Growth and photoluminescence studies of Zn-doped AlN epilayers

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Deep ultraviolet time-resolved photoluminescence (PL) spectroscopy has been employed to study Zn-doped AlN epilayers grown by metal-organic chemical vapor deposition. The PL spectra of Zn-doped AlN epilayer exhibited two impurity emission lines at 5.40 and 4.50 eV, which were absent in undoped epilayers and assigned to the transitions of free electrons and electrons bound to nitrogen vacancies with three positive charges (0.90 eV deep) to the Zn^0 acceptors. By comparing PL spectra of Zn- and Mg-doped AlN epilayers with undoped epilayers, it was deduced that Zn energy level is about 0.74 eV, which is about 0.23 eV deeper than the Mg energy level (0.51 eV) in AlN. It is thus concluded that contrary to theoretical prediction, Zn would not be a better candidate than Mg as an acceptor dopant in AlN. © *2006 American Institute of Physics.*
[DOI: 10.1063/1.2387869]

AlN is emerging as an active semiconductor material due to the recent development of high quality AlN epilayer growth on sapphire, SiC, and AlN bulk substrates. Because of its large direct band gap ($\sim$6.1 eV), AlN can be used for the development of optoelectronic devices operating from 200 to 350 nm by alloying with GaN. A recent demonstration of an AlN light emitting diode with emission wavelength at 210 nm has shown its high potential for obtaining optoelectronic devices active in the ultraviolet *C*-band (UVC) spectral range.[1] Potential applications of compact light sources and detectors operating in the UVC spectral region range from sterilization, bioagent detection, and acoustic sound wave devices, to x-ray detectors.[2–5]

For the applications of AlN as an active material, conductive *n*- and *p*-type materials are required. While *n*-type AlN epilayers with reasonable conductivities have been achieved by Si doping,[6–9] *p*-type conductivity is extremely difficult to obtain due to the large activation energy of Mg acceptors. GaN with *p*-type conductivity can be reproducibly grown by metal-organic chemical vapor deposition (MOCVD) by Mg doping and subsequent annealing.[10] The activation energy of Mg is about 160 meV in GaN, increases with Al content in AlGaN alloys, and is about 0.51 eV in AlN.[11–14] Zn elements have been previously utilized as *p*-type dopants in GaN,[15] which, however, rendered semi-insulating materials. The binding energy of Zn in GaN is about 0.34 eV, as determined by optical measurements.[15–17] A previous calculation predicted that Zn occupies Al site in AlN and the activation energy of Zn acceptor in AlN is in the range of 0.22–0.44 eV,[18] which is significantly smaller than that of Mg in AlN. Since the free hole concentration increases exponentially with a decrease of the acceptor activation energy, any strategies that have the potential to reduce the activation energies of acceptors in AlN are worth pursuing. In this letter, we report on the growth and photoluminescence (PL) studies of Zn-doped AlN epilayers.

Zn-doped AlN epilayers of thickness $\sim$1 μm were grown by MOCVD. Prior to the growth of Zn-doped layer, a 0.5 μm thick undoped AlN epilayer was first grown on sapphire substrate as a template and was then followed by the growth of Zn-doped AlN. Trimethyl aluminum and blue ammonia were used as aluminum and nitrogen sources, respectively. Dimethyl zinc was used as Zn source. The Zn dopant concentration was on the order of 10^{20} cm^{-3} as determined by secondary ion mass spectrometry measurement. The growth temperature and pressure were 1200 °C and 40 torr, respectively. Hall-effect measurements were attempted to measure the conductivity of Zn-doped AlN epilayers. However, as-grown epilayers were highly resistive. Furthermore, subsequent postgrowth annealing of Zn-doped AlN in nitrogen ambient did not result in *p*-type conduction. Deep UV PL spectroscopy[19] was employed to study the optical properties of Zn-doped AlN.

Low temperature (10 K) PL spectra of Zn- and Mg-doped AlN and undoped AlN epilayers are shown in Fig. 1. The PL spectrum of undoped AlN exhibits a strong band edge emission at 6.06 eV due to the free exciton[20] (FX) transition and virtually no impurity transitions. Since FX binding energy in AlN is around 0.08 eV,[21,22] the band gap of AlN at 10 K is thus around 6.14 eV ($\approx$6.06 eV+0.08 eV). The
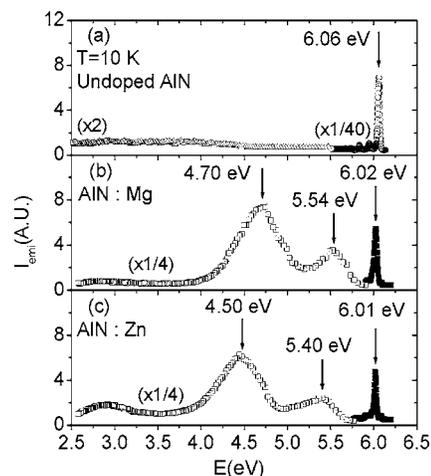
FIG. 1. PL spectra of (a) undoped, (b) Mg-doped, and (c) Zn-doped AlN epilayers measured at 10 K. For the Mg-(Zn-) doped AlN epilayers, the band edge transition at 6.06 eV disappears and a new band edge emission line is observed at 6.02 (6.01) eV. Additional impurity emission lines observed in Mg-(Zn-) doped AlN at 4.70 (4.50) and 5.54 (5.40) eV are related with Mg (Zn) acceptor impurities.

