Acceptor-bound exciton transition in Mg-doped AlN epilayer

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Mg-doped AlN epilayers grown by metalorganic chemical-vapor deposition have been studied by deep ultraviolet time-resolved photoluminescence (PL) spectroscopy. A PL emission line at 6.02 eV has been observed at 10 K in Mg-doped AlN, which is about 40 meV below the free-exciton transition in undoped AlN epilayer. Temperature dependence of the PL intensity of this emission line also reveals a binding energy of 40 meV. This transition line is believed to be due to the recombination of an exciton bound to neutral Mg acceptor (I_1) with a binding energy of E_{bx} =40 meV. This value is also about 10% of the energy level of Mg impurity in AlN satisfying Haynes' rule. The recombination lifetime of the I_1 transition in Mg-doped AlN has been measured to be 130 ps, which is close to the expected value. The larger E_{bx} of the acceptor-bound exciton in AlN than that in GaN is due to large effective masses of the electrons and holes, as well as the energy level of Mg impurity. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1796521]

Aluminum nitride (AlN), a group-III nitride semiconductor of direct band gap 6.1 eV, is emerging as an important semiconductor due to its applications in light emitters, laser diodes (LDs), and other optoelectronic devices. It has high mechanical hardness, high thermal conductivity, large dielectric constant, and high resistance to harsh environments.[1] By alloying AlN with GaN, the band gap changes systematically from 3.4 to 6.1 eV. For device applications, conductive AlN and $Al_xGa_{1-x}N$ with high x are essential. P-type doping in $Al_xGa_{1-x}N$ has been proven to be extremely difficult, due to high activation energy of Mg dopant as well as reduced crystalline quality of the alloys. The resistivity of Mg-doped $Al_xGa_{1-x}N$, ρ, was found to increase with increasing x and it is expected to be extremely high in Mg-doped AlN. Our group has obtained p-type $Al_xGa_{1-x}N$ alloys with x up to 0.27 with Mg doping.[2] The electric properties of Mg-doped $Al_xGa_{1-x}N$ alloys with higher $x(>27\%)$ has not been reported. Our group has also grown high optical quality AlN epilayers on sapphire substrate by metalorganic chemical vapor deposition (MOCVD).[3] Binding energy and recombination lifetime of free exciton (FX) and donor-bound exciton (I_2) have been determined previously in undoped AlN epilayer.[4] A photoluminescence (PL) study on Si-doped AlN has found the I_2 transition to be the dominant emission line at low temperatures.[5] We have also studied optical transition lines involving Mg in AlN from which the Mg impurity binding energy in AlN was obtained.[6] However, excitonic transitions in Mg-doped AlN were not observed.

In this letter, we report on the observation and optical studies of neutral acceptor-bound exciton (I_1) transition in Mg-doped AlN epilayers by deep UV time-resolved PL. The recombination lifetime and the binding energy of the I_1 transition in the Mg-doped AlN have been measured. The measured values in AlN are also compared with those in Mg-doped GaN.

The 1-μm-thick Mg-doped AlN epilayers were grown by MOCVD on sapphire (0001) substrates with low-temperature AlN nucleation layers.[6] Trimethylaluminum and blue ammonia (NH_3) were used as Al and N sources. For Mg doping, bis-cylopentadienylmagnesium (Cp_2Mg) was used as a Mg source. Secondary ion mass spectroscopy measurements (performed by Charles Evans & Associates) revealed that Mg-dopant concentration was about 6×10^{18} cm^{-3} in Mg-doped AlN epilayer. Atomic force microscope (AFM) and scanning electron microscope (SEM) were used to characterize the surface morphology of these epilayers. Structural characterization was done with x-ray diffraction (XRD) measurement. Full width at half maximum (FWHM) of XRD rocking curve of (0002) peak of as-grown AlN epilayers was between 50 and 300 arc sec. Deep UV time-resolved PL spectroscopy was employed to investigate the sample. The PL system consists of a frequency quadrupled 100 fsec Ti: sapphire laser with an average power of 3 mW with excitation photon energy set at 6.28 eV (repetition rate of 76 MHz), 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.[7]

Figure 1 compares the low-temperature (10 K) PL spectra of (a) undoped and (b) Mg-doped AlN epilayers. The arrows indicate the peak positions of the spectra. The un-

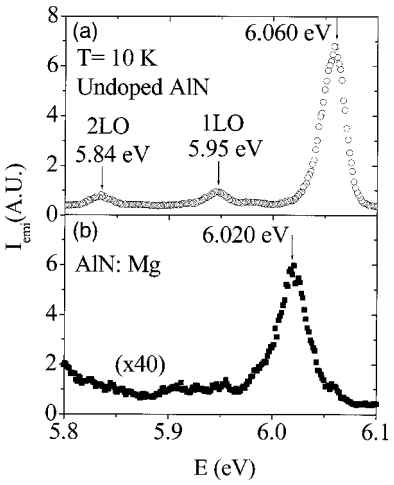

FIG. 1. PL spectra of (a) undoped AlN and (b) Mg-doped AlN epilayer measured at 10 K. For the Mg-doped AlN epilayer, the transition at 6.06 eV disappears and a new emission line is observed at 6.02 eV.

