Time-resolved photoluminescence studies of Mg-doped AlN epilayers

N. Nepal, M. L. Nakarmi, J. Y. Lin, and H. X. Jiang[a)]

Department of Physics, Kansas State University, Manhattan, KS 66506-2601

ABSTRACT

Mg-doped AlN epilayers grown by metalorganic chemical vapor deposition have been studied by deep UV 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 (FX) transition in undoped AlN epilayer. Temperature dependent measurement 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, E_{bx} of 40 meV. The recombination lifetime of the I_1 transition in Mg doped AlN have been measured to be 130 ps, which is close to the expected value. Excitation intensity dependence of time-resolved PL for Mg-doped AlN epilayer is also measured to understand carrier and exciton dynamics.

Keywords: Mg-doped AlN, time-resolved PL, exciton, lifetime, carrier dynamics, ultrafast spectroscopy

1. INTRODUCTION

AlN with a bandgap 6.1 eV is emerging as an important semiconductor due to its applications in ultraviolet (UV) 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 environment[1]. AlN is unique due to the fact that no other semiconductor possesses such a large direct bandgap as well as the ability of bandgap engineering through the use of heterostructures. By alloying AlN with GaN, the band-gap changes systematically from 3.4 to 6.1 eV, that can be used to tune the wavelength of optoelectronic devices in UV and deep UV spectral ranges. 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 $Al_xGa_{1-x}N$ 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]. We have obtained a room temperature resistivity of around 10^5 Ωcm for $Al_{0.7}Ga_{0.3}N$ and confirmed p-type conduction at elevated temperatures (>700 K) with a resitivity of 40 Ωcm at 800 K [3]. Our group has grown high optical quality AlN epilayers on sapphire substrate by metalorganic chemical vapor deposition (MOCVD)[4]. Very efficient bandedge PL emission lines have been observed with above bandgap excitation. Binding energy and recombination lifetime of free exciton (FX) and donor-bound exciton (I_2) have been determined previously in undoped AlN epilayer [5]. A photoluminescence (PL) study on Si-doped AlN has found that the I_2 transition to be the dominant emission line at low temperatures[6]. We also have studied transition lines involving Mg in AlN from which energy level of Mg impurity in AlN was obtained [7]. However, excitonic transitions in Mg-doped AlN were not observed and the dominant transitions were donor-acceptor pair (DAP) type involving Mg acceptors and two donors, one shallow and another deep. Significant improvement in material quality of Al-rich Si- and Mg-doped $Al_xGa_{1-x}N$ alloys allowed us to investigate the fundamentally important optical processes as well as basic parameters in $Al_xGa_{1-x}N$ alloys with high x [3-7].

Due to high insulating nature of Mg-doped Al-rich $Al_xGa_{1-x}N$ alloys, PL is proven to be a powerful characterization method to study optical properties of these materials. Understanding optical properties not only helps to characterize materials but also is very useful to probe their fundamental properties. We report on optical studies of Mg-doped AlN epilayers by deep UV time-resolved PL. Recombination lifetime and binding energy of the neutral acceptor-bound exciton (I_1) transition in Mg-doped AlN have been measured. The measured values in AlN are compared with those in Mg-doped GaN. We also measured the decay lifetimes of impurity transitions in Mg-doped AlN epilayers.

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2. EXPERIMENT

The 1 μm thick Mg-doped AlN epilayers were grown by MOCVD on sapphire (0001) substrates with low temperature AlN nucleation layers [7]. Trimethylaluminum (TMAl) and blue ammonia (NH_3) were used as Al and N sources. For Mg doping, bis-cylopentadienylmagnesium (Cp_2Mg) was used as 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 to 300 arcsec. Deep UV time-resolved PL spectroscopy was employed to investigate the sample. The PL system consists of a frequency quadrupled 100 femtosecond 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 – 800 nm and a time resolution of 2 ps [8].

3. RESULTS AND DISCUSSIONS

Figure 1 shows the low temperature (10 K) PL spectra of (a) undoped and (b) Mg-doped AlN epilayers covering a broad spectral range from 2.4 to 6.2 eV. The arrows indicate the peak positions of the spectra. The undoped AlN epilayers exhibit a strong band-edge emission line at 6.06 eV due to FX transition and its second order at 3.03 eV due to grating of the monochromator, however Mg-doped AlN has two broad and intense impurity emission lines at 4.70 and 5.55 eV and a weak bandedge transition at 6.02 eV. Impurity transition at 4.7 eV is several orders stronger than the bandedge transition in Mg-doped AlN. It was observed that the optical and electrical quality of Mg-doped AlN depends strongly on the growth conditions.

