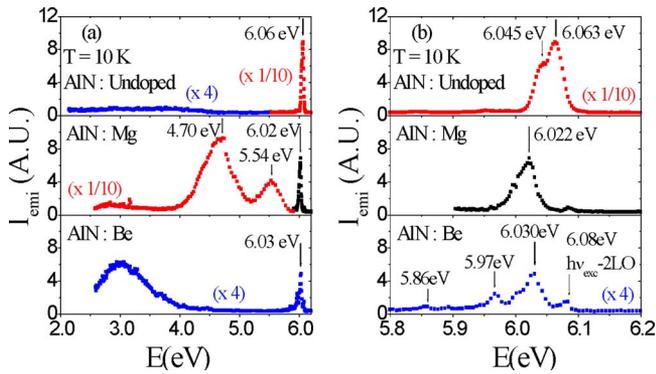


FIG. 1. (Color online) Low temperature (10 K) PL spectra of undoped, Mg-doped, and Be-doped AlN epilayers measured in (a) a broad spectral range from 2 to 6.2 eV and (b) a narrower spectral range from 5.8 to 6.2 eV.

tral range from 5.8 to 6.2 eV. PL spectra of undoped and Mg-doped AlN are plotted together for comparison. Two band-edge peaks are well resolved in undoped AlN with virtually no impurity related emission lines. We attribute in undoped AlN the dominant emission peak at 6.063 eV to the recombination of free exciton (FX) and the emission line at 6.045 eV (18 meV below the FX peak) to the donor-bound exciton transition (the I_2 line). The energy difference (18 meV) between the two peaks provides the BE of the donor-bound exciton in AlN, which agrees well with a previous reported value.²⁰

In the near-band-edge PL spectra of Mg-doped AlN epilayers, FX transition disappears and a new emission line with a peak position at 6.022 eV is observed, which is attributed to the recombination of excitons bound to neutral Mg acceptors (A_0, X) or the I_1 line in Mg-doped AlN.²¹ Weak emission lines at 6.08, 5.97, and 5.86 eV in Be-doped AlN are 2LO, 3LO, and 4 LO phonon replica of excitation laser (6.30 eV) with LO phonon energy of 110 meV in AlN. The emission peak at 6.030 eV in Be-doped AlN appears at a higher energy position (by 8 meV) than the I_1 transition in Mg-doped AlN. The temperature dependence of the 6.030 eV emission line follows that of the energy band gap. The spectral linewidth and shape are very similar to those of the I_1 transition in Mg-doped AlN. Therefore, we assign the emission line at a 6.030 eV peak in Be-doped AlN to the recombination of excitons bound to neutral Be impurities.

The energy difference between the FX peak position in undoped AlN and the I_1 line in Be-doped AlN gives the BE of the excitons bound to Be impurities to be 33 meV ($=6.063-6.030$ eV). According to Haynes' rule, the BE of the exciton-neutral impurity complex is about 10% of the impurity BE, neglecting the central cell correction.²² The I_1 spectral peak position measurement thus implies that Be acceptor BE is about 0.33 eV, which agrees quite well with the calculation value of ~ 0.34 eV for the substitutional Be at the Al site.¹⁸ In the case of Mg-doped AlN, the BE of the acceptor-bound exciton is about 41 meV ($=6.063-6.022$ eV), which is very close to the previously reported values of 40 meV (Ref. 18) and 8 meV larger than that of the Be acceptor-bound exciton in AlN. Based on Haynes' rule, our results suggest that the Be acceptor level is about 80–150 meV shallower than that of the Mg in AlN.

The temperature dependence of the PL intensity of the I_1 transition on Be-doped AlN has been measured, which is

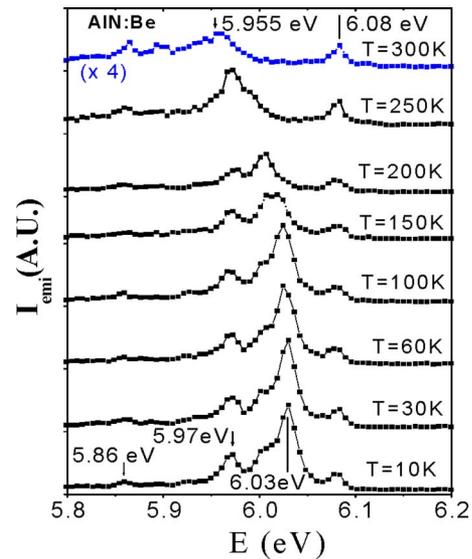


FIG. 2. (Color online) Temperature dependence of the I_1 transition on Be-doped AlN epilayers measured from 10 to 300 K.

