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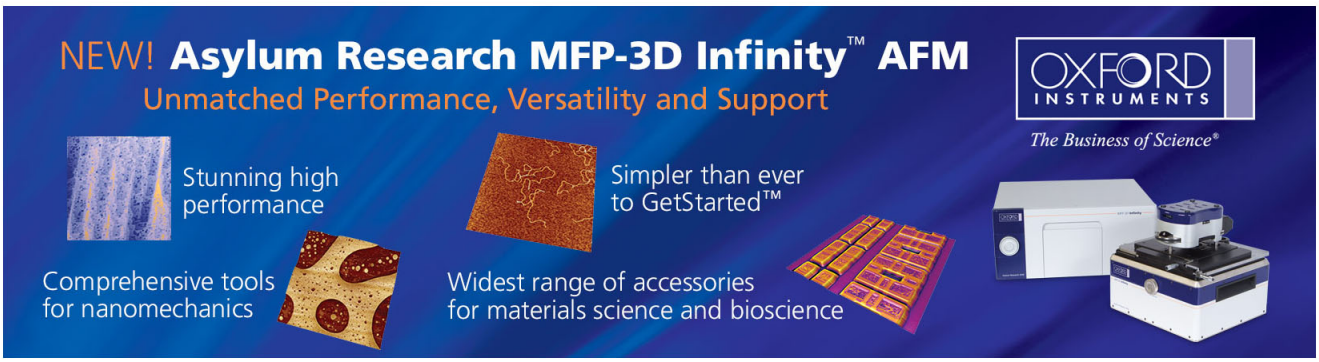

Deep ultraviolet picosecond time-resolved photoluminescence studies of AlN epilayers

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AlN epilayers with high optical qualities have been obtained 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 AlN epilayers. Two PL emission lines associated with the donor bound exciton (D^0X, or I_2) and free exciton (FX) transitions have been observed, from which the binding energy of the donor bound excitons in AlN epilayers was determined to be around 16 meV. Time-resolved PL measurements revealed that the recombination lifetimes of the I_2 and free exciton transitions in AlN epilayers were around 80 and 50 ps, respectively. The temperature dependencies of the free exciton radiative decay lifetime and emission intensity were investigated, from which a value of about 80 meV for the free exciton binding energy in AlN epilayer was deduced. This value is believed to be the largest free exciton binding energy ever reported in semiconductors, implying excitons in AlN are an extremely robust system that would survive well above room temperature. This together with other well-known physical properties of AlN may considerably expand future prospects for the application of III-nitride materials. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1559659]

Recently, AlGaN alloys, particularly Al rich AlGaN alloys have attracted much interest due to their applications in solid-state UV light sources for bioagent detection as well as for general lighting. AlN has many attractive properties,[1,2] such as high mechanical hardness and thermal conductivity, large dielectric constant, and high resistance to harsh environments. Moreover, AlN is unique due to the fact that no other semiconductor possesses such a large direct band gap as well as the ability of band gap engineering through the use of heterostructures.

In spite of the recognition of the importance of AlN, many of its fundamental optical emission properties, particularly the recombination dynamics associated with the fundamental optical transitions in AlN, are still unknown due to the lack of high quality materials as well as technical difficulties involved for the deep UV (down to 200 nm) time-resolved photoluminescence (PL) measurements. Recently, our group has obtained AlN epilayers with high optical qualities on sapphire substrates by metalorganic chemical vapor deposition (MOCVD). Very efficient band edge PL emission lines have been observed with above band gap deep UV laser excitation.[3] We have also developed a unique deep UV picosecond time-resolved optical spectroscopy system for probing the emission properties of III nitrides with high Al contents with a time-resolution of a few picoseconds and wavelength down to deep UV (195 nm) to cover pure AlN.[4]

In this letter, we present the deep UV picosecond time-resolved PL results of fundamental optical transitions in AlN epilayers. Two band edge emission lines were observed at 10 K and were assigned to the donor bound exciton (I_2) and free exciton (FX) transitions, respectively. The recombination lifetimes were also measured for the I_2 and FX transitions at different temperatures; from which the binding energies associated with the donor bound excitons and free excitons in AlN epilayers have been deduced.