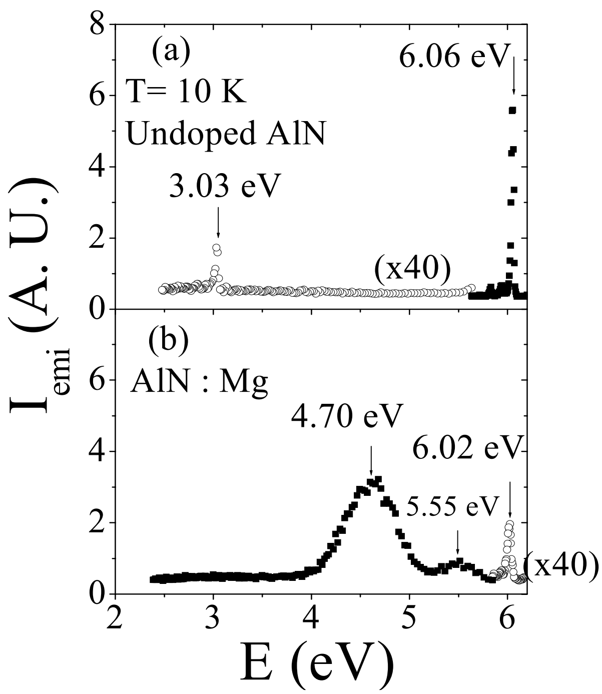

Fig. 1. PL spectra of (a) undoped AlN and (b) Mg-dope Mg-doped AlN epilayer measured at 10 K which covers a broad spectral range from 2.4 to 6.2 eV. Mg-doped AlN has two broad impurity emission lines at 4.70 and 5.55 eV.

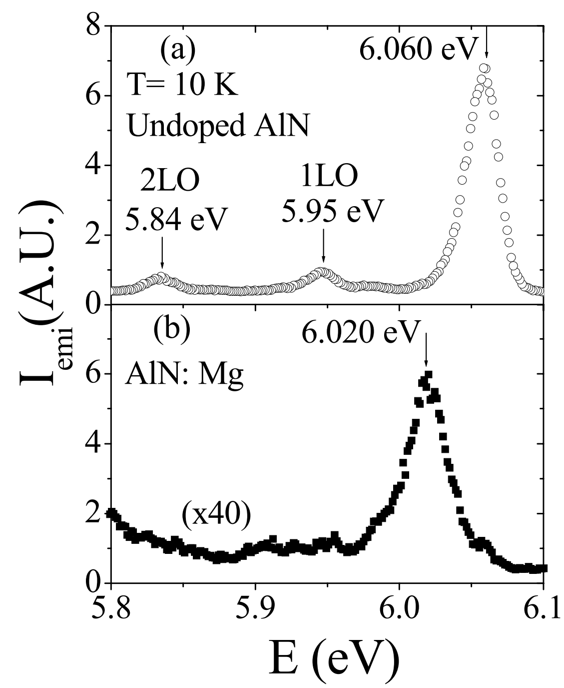

Fig. 2. PL spectra of (a) undoped AlN and (b) Mg-doped AlN epilayer measured at 10 K in the small spectral range. For the Mg-doped AlN epilayer, the transition at 6.06 eV disappears and a new emission line at 6.02 eV appears.

Figure 2 compares the low temperature (10 K) PL spectra of (a) undoped and (b) Mg-doped AlN epilayers in the smaller spectral range. The undoped 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 LO phonon energy of 110 meV. As undoped GaN is n-type, the neutral donor-bound 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 very low concentration of neutral donor; 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, the 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 I_1 line in AlN. With Mg doping, the I_1 transition is expected to be dominant instead of FX, which is consistent with the results. The intensity of this new emission line is about 50 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] [9]. 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.