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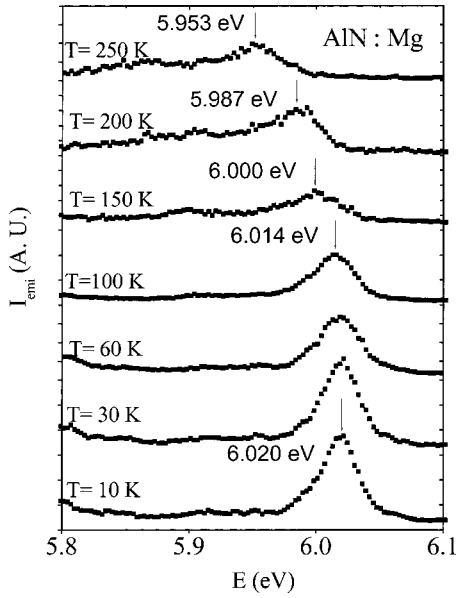

FIG. 2. PL spectra of Mg-doped AlN epilayer measured from 10 to 250 K.

doped AlN epilayers exhibit a strong band-edge emission line at 6.06 eV, due to FX transition and its longitudinal optical (LO) phonon replica at 5.95 eV(1 LO) and 5.84 eV(2 LO), with a LO phonon energy of 110 meV. As undoped GaN is *n* type, the neutral donor-bond exciton (I_2) transition is often dominant at low temperatures. However, undoped AlN is highly insulating due partly to the presence of native defects, such as Al vacancy or vacancy complex, which are deep acceptors and act as compensating centers for electrons. Thus, in undoped AlN, there is either a very low concentration of neutral donors, D^0 (if $D^0 > A^0$), or no D^0 at all (if $D^0 < A^0$) at low temperatures, and FX would be dominant due to large binding energy of FX.

For the Mg-doped AlN epilayer, a new emission line with a peak position at 6.02 eV is evident, which is attributed to excitons bound to the neutral Mg acceptor impurities (A^0,X) or the I_1 line in AlN. The intensity of this new emission line is about 40 times smaller than that of FX transition in undoped epilayer. The new emission line in Mg-doped AlN is 40 meV below the FX transition in undoped AlN, which corresponds to the binding energy, E_{bx}, of the I_1 transition in AlN. This value is about two times larger than that of I_1 in Mg-doped GaN(E_{bx}[(GaN)=20.0–21.5 meV].[8] Mg-doped AlN epilayers were thermally annealed in nitrogen ambient up to 1325 °C; however, the peak position of the I_1 transition is almost the same when compared with as-grown samples.

Temperature evolution of the 6.02 eV emission line in the Mg-doped AlN epilayer measured from 10 to 250 K is shown in Fig. 2. The intensity decreases monotonically and the spectral peak position of this emission line is redshifted with increasing temperature. The thermal quenching of the I_1 transition is due to the dissociation of neutral acceptor-bound exciton described by

$$(A^0,X) \rightarrow A^0 + X, \tag{1}$$

where A^0 and X are neutral acceptor and free exciton, respectively.

Figure 3 shows the Arrhenius plot of the PL intensity of the 6.02 eV emission line for the temperature range between 10 and 250 K. The solid line is the least-squares fit of the data with equation

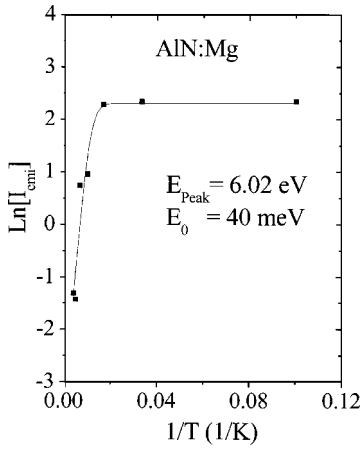

FIG. 3. The Arrhenius plot of the integrated PL emission intensity at 6.02 eV(10 K) between 10 and 250 K. The solid line is the least-squares fit of data with Eq. (2). The fitted value of the activation energy (E_0) is also indicated.

$$I_{emi} = \frac{I_0}{1 + ce^{-E_0/KT}}, \tag{2}$$

where c is a constant. The fitted value is E_0=40 meV and is consistent with the value obtained from the difference between the peak position of FX in undoped AlN and the I_1 peak position in Mg-doped AlN epilayers. This value of activation energy is in rough agreement with Haynes' rule; for Mg-doped AlN the binding energy of the exciton-neutral-impurity complex is about 10% of the impurity binding energy if we neglect the central-cell correction.[9] Using Haynes' rule, the expected energy level of Mg impurity in AlN is 400 meV, which is close to our reported value of 510 meV.[6] The binding energy of 20 meV for the I_1 transition in GaN is also roughly about 10% of the energy level for Mg impurity.