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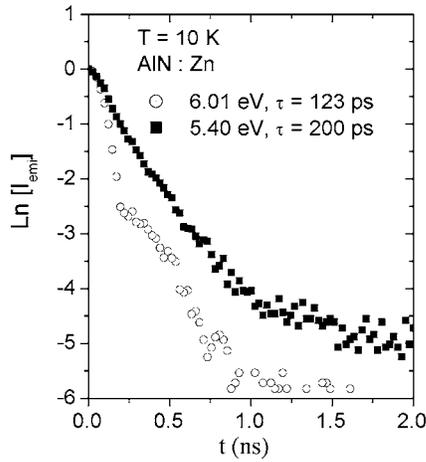
FIG. 2. Temporal responses of the I_1 and 5.40 eV emission lines in Zn-doped AlN epilayers measured at 10 K.

FIG. 3. Energy diagram showing the energy levels of Mg and Zn acceptors in AlN. Zn energy level in GaN is also included.

PL spectrum of Mg-doped AlN comprises a band edge transition at 6.02 eV due to the recombination of excitons bound to neutral Mg acceptors (I_1 transition). Two additional impurity emission lines at 4.70 and 5.54 eV in Mg-doped AlN are also observable and believed to be donor-acceptor-pair (DAP) transitions involving two different donors (deep and shallow level donors) and Mg acceptor.[14] The deep level donors participated in the 4.70 eV transition in Mg-doped AlN were identified as nitrogen vacancies with three positive charges (V_N^{3+}) that act as compensating centers for p-type doping.[23]

Compared to the PL spectrum of Mg-doped AlN, the PL spectrum of Zn-doped AlN has a very similar line shape, however, with the two impurity transitions redshifted to 4.50 and 5.40 eV (with respect to 4.70 and 5.54 eV in Mg-doped AlN). The band edge emission line at 6.01 eV in Zn-doped AlN can be indisputably assigned to the recombination of excitons bound to neutral Zn acceptors (I_1 transition). The measured recombination lifetime of the 4.50 eV emission line is rather long (~ 1 μs) and is comparable to that of the 4.70 eV line in Mg-doped AlN. Based on the assignment of the 4.70 eV emission line in Mg-doped AlN, we assign the emission line at 4.50 eV in Zn-doped AlN to a DAP transition of electrons bounded to nitrogen vacancies with three positive charges (V_N^{3+}) to neutral Zn acceptors, which is consistent with the measured long recombination lifetime. The width of the V_N^{3+} related emission line is very broad, which is comparable to those of the cation vacancy (V_{cation}) related emission lines in Si-doped AlN (Ref. 24) and is a typical characteristic of deep level impurity transitions. The binding energy of V_N^{3+} in AlN has been calculated to be about 0.9 eV,[25] from which an energy level for Zn acceptors in AlN is thus deduced to be about 0.74 eV ($E_A \approx 6.14$ eV -4.50 eV -0.90 eV $=0.74$ eV) with neglecting Coulomb interactions between the ionized acceptors and donors.

Figure 2 shows the temporal responses of the I_1 transition at 6.01 eV and the impurity transition at 5.40 eV in Zn-doped AlN epilayer measured at 10 K, which revealed a roughly single exponential decay kinetics with a decay time constant of about 123 ps for the I_1 transition and 200 ps for the 5.40 eV impurity transition. The measured decay time constant of I_1 is comparable to a value of 130 ps observed in Mg-doped AlN.[20] The recombination lifetime of 200 ps ob-