shown in Fig. 2. The general trends of decreasing the PL intensity and redshifting the emission peak position with temperature are evident. The decrease in the I_1 intensity is due to the dissociation of acceptor-bound exciton into the neutral acceptor (A^0) and free-exciton (X) following $A^0X \rightarrow A^0+X$. Figure 3 shows the Arrhenius plot of the I_1 emission intensity and the solid line is the least squares fit of the data with the equation

$$I(T) = \frac{I_0}{1 + Ce^{-E_0/K_B T}} \quad (1)$$

Here I_0 represents the PL intensity at 10 K. The fitted value of E_0 , the activation energy of the I_1 emission intensity, is around 36 meV, which measures the BE of the acceptor-bound exciton in Be-doped AlN and is in good agreement

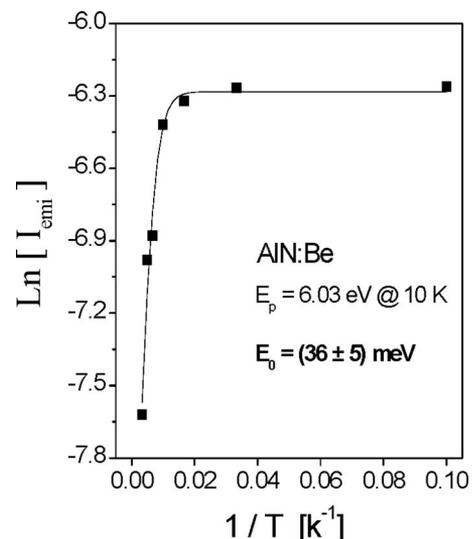


FIG. 3. Arrhenius plot of the PL intensity [$\ln(I_{\text{emi}})$ vs $1/T$] in Be-doped AlN epilayers in the temperature range from 10 to 300 K. We have excluded the PL intensity at 250 K because of the overlap of the I_1 peak position with 3LO phonon of excitation laser. The solid line represents the least squares fit of the data with Eq. (1).

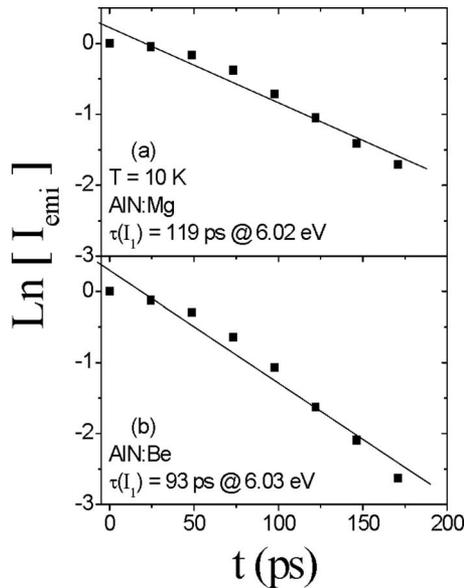


FIG. 4. Temporal responses of the I_1 transition in (a) Mg- and (b) Be-doped AlN epilayers measured at 10 K. The measured decay lifetimes were 119 and 93 ps for Mg- and Be-doped AlN epilayers, respectively.

with a value of 33 meV obtained from the spectral peak measurement of Fig. 1.

Figure 4 shows the temporal response of the I_1 transitions in Be- and Mg-doped AlN epilayers. The measured decay lifetimes of the I_1 transitions in Be- and Mg-doped AlN are 93 and 119 ps, respectively. The relation between the oscillator strength of the impurity-bound exciton (F) and the free exciton (F_{ex}) is expressed as^{23,24}

$$F = (E_0/E_{bx})^{3/2} F_{ex}, \quad (2)$$

where E_{bx} is the BE of the impurity-bound exciton and E_0 is the BE of the free exciton. The ratio between the decay lifetimes of the I_1 transition in Be- and Mg-doped AlN can thus be obtained as

$$\begin{aligned} \tau_{I_1}(\text{Be})/\tau_{I_1}(\text{Mg}) &= F_{I_1}(\text{Mg})/F_{I_1}(\text{Be}) \\ &= [E_{bx}(\text{Be})/E_{bx}(\text{Mg})]^{3/2}. \end{aligned}$$

$[E_{bx}(\text{Be})/E_{bx}(\text{Mg})]^{3/2}$ lies within 0.72–0.85 and is in agreement with the ratio of (93 ps/119 ps)=0.78 of the measured decay lifetimes. Time-resolved PL results are thus further corroborating our conclusion that the Be acceptor energy level in AlN is shallower than that of Mg.

In summary, Be-doped AlN epilayers were grown by MOCVD and their optical properties were investigated by time-resolved DUV PL. Be impurity related acceptor-bound exciton transition is observed at 6.03 eV with a BE of about 33 meV, which indicates that the Be level in AlN is about 80–150 meV shallower than Mg. Our additional experimental data from temperature dependent PL and decay lifetime

measurements of the I_1 transition provided a coherent picture to support the fact that the Be energy level is shallower than that of Mg in AlN. As our Be-doped AlN layers are highly resistive at this point, direct transition from free electron to neutral Be acceptor could not be observed, which would have provided a direct measure of the energy level of Be_{Al} acceptor in AlN. Much more work is required to obtain Be-doped AlN epilayers that exhibit a higher p -type conductivity than Mg-doped layers.

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