The 1-μm-thick AlN epilayers were grown by MOCVD on sapphire (0001) substrates with low temperature AlN nucleation layers. Trimethylaluminum and NH_3 were used as Al and N sources. Atomic force microscopy studies upon the AlN epilayers revealed smooth surfaces (with a typically 1 nm roughness across a 2 μm$\times$2 μm scanning area) free of cracks. The deep UV picosecond time-resolved laser spectroscopy system used here basically 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), a streak camera with a detection capability ranging from 185 to 800 nm, and a time resolution of 2 ps.[4,5]

Figure 1 shows the low temperature (10 K) PL spectrum for an AlN epilayer. Two emission peaks are well resolved, and the spectral shapes can be described by Gaussian functions. The dominant emission line at 6.015 eV is attributed to the neutral donor-bound-exciton recombination (D^0X) or I_2. A second emission line at the higher energy side around 6.031 eV is also clearly resolved, which is attributed to free-exciton transition (FX). The emission spectral line shape resembles those of GaN epilayers in which both free- and bound-excitons emission lines were present.[6,7] The separation between the two peaks is around 16 meV, which corresponds to the binding energy of I_2, E_{bx}, in AlN epilayer. This value is about 2.5 times larger than in GaN (E_{bx}=6–7 meV).[6–10] This enhanced binding energy of the donor bound exciton in AlN is attributed to the fact that the free exciton binding energy, E_x, in AlN is larger than that in GaN due to the larger effective masses of electrons and holes in AlN. The full widths at half maxima (FWHM) of the emission lines indicated are 15.5 and 12.5 meV for the I_2 and FX transi-

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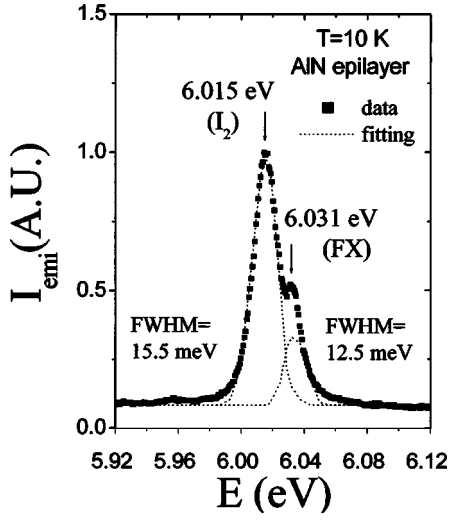

FIG. 1. Low-temperature (10 K) cw PL spectrum of an AlN epilayer grown on sapphire.

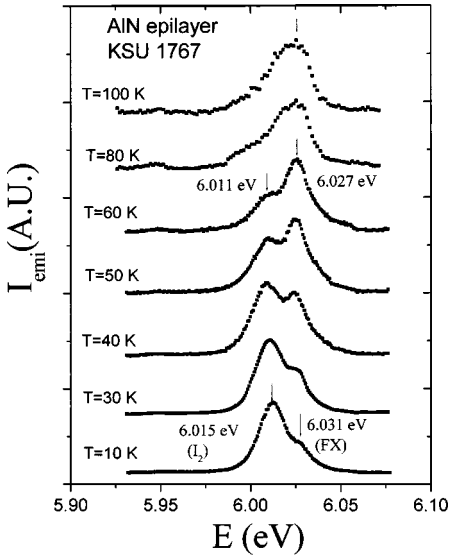

FIG. 2. PL spectra measured at different temperatures for an AlN epilayer. The arrows indicate the PL spectral peak positions of the bound exciton (I_2) and free exciton (FX) transition lines.

tions, respectively, which are larger than those in GaN epilayers.[6–9]

The temperature evolution of the time-integrated PL spectra is shown in Fig. 2. Other than the larger separation energy between the I_2 and FX emission lines seen in AlN than in GaN (16 vs 6 meV), the temperature variation of the PL spectra of AlN shown here is very similar to that of GaN epilayers.[10–12] The PL intensity of the bound exciton transition decreases with temperature more rapidly than that of the FX transition, which is expected because the donor bound excitons dissociate into free excitons (FX) and neutral donors D^0, ($D^0X \rightarrow FX + D^0$).

