Epitaxial Growth and Time-Resolved Photoluminescence Studies of AlN Epilayers

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ABSTRACT

AlN epilayers with high optical qualities have been grown on sapphire substrates by metal organic chemical vapor deposition (MOCVD). Deep ultraviolet (UV) photoluminescence (PL) spectroscopy has been employed to probe the optical quality as well as optical transitions in the grown 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 ps 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. The PL emission properties of AlN have been compared with those of GaN. It was shown that the optical quality as well as quantum efficiency of AlN epilayers is as good as that of GaN. It was shown that the thermal quenching of PL emission intensity is greatly reduced in AlN over GaN, which suggests that the detrimental effect of impurities and dislocations or non-radiative recombination channels in AlN is much less severe than in GaN. The observed physical properties of AlN may considerably expand future prospects for the application of III-nitride materials.

Key words: AlN, wide bandgap semiconductors, time-resolved photoluminescence, excitons, UV light emitters

1. BACKGROUND

Tremendous progress has been made for III-nitrides research and development in terms of both fundamental understanding as well as devices applications. However, the materials we understand relatively well include only the binary GaN and ternary alloys In(Al)GaN with In (Al) content less than 30% (50%). Recently, AlGaN alloys, particularly Al rich AlGaN alloys have attracted much interest due to their applications in solid-state UV light sources for bio-agent detection as well as for general lighting. AlN is an end point of the AlGaN alloy system. A full understanding for the AlGaN alloy system, particularly Al rich AlGaN alloys could not be achieved before the binary AlN material is well understood. 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 bandgap as well as the ability of bandgap engineering through the use of heterostructures.

Currently there is a great need of solid-state ultraviolet (UV) emitters for many applications, including next generation lighting and chem-bio-agent detections. In such applications based on III-nitride wide bandgap semiconductors, both n-type and p-type high quality AlGaN alloys with high Al contents are indispensable. However, achieving device quality AlGaN with high conductivities and quantum wells with high Al-contents remains as one of the foremost challenging tasks for the Nitride community. In particular, our knowledge concerning the optical properties of AlN is very scarce, despite its importance for fundamental understanding of wide band gap semiconductor properties as well as for device applications. Band-edge PL emission lines in AlN have not been reported previously due to the lack of high quality materials as well as technical difficulties involved

in the deep UV (down to 200 nm) PL measurements. As a consequence, very little is known of all fundamentally important optical transitions in AlN. The reported bandgap and optical data were mostly obtained through the optical absorption measurements [3]. Although band-edge emission lines near 6.0 eV have been observed in AlN at room temperature by cathodoluminescence (CL) measurement [4,5], the broad feature of the emission bands (linewidth larger than 100 meV) due to the presence of high concentration of defects/impurities as well as the use of the high-energy electron beam excitation made the identify of the transition mechanisms in AlN epilayers very difficult.

With its large direct bandgap of about 6.1 eV at room temperature, high thermal conductivity and hardness, and high resistance to chemicals [1], AlN has many other attractive features [2]. For example, AlN has applications for surface acoustic wave (SAW) devices because of its piezoelectric properties [6]. It is needless to say that the future applicability of AlN devices depends on the development of methods for producing high quality materials and device structures as well as on the full understanding of the basic properties of this material. From the materials growth point of view, feedbacks from different materials characterization techniques are essential for achieving further improvements in materials quality. Due to its insulating nature, electrical characterization methods such as Hall effect measurement, which has been extremely effective for optimizing GaN growth, is no longer applicable to AlN. It has also been difficult to characterize the optical properties of AlN due to its wide bandgap. Although X-ray diffraction measurement can provide information about crystalline quality, it provides very little information about electrical and optical qualities of AlN epilayers. Because of our unique optical measurement capabilities for working with AlN [7,8], for the first time, we are equipped with "eyes" for monitoring the optical quality, as well as for probing the fundamental optical properties of AlN. In this paper, we summarize recent experimental results of epitaxil growth and time-resolved PL studies of AlN obtained by our group. High quality AlN epilayers that emit exciton PL emission have been obtained by metal organic chemical vapor deposition (MOCVD) [9]. 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 [10].