Time-resolved PL was employed to measure the recombination lifetime of the I_1 transition at 6.02 eV, which is shown in Fig. 4. The measurement reveals that the decay kinetics was a single exponential with a decay lifetime constant about 130 ps at 10 K, which is about three to five times shorter than the PL decay lifetime of the I_1 transition in GaN (370–660 ps).[8]

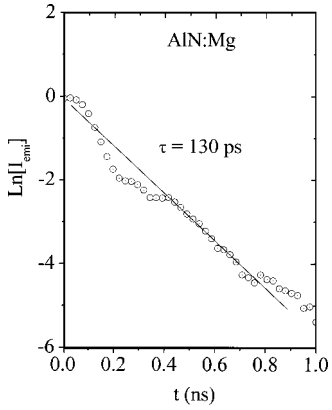

FIG. 4. Temporal response of the I_1 transition in Mg-doped AlN epilayer measured at 10 K. Observed recombination lifetime is 130 ps.

TABLE I. Binding energy (in meV) and decay lifetime (in ps) of the fundamental transitions as well as energy levels (in meV) of Si donor and Mg acceptor impurities in AlN and GaN.

	E_{FX}	$E_{bx}(I_1)$	$E_{bx}(I_2)$	E_A	E_D	τ_{FX}	$\tau(I_1)$	$\tau(I_2)$
GaN	20–25	20-21	6-7	160–180	25–29	50–350	370–660	35–100
AlN	80	40	16	510	86	50	130	80
AlN/GaN	3.6–4.0	2.0	2.6	3.2	3.4	1.0–0.1	0.4–0.2	2.3–0.8

The relation between the oscillator strength of the impurity-bound exciton (F) and the free excitons (F_{eX})is[10]

$$F = \left(E_0/E_{bx}\right)^{\frac{3}{2}} F_{eX}, \tag{3}$$

where E_{bx} is the binding energy of the impurity-bound excitons, $E_0=(2\eta^2/m)(\pi/\Omega_0)^{2/3}$, m is the effective mass of the FX, and Ω_0 is the volume of the unit cell. From Eq. (3), we thus have the ratio of radiative decay lifetime of I_1 and I_2 transitions as

$$\tau(I_1)/\tau(I_2) = F(I_2)/F(I_1) = \left(E_{bx}(I_1)/E_{bx}(I_2)\right)^{\frac{3}{2}}. \tag{4}$$

From Eq. (4), the ratio $\tau(I_1)/\tau(I_2)=3.9$ is obtained by using the binding energy of I_1 and I_2 transitions in AlN as 40 and 16 meV,[4] respectively. The decay lifetime of the I_2 transition in Si-doped AlN decreases from 80 to about 40 ps with increasing Si concentration (N_{Si}) from 1.5×10^{17} to 1.5×10^{18} cm^{-3}.[5] If we use 80 (40)ps as the lifetime for the I_2 transition in Si-doped AlN, we get the expected lifetime of 312 (158) ps for the I_1 transition in Mg-doped AlN, which is close to the observed value of 130 ps. The trend of increased decay lifetime with increased binding energy is also clearly demonstrated.

Table I displays the binding energy and lifetime of FX, I_1, and I_2 transitions in AlN and GaN. The table summarizes the results of this work and a survey of references.[4–16] Energy levels of Mg acceptor and Si donor in AlN and GaN are also listed. All parameters in AlN are almost a factor of 2–3 times larger than that in GaN. Decay lifetimes of excitonic transitions in AlN are larger compared to GaN, due to the increased effective masses of electrons and holes.

In summary, MOCVD-grown Mg-doped AlN epilayers have been studied by deep UV time-resolved PL. An emission line at 6.02 eV has been observed, which was absent in undoped AlN epilayers and is 40 meV below the FX transition in undoped AlN. This emission line is due to the recombination of the exciton bound to neutral Mg acceptor transition (I_1) in AlN. This assignment has been confirmed by the time-resolved measurement at 10 K and the temperature dependence of the PL intensities. Measured binding energy of exciton bound to Mg impurity in AlN is 40 meV, which is twice as that in GaN, as expected with larger effective masses of electrons and holes in AlN than in GaN. The measured PL decay lifetime of the I_1 transition in Mg-doped AlN is 130 ps.

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