The temporal responses of the I_2 and FX recombination lines were measured at their respective spectral peak positions at 10 K as displayed in Fig. 3. The decay lifetimes were found to be around 80 ps for I_2 and 50 ps for FX transition at $T=10$ K. The bound exciton lifetime in AlN is slightly shorter than the approximately 100 ps reported for GaN epilayers.[6–8] Values ranging from 50 to 350 ps for the lifetime of free excitons in GaN epilayers depending on the purity and crystalline quality of the materials have been reported.[6–8] We believe that the observed low temperature free exciton lifetime of 50 ps is predominantly the radiative recombination lifetime in AlN.

Figure 4(a) plots the decay lifetime (τ_{eff}) of the I_2 transition line as a function of the emission energy (E_{emi}) measured at $T=10$ K. The decay lifetime decreases monotonically from 102 ps at $E=6.004$ eV to 78 ps at $E=6.027$ eV. Similar behaviors have been observed for the I_2 and I_1 (acceptor bound exciton) transition lines in GaN epilayers,[13,14] which was attributed to the existence of a distribution of the binding energy of the bound exciton. The measured decay lifetime of the FX transition is almost independent of E_{emi}. Figure 4(b) exhibits the temperature dependence of the recombination lifetime of the I_2 and FX transitions measured at their respective spectral peak positions. Decay lifetimes of both I_2 and FX transitions decrease with increasing temperature; however, the FX decay lifetime decreases slower than the I_2 transition, which corroborates the results shown in Fig. 2—the bound exciton dissociates first into a neutral donor and a free exciton with increasing temperature.

The radiative recombination lifetime of free excitons, τ_{rad}, can be obtained from the measured decay lifetimes (τ_{eff}) and quantum efficiency, $\eta = I_{\text{emi}}(T)/I_{\text{emi}}(0)$, with the assumption that the radiative recombination is the dominant process at low temperature, where $I_{\text{emi}}(T)$ and $I_{\text{emi}}(0)$ are the PL emission intensities at temperature T and 0 K, respectively. The radiative lifetime (τ_{rad}) can be obtained from the following equation:[15]

$$\tau_{\text{rad}} = \tau_{\text{eff}}/\eta. \tag{1}$$

By taking $I_{\text{emi}}(0) \approx I_{\text{emi}}$ (10 K), we have obtained the temperature dependence of τ_{rad} for AlN epilayers for $T>100$ K, as shown in Fig. 5. From Fig. 2, the process of the bound exciton dissociation into FX transition affects the measured decay lifetime and quantum efficiency largely at $T<100$ K. As shown in Fig. 5, τ_{rad} increases with T according to $T^{3/2}$ in the temperature range of $100<T<200$ K for AlN, a well known feature of free excitons or free carriers in semiconductors.[16] A similar behavior has been observed in

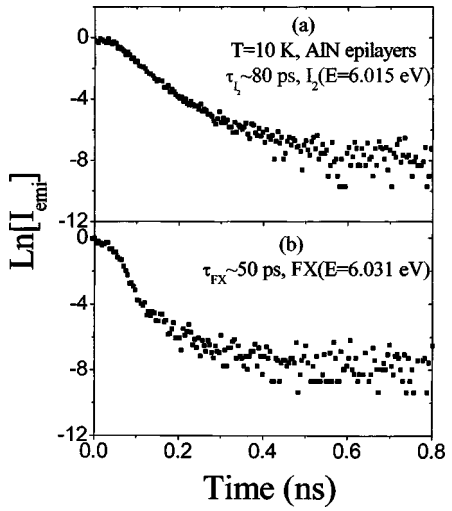

FIG. 3. Temporal responses of PL emissions measured at 10 K at the bound exciton and free exciton spectral peak positions in an AlN epilayer.