served for the 5.40 eV emission line in Zn-doped AlN is rather short, which seems to suggest that it is of a band-to-impurity type of transition. Based on this, we assign the 5.40 eV emission peak to the transition of free electrons to neutral Zn acceptors (Zn^0), although a DAP type of transition involving a shallow donor and Zn^0 cannot be totally precluded. This assignment provides an energy level of Zn acceptors in AlN to be $E_A \approx 6.14$ eV -5.40 eV $=0.74$ eV, which agrees with the value deduced from the energy position of the 4.50 eV emission line discussed above. It is worth noting that the identified origins of the two impurity transitions at 5.40 and 4.50 eV in Zn-doped AlN provide an identical activation energy of 0.74 eV for Zn acceptors in AlN, which offers confidence in our assignments. Our results thus point to the fact that the energy level of Zn is about 0.23 eV deeper than that of Mg in AlN (0.51 eV). The energy levels related to Zn acceptors and corresponding transitions in AlN are shown in Fig. 3. Optically measured Zn level in GaN is also indicated in Fig. 3.[15,16]
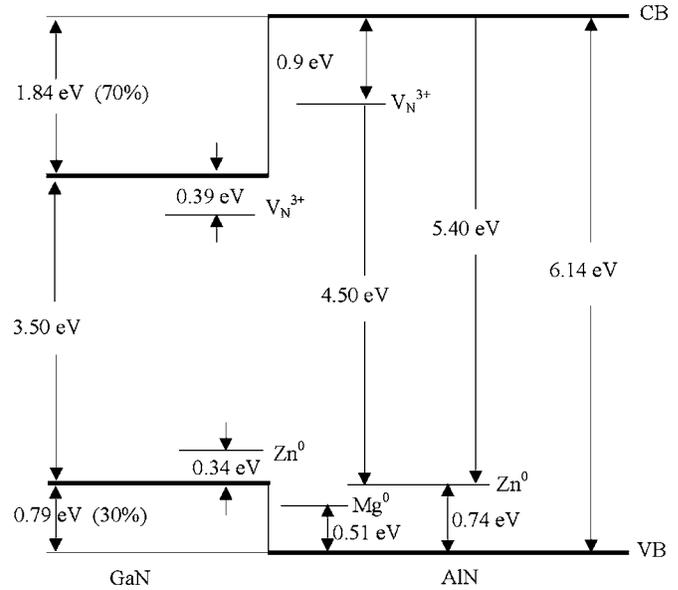
To determine the binding energy of the Zn acceptor bound exciton in AlN, we have measured the temperature dependence of the I_1 emission intensity in Zn-doped AlN and the result is shown in the inset of Fig. 4. The spectral peak position is redshifted with increasing temperature following the variation of the band gap. The thermal quenching of the I_1 transition is due to the dissociation of neutral acceptor bound excitons in Zn-doped AlN. Figure 4 shows the Arrhenius plot of the I_1 emission intensity in Zn-doped AlN. The solid line is the least-squares fit of the data with equation

$$I_{emi} = \frac{I_0}{1 + ce^{(-E_{BX}/KT)}}, \tag{1}$$

where c is a constant and E_{BX} is the binding energy of neutral Zn acceptor bound excitons in AlN. The fitted value of E_{BX} is 50 meV and is consistent with the value obtained from the difference between the spectral peak positions of FX in undoped AlN and I_1 in Zn-doped AlN epilayers (6.06 eV -6.01 eV $=0.05$ eV). Experimentally measured binding energy of neutral Mg acceptor bound excitons in
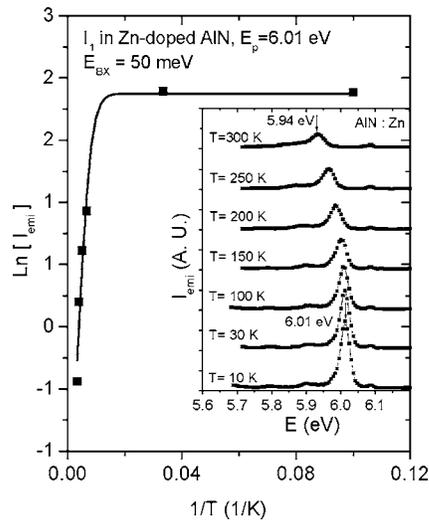
FIG. 4. Arrhenius plot of the integrated PL emission intensity of the I_1 emission peak in Zn-doped AlN between 10 and 300 K. The solid line is the least-squares fit of data with Eq. (1). The fitted value of the binding energy of neutral acceptor bound exciton I_1 (E_{BX}) is also indicated. The inset is the temperature evolution of PL spectra of Zn-doped AlN epilayer measured from 10 to 300 K.

AlN is about 0.04 eV.[20] From Haynes' rule,[26] the larger E_{BX} value in Zn-doped AlN compared to that in Mg-doped AlN also hints a deeper energy level of Zn than Mg in AlN.

In summary, Zn-doped AlN epilayers were grown by MOCVD and their optical properties were probed by deep UV time-resolved PL. Zn related impurity transitions were observed at 5.40 and 4.50 eV in Zn-doped AlN, which are absent on undoped AlN layers. By comparing the PL spectra of Zn- and Mg-doped and undoped AlN epilayers, the energy level of Zn acceptor in AlN was deduced to be about 0.74 eV, which is about 0.23 eV deeper than the Mg level in AlN. Contrary to a previous theoretical prediction, our results thus suggest that Zn is not a better candidate than Mg as a *p*-type dopant in AlN. More theoretical and experimental investigations are required to further understand doping issues in AlN, particularly pertaining to *p*-type doping. Besides the search for suitable acceptor elements, innovative doping methods also need to be developed to bring a breakthrough in this field.

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