2. Experiment

The 1 μm thick AlN epilayers were grown by MOCVD on sapphire (0001) substrates with low temperature AlN nucleation layers. Trimethylaluminum (TMAl) and NH_3 were used as Al and N sources. X-ray diffraction measurements (XRD) revealed that the full width at half-maximum (FWHM) of the AlN (0002) rocking curves varied from 150 to 500 arcsec, which are among those best values reported in the literatures for AlN epilayers [5,11,12]. Atomic force microscopy (AFM) studies upon the AlN epilayers revealed smooth surfaces (with a typically 1 nm roughness across a 2 μm^2 scanning area) free of cracks [13]. For PL measurements carried out on AlN, a specially designed deep UV laser spectroscopy system was utilized, which basically consists of a quadrupled 100 femtosecond Ti:sapphire laser together with a streak camera, providing an excitation power of about 3 mW at 196 nm (with a 76 MHz repetition rate and a 3 mW average power) [7]. The streak camera has a detection capability ranging from 185 – 800 nm and a time resolution of 2 ps. For GaN, in addition to the 196 nm deep UV laser, a second laser system with excitation wavelength tunable from 285 nm to 320 nm was also used as an excitation source. This second laser system consisted of a cavity-dumped dye laser with 6G dye solutions, which was pumped by a YAG laser with a frequency doubler, while the output of the dye laser was frequency doubled again to provide a tunability from 285 – 320 nm [7]. The PL results of GaN obtained by the two laser systems of different excitation wavelengths are similar. For example, the ratio of the PL emission intensity at room temperature to that at 10 K in GaN obtained by the two laser systems of different excitation wavelengths was the about same. Hence we believe that the effect due to the variation in optical absorption depth as a result of the use of different excitation wavelengths or different materials (AlN versus GaN) is negligibly small.

3. Results and Discussion

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 [14,15]. 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) [14-17]. 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 transitions, respectively, which are larger than those in GaN epilayers [14-17].
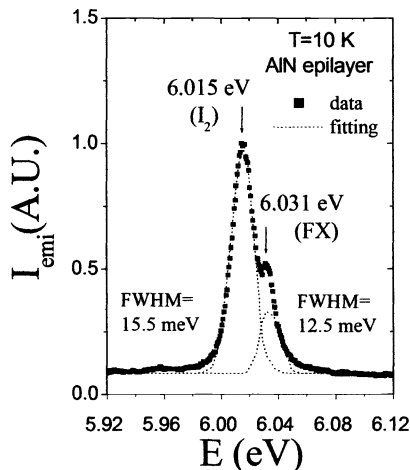

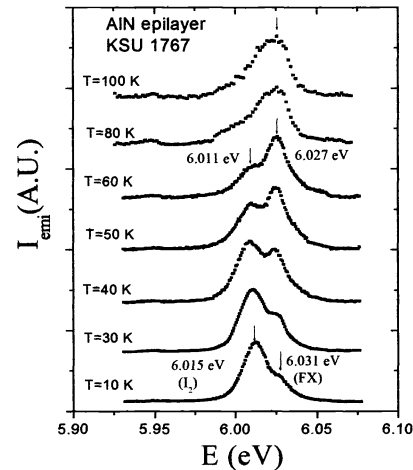Fig. 1.   Low-temperature (10 K) cw PL spectrum of an AlN epilayer grown on sapphire.

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. The spectra are vertically shifted for a better illustration. The dissociation of the bound excitons into the free excitons with increasing temperature is clearly shown.

The temperature evolution of the time-integrated PL spectra is shown in Fig. 2. In general, the FWHM of PL emission lines increases and the spectral peak positions red-shift with increasing temperature, which is quite typical for an exciton transition in semiconductors due to the bandgap variation with temperature as well as thermal broadening. 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 [18,19]. 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 excitation intensity (I_{exc}) dependence of the integrated PL emission intensities (I_{emi}) for both the I_2 and FX transitions revealed that the emission intensity increases with excitation intensity super linearly following $I_{emi} \propto I^\beta_{exc}$ and the fitted exponents (β) were 1.34 and 1.65 for the I_2 and FX transitions, respectively. No significant change in the emission peak positions of the I_2 and FX transitions was observed when I_{exc} was varied over three orders of magnitude, ruling out the possibility for a band-to-band recombination [20].