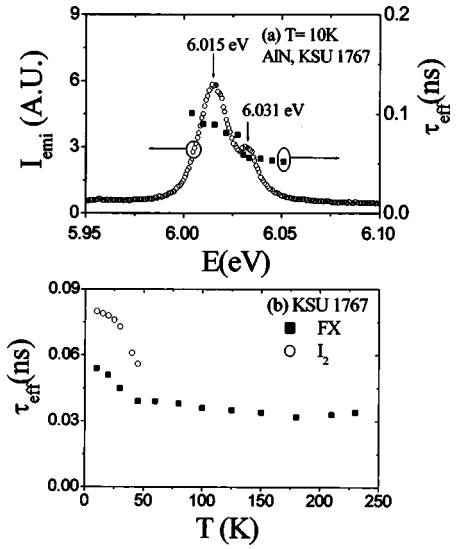

FIG. 4. (a) Emission energy dependence of the decay lifetime of the bound exciton and free exciton transition lines in an AlN epilayer measured at 10 K. The time-integrated emission spectrum is also included. (b) Temperature dependence of the recombination lifetime of the bound and free excitons measured at their respective spectral peak positions.

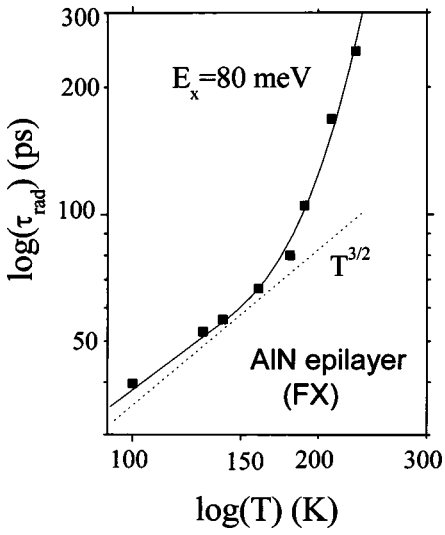

FIG. 5. Temperature dependence of the radiative decay lifetime of free excitons in AlN. The solid line is the fit based on a theory of free exciton dissociation in Ref. 15.

GaN between 50 and 100 K.[15] The temperature range for the relation $\tau_{\mathrm{rad}} \propto T^{3/2}$ to hold in AlN is higher than in GaN, which is due to a larger binding energy of the bound exciton in AlN. At temperatures higher than 200 K, the measured decay lifetime of *FX* transition is dominated by the dissociation of free excitons. However, the *FX* transition can be observed and is the dominant transition at room temperature.

The observed temperature dependence of τ_{rad} shown in Fig. 5 corresponds very well to a theory based on free exciton dissociation (solid line),[15] from which a free exciton binding energy of $E_x = 80$ meV is deduced for AlN. This value also agrees fairly well with the thermal activation energy of the free exciton emission line obtained by measuring the temperature dependent free exciton emission intensity at higher temperatures, i.e., the slope of the $\ln(I_{\mathrm{emi}})$ vs $1/T$ plot. We believe this value represents the largest free exciton binding energy ever observed in semiconductors and implies that the excitons are highly robust in AlN, which could have a great significance upon deep UV photonic device applications based on AlN. From the peak position of *FX* transition line at 6.031 eV at 10 K, the energy gap of AlN (E_g) is thus deduced to be around 6.11 eV at 10 K, which is lower than the better-known value of 6.2 eV obtained from the optical absorption measurements at room temperature.[1]

In summary, we have investigated the optical properties of the band edge transitions in AlN epilayers by using deep UV picosecond time-resolved PL measurements. The bound exciton (I_2) and free exciton (FX) transitions in AlN epilayers were well resolved and their recombination dynamics have been probed. The PL decay lifetimes were found to be around 80 ps for the bound exciton and 50 ps for the free exciton at 10 K in AlN epilayers, which are shorter than those in GaN. The extrapolated radiative decay lifetimes in AlN epilayers increases with temperature according to $T^{3/2}$ between 100 and 200 K and are affected by the free exciton dissociation at temperatures above 200 K, following the same trend as GaN. From the low temperature (10 K) emission spectra, the temperature dependence of the recombination lifetime, and the PL emission intensity activation energy, the binding energies of the bound excitons and free excitons in AlN were deduced to be around 16 and 80 meV, respectively. From this, the energy band gap of AlN epilayers grown on sapphire was found to be around 6.11 eV at 10 K. The observed large free exciton binding energy implies that excitons in AlN are extremely robust entities.

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