The 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. 3. 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 dissociation of neutral acceptor-bound exciton described by

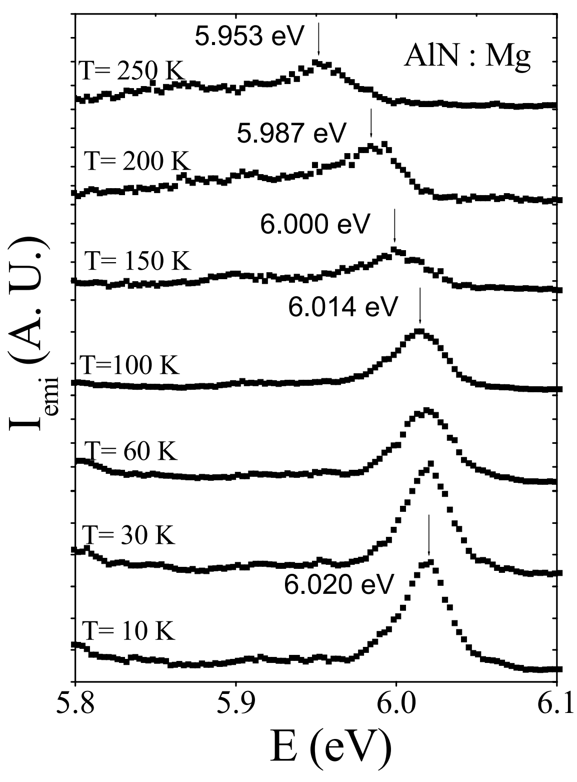

Fig. 3. PL spectra of Mg-doped AlN epilayer measured from 10 to 250 K.

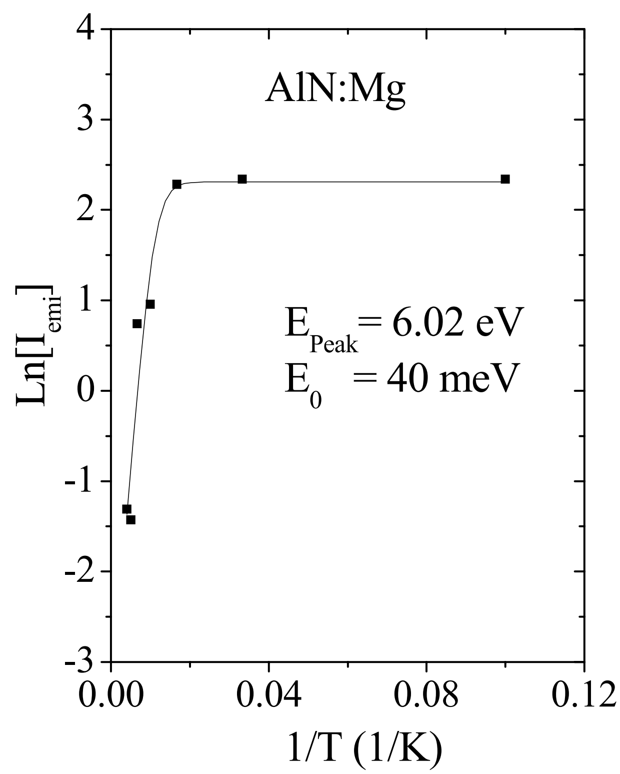

Fig. 4. The Arrhenius plot of the integrated PL emission intensity at 6.02 eV (10 K) between 10 and 250 K. The solid line is the least squares fit of data with Eq. (2). The fitted vale of the activation energy (E_0) is also indicated.

$$(A^0,X) \longrightarrow A^0 + X, \qquad (1)$$

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

Figure 4 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

$$I_{emi} = \frac{I_0}{1 + c e^{-E_0/KT}}, \qquad (2)$$

where c is a constant. The fitted value of E_0 is 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 a 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 [10]. Using Haynes' rule, the expected energy level of Mg impurity in AlN is 400 meV, which is close to our reported value of 500 meV [7]. The binding energy of 20 meV for the I_1 transition in Mg-doped GaN is also roughly about 10% of the energy level for Mg impurity (~ 170 meV).

Time-resolved PL was employed to measure the recombination lifetime of the I_1 transition at 6.02 eV, which is shown in Fig. 5. The measurement reveals that the decay kinetics was a single exponential with a decay lifetime constant of about 130 ps at 10 K, which is about three to five times smaller than the PL decay lifetime of the I_1 transition in GaN (370 - 660 ps) [9].