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 [14-16]. Values ranging from 50 ps 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 [14-16].   In semiconductors, the radiative recombination rate of fundamental optical transitions increases quadratically with the bandgap, $r_r \propto E_g^2$, while the non-radiative recombination rate decreases exponentially with an increase of the bandgap [21,22]. This means that the estimated ratio of the exciton lifetime in AlN to GaN would be roughly (3.4 eV /6.1 eV)^2 ≈ 0.3.   Thus, we believe that the observed low temperature free exciton lifetime of 50 ps is predominantly the radiative recombination lifetime in AlN.
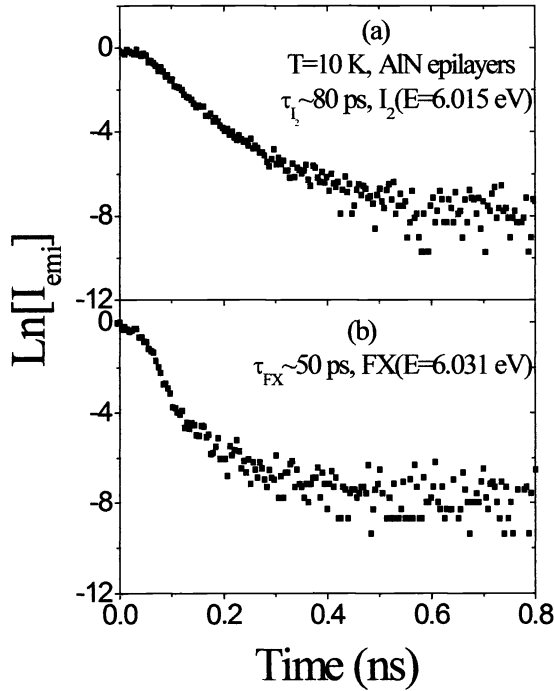
Fig. 3.   Temporal responses of PL emissions measured at 10 K at the bound exciton and free exciton spectral peak positions in an AlN epilayer.
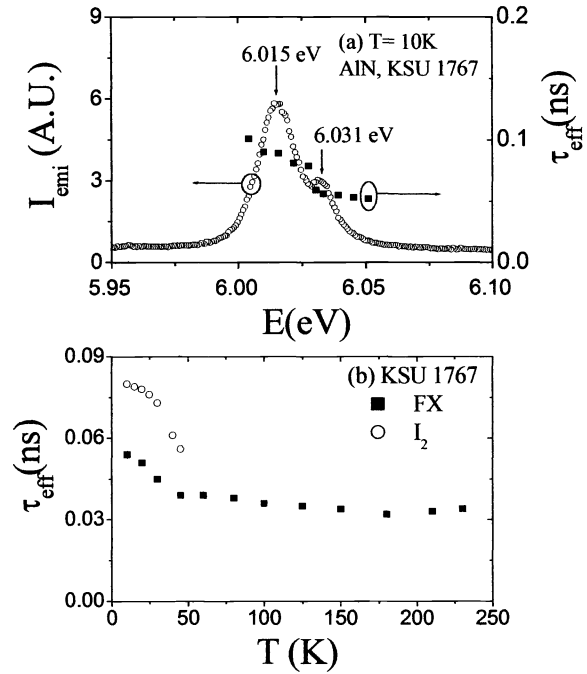

Fig. 4.   (a) Emission energy dependence of the decay lifetime of the bound exciton and free exciton transition lines in an AlN epilayer measured at 10 K. The time-integrated emission spectrum is also included. (b) Temperature dependence of the recombination lifetime of the bound and free excitons measured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

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 [23,24], 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}. Fig. 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, $\eta = I_{emi}(T)/I_{emi}(0)$, with the assumption that the radiative recombination is the dominant process at low temperature, where $I_{emi}(T)$ and $I_{emi}(0)$ are the PL emission intensities at temperature T and 0 K, respectively. The radiative lifetime (τ_{rad}) can be obtained from the following equation [25]

$$\tau_{rad} = \tau_{eff}/\eta. \hspace{3cm} [1]$$

By taking $I_{emi}(0) \approx I_{emi}(10\ K)$, 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 [26]. A similar behavior has been observed in GaN between 50 and 100 K [25]. The temperature range for the relation $\tau_{rad} \propto T^{3/2}$ 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.
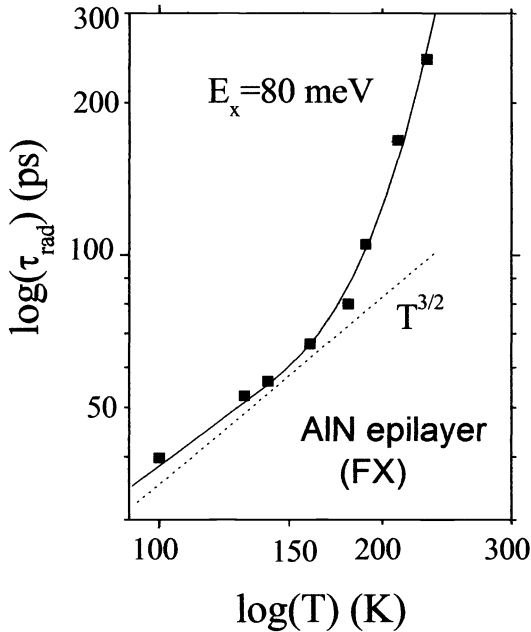
Fig. 5. Temperature dependence of the radiative decay lifetime of free excitons in AlN. The solid line is the fit based on a theory of free exciton dissociation in Ref. 25.
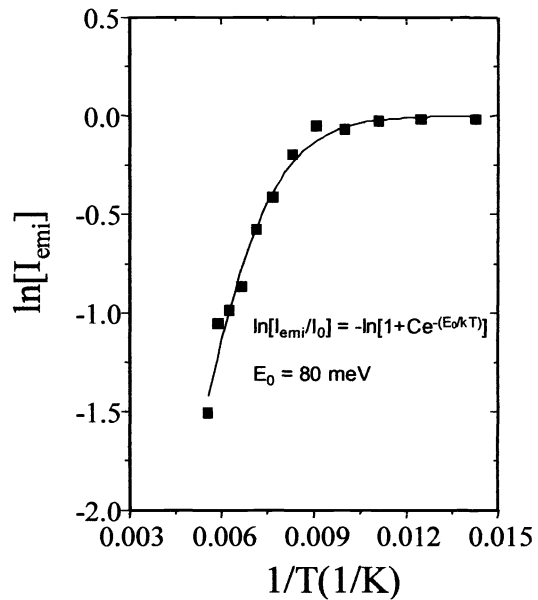
Fig. 6. The Arrhenius plot of PL intensity [ln(I$_{emi}$) vs. 1/T] for the free exciton emission lines in AlN epilayer. The solid line is the least squares fit of data to Eq. (1), from which a free exciton binding energy of 80 meV is obtained.

The observed temperature dependence of τ_{rad} shown in Fig. 5 corresponds very well to a theory based on free exciton dissociation (solid line) [25], 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. Fig. 6 shows the Arrhenius plot of PL intensity [ln(I$_{emi}$) vs. 1/T] for AlN epilayer for T > 80 K, at which the free exciton recombination is the dominant process. The solid line is the least squares fit of data to

$$I_{emi}(T) = I_0 \left[1 + Ce^{(-E_0 / kT)} \right]^{-1} ,$$
[2]

from which a thermal activation energy (or a free exciton binding energy) of 80 meV is obtained. 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 [3].

Figure 7 compares the low temperature (10 K) PL spectra of our AlN and GaN epilayers covering a broad spectral range from 2.2 to 6.2 eV for AlN and 1.8 to 3.6 eV for GaN. One can see that the peak emission intensity of the deep level impurity related transition at 2.16 eV (the yellow line) in our GaN epilayers is about four orders of magnitude lower than that of the band-edge transition at about 3.48 eV, revealing the high optical quality of our GaN. In AlN, there are two broad emission bands related with deep level impurities at about 2.94 and 4.36 eV, however with peak (integrated) emission intensity being only 1% (3%) of that of the band-edge emission line, which indicates that the optical quality of our AlN epilayers is also sufficiently high. It was observed that the optical quality or the intensity ratio of the band-edge to the deep level impurity transitions depends strongly on the growth conditions. On the other hand, the ratio at room temperature remains roughly the same as the excitation intensity was varied by one order of magnitude.

Figure 8 compares the room temperature PL spectra of AlN and GaN epilayers, again covering broad spectral ranges. One sees that at room temperature the PL emission intensity of the deep level impurity related

transition is also about 2 orders of magnitude lower than that of the band-edge transition in our AlN epilayers. This points to a much-improved optical quality of our AlN epilayers over those in previous CL studies, in which a comparable peak emission intensity for the deep level impurity related and the band-edge transition lines was observed in AlN grown on sapphire substrates [4,5]. It is interesting to note from Figs. 7 and 8 that although the 10 K band-edge emission intensity is about one order of magnitude lower in AlN than in GaN, the room temperature emission intensities are comparable for both compounds. This implies that the thermal quenching of PL emission intensity is greatly reduced in AlN over GaN, which suggests that the detrimental effect of impurities and dislocations or non-radiative recombination channels in AlN is much less severe than in GaN. This points to the great potential of AlN for many device applications, because it is already well known that the detrimental effect of dislocations/impurities in GaN is much smaller than in other III-V and II-VI semiconductors.
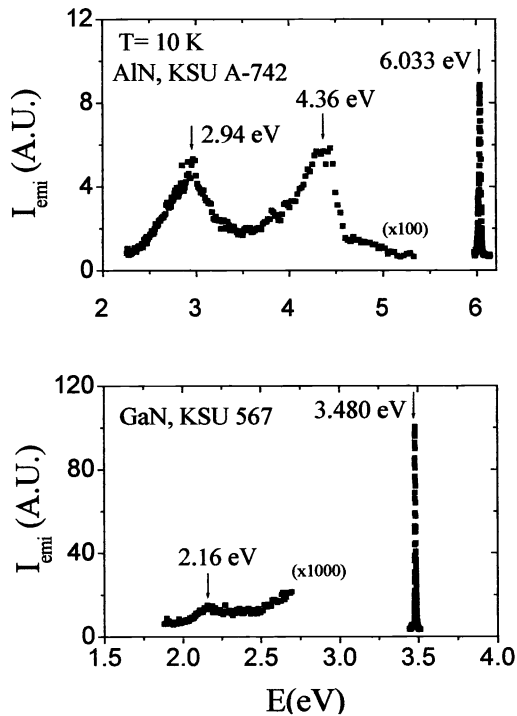