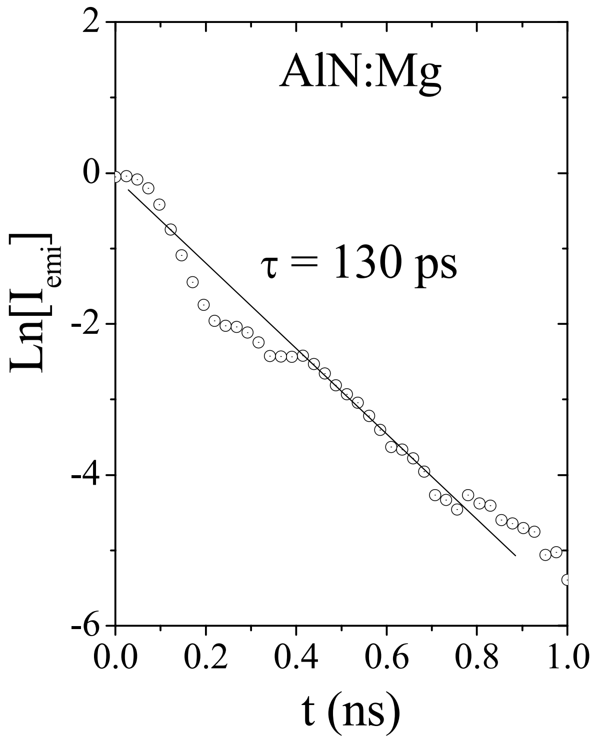

Fig. 5. Temporal response of the I_1 transition in Mg-doped AlN epilayer measured at 10 K. Observed recombination lifetime is 130 ps.

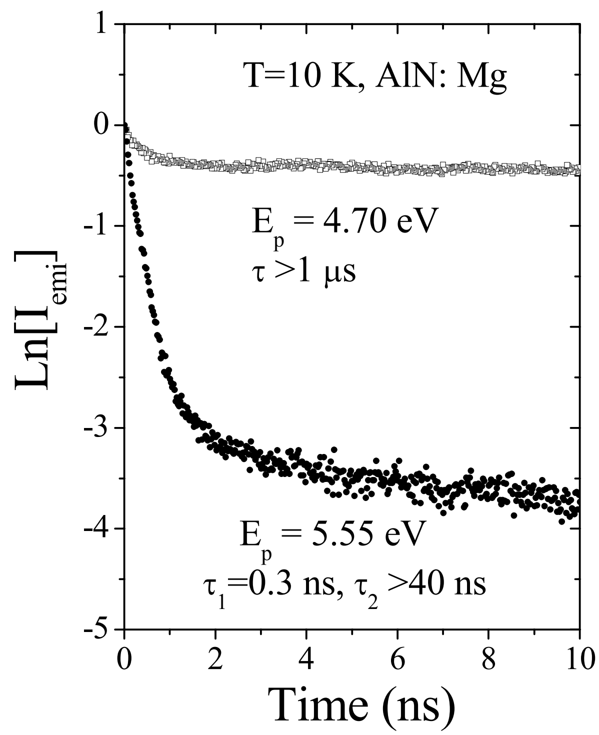

Fig. 6. Temporal response of the 5.55 eV and 4.7 eV emission peaks in Mg-doped AlN epilayer measured at 10 K. τ >1 μs for E_p = 4.70 eV and lifetime of 5.55 eV emission peak is two-exponential.

The relation between the oscillator strength of the impurity-bound exciton (F) and the free excitons (F_{eX}) is [11]

$$F = \left(E_1 / E_{bx} \right)^{\frac{3}{2}} F_{eX} \,, \tag{3}$$

where E_{bx} is the binding energy of the impurity-bound excitons, $E_1 = (2\hbar^2 / m)(\pi / \Omega_0)^{2/3}$, 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 [5], 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 $1.5\text{x}10^{17}$ to $1.5\text{x}10^{18}$ cm^{-3} [6]. If we use 80 (40) ps as the decay 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 in reasonable agreement with the observed value of 130 ps. The trend of increased decay lifetime with increased binding energy is also clearly demonstrated.