Fig. 7. PL spectra of AlN and GaN epilayers measured at 10 K, which covers a broad spectral range from 2.2 to 6.2 eV for AlN and 1.8 to 3.6 eV for GaN.
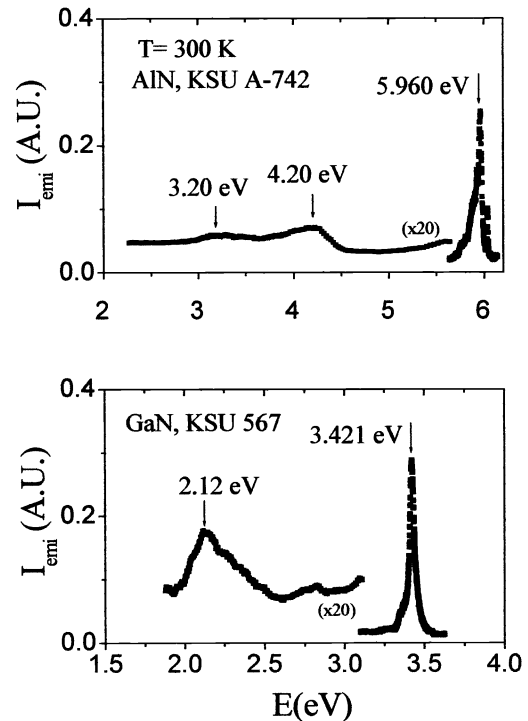
Fig. 8. PL spectra of AlN and GaN epilayers measured at 300 K, which covers a broad spectral range.

In the past, AlN is referred as a ceramic due to its very large bandgap, poor quality, and highly insulating nature and is considered useful as a semiconductor only when alloyed with GaN or used as buffer and spacer layers in nitride structures and devices. Our results show that it is now emerging as an important semiconductor material, namely AlN epilayers of high optical qualities can be achieved by MOCVD. Since it is still at a very early stage for AlN epilayer growth, significant improvements in materials quality are anticipated. For example, during the last a few months, we have enhanced (suppressed) the emission intensity of the band-edge transition (deep level impurity related transition) by three orders of magnitude. However, an important issue for achieving a true semiconducting AlN is how to control its conductivity. Indeed, it was shown recently that the conductivity of AlN can be controlled and n-type conduction with a free electron concentration of about $1 \times 10^{17} cm^{-3}$ has been achieved by Si doping [27]. With the demonstrated abilities of achieving high optical quality here and the n-type conductivity control of AlN epilayers, many novel applications of III-nitrides are conceivable. The most important message we want to deliver in this letter is that AlN can be grown as good as GaN and that the detrimental effect of non-radiative recombination channels in AlN is much less severe than in GaN.

In summary, AlN epilayers with high optical qualities have been grown by MOCVD on sapphire substrates. Deep ultraviolet (UV) picosecond time-resolved photoluminescence (PL) spectroscopy has been employed to study the optical transitions in AlN epilayers. Very efficient band-edge PL emission lines have been

observed with above bandgap deep UV laser excitation. The emission intensities of the deep level impurity transitions are about two orders of magnitude lower than that of the band-edge transition at room temperature. We have shown that the optical quality of AlN can be as good as GaN as demonstrated by quantum efficiency of PL especially at room temperatures. 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. This is a direct consequence of the large energy bandgap of AlN. 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. 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 meV and 80 meV, respectively. From this, the energy bandgap 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. This together with other well-known physical properties of AlN may considerably expand future prospects for the application of III-nitride materials.

4. References

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