Temporal response of the 5.55 and 4.7 eV emission peaks in Mg-doped AlN epilayer measured at 10 K is shown in Fig. 6. Decay lifetime of 5.55 eV peak is two exponential while 4.7 eV peak has a very long decay lifetime. The emission peak at 5.55 eV has been assigned to the free electrons to the neutral Mg level transition [12]. Observed two exponential decay of 5.55 eV peak with one very short lifetime and another very long lifetime supports this assignment. Very long (`> 1μm) decay lifetime of 4.70 eV peak in Mg-doped AlN indicates that it is DAP type transition involving deep donor and neutral magnesium, which is consistent with our previous results [7, 12]. We previously attributed the 4.70 eV peak to be the transition from nitrogen vacancy with positive three-charge state (V_N^{3+}) to the neutral magnesium level [12]. Suppressing the 4.70 eV emission peak and increasing the intensity of I_1 transition improves the optical and electrical quality of the Mg-doped AlGaN alloys. Conductive Al-rich $Al_xGa_{1-x}N$ alloy of x = 0.7 has been obtained by suppressing V_N^{3+} related transition [3]. Time-resolved PL has been used as a characterization tool to characterize and hence improve Mg-doped AlN epilayers and the resistivity of about (1 - 5)$\text{x}10^3$ Ωcm was measured at room temperature [12].

In Fig. 7 we plot the decay lifetimes of the I_1 transition as a function of relative excitation intensity I_{exc} measured at 10 K. The lifetime decreases as the excitation intensity increases. We attribute the observed behavior to the exciton–exciton interaction, however, such an interaction is absent at low exciton densities. The radiative quantum efficiency η is given by,

$$\eta = \frac{1}{1 + \tau_r / \tau_n} \tag{5}$$

where τ_r and τ_n are radiative and non radiative recombination lifetimes, respectively. Our results show that η is enhanced under the influence of the exciton-exciton interaction through decreasing τ_r with I_{exc} and the PL quantum yield increases superlinearly with I_{exc} in Mg-doped AlN. Similar results have been observed for FX transition in GaN[13,14]. At the lowest excitation intensity, the recombination lifetime of I_1 transition in Mg-doped AlN is about 172 ps.

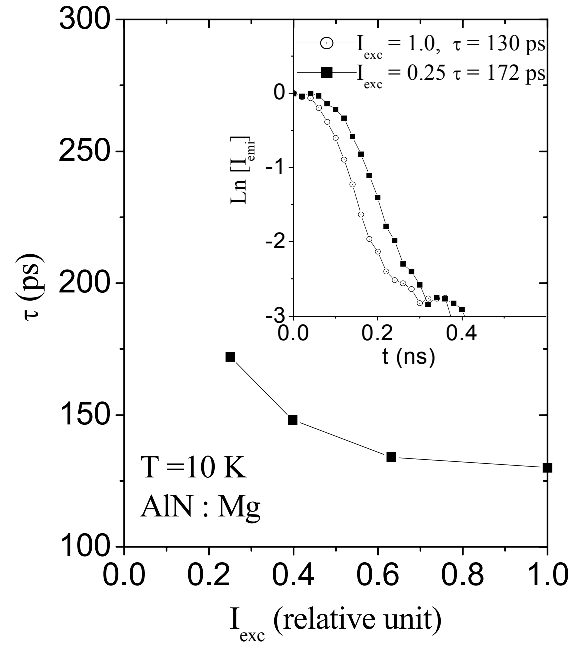

Fig. 8. Excitation intensity, I_{exc} dependence of the recombination lifetimes of the I_1 transition in Mg-doped AlN. Inset shows the temporal responses of the I_1 transition measured at two representative excitation intensities for I_{exc} =1 and I_{exc} = 0.25.

Table I displays the binding energy and decay 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 [5--19]. 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 smaller compared to GaN, which is due to large bandgap and increased effective masses of electrons and holes.

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}	τ (I_1)	τ (I_2)
GaN	20-25	20-21	6-7	160-180	25-29	50-350	370-660	35-100
AlN	80	**40**	16	500	80 -250	50	**130**	80
AlN/GaN	3.6-4.0	2.0	2.6	3.1	3.2 – 8.6	1.0-0.1	0.4-0.2	2.3-0.8

4. SUMMARY

MOCVD grown Mg-doped AlN epilayers have been studied by deep UV time-resolved PL spectroscopy. 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 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 that is twice as that in GaN, as expected with larger effective masses of electrons and holes in AlN than in GaN. The observed large acceptor-bound exciton binding energy implies that excitons in AlN are extremely robust entities. The measured PL decay lifetime of the I_1 transition in Mg-doped AlN is 130 ps. The decay lifetime increases with decreasing excitation intensity, which indicates that the PL quantum yield increases with increasing excitation intensity.

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(a) Eectronic mail: jiang@phys.ksu.edu

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