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Excitonic recombination in GaN grown by molecular beam epitaxy

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Time-resolved photoluminescence has been employed to probe the free-excitonic transitions and their dynamic processes in GaN grown by molecular beam epitaxy (MBE). The exciton photoluminescence spectral line shape, quantum yield, and recombination lifetimes have been measured at different excitation intensities and temperatures, from which the binding energy of an exciton, the energy band gap, and the free-exciton radiative recombination lifetimes of GaN grown by MBE have been obtained. Our results have demonstrated the superior crystalline quality as well as ultrahigh purity of the investigated sample, implying a new major breakthrough in MBE growth technologies for GaN. © *1995 American Institute of Physics.*

GaN has been recognized as one of the most important semiconductors due to its potential applications for many optoelectronic devices which are active in the UV-blue wavelength regions and electronic devices capable of operation at high-temperture and high-power conditions.[1,2] The recent success of high efficiency blue and green GaN light emitting diodes (LEDs)[3] has led to the conviction that green/blue /UV lasers can also be fabricated from GaN and its alloys systems (InGaN and AlGaN). However, the understanding of its fundamental optical properties, which are crucial to the realization of laser diodes, is far from complete due to the lack of high quality crystals in the past. The detailed band structure near the band edge, the hole effective masses, and the exciton binding energies have not yet been well-established. In particular, the investigation and understanding of the dynamic processes of fundamental optical transitions, including the band-to-band and exciton transitions, are just in their infancy. Yet the history of GaAs and ZnSe laser development has shown that the understanding of the fundamental optical recombination dynamics is the key to the understanding of lasing origins in these materials.

Recently, we have employed time-resolved photoluminescence spectroscopy to study the band-edge emissions in GaN epitaxial layers grown by plasma-assisted molecular beam epitaxy (MBE),[4] in which the neutral-donor-bound exciton (I_2) transition and a band-to-impurity transition were the dominant emission lines. In this letter, we report time-resolved photoluminescence results for an insulating GaN epitaxial layer grown very recently by MBE. In a remarkable contrast to the previous samples, only free-excitonic transitions have been observed. The recombination lifetimes of the free-exciton transitions associated with different valence bands have also been measured, which are fundamentally important quantities for laser applications based on the GaN system. Time-resolved photoluminescence results have demonstrated that the quality of the recent MBE grown GaN crystals has reached the state-of-the-art, which is a significant step toward the realization of reliable optoelectronic devices based on GaN.

The wurtzite GaN epitaxial layer of about 4 μm thick used here was grown very recently by MBE on a sapphire (Al_2O_3) substrate with a 50 nm AlN buffer layer. It is nominally undoped, insulating, and consequently, its intrinsic carrier concentration and mobility cannot be measured. The detailed growth processes, structural, optical, and electrical characterization of these epitaxial layers will be reported in a forthcoming paper.[5] Low-temperature time-resolved photoluminescence spectra were measured by using a picosecond laser spectroscopy measurement system.[4] The excitation intensity was controlled by a set of neutral density filters with different values of optical densities D, and was proportional to 10^{-D}. Photoluminescence was collected in a reflection mode and the excitation laser polarization direction was perpendicular to the c axis of the sample.

In Fig. 1(a) we plot the continuous-wave (cw) photoluminescence (PL) emission spectrum of the insulating sample obtained at 10 K, which clearly reveals three different emission lines in the energy region shown. For comparison, a PL spectrum is also shown for one representative n-type ($n = 10^{18}$ cm^{-3} due to unintentional doping) epitaxial layer deposited earlier by conventional plasma-assisted MBE in Fig. 1(b), in which a dominant emission line at 3.475 eV is observed. The 3.475 eV emission line in the n-type layer shown in Fig. 1(b) is the well-known transition due to the recombination of the excitons bound to neutral donors associated with nitrogen vacancies or the I_2 line.[6–8]

The two dominant emission lines at 3.483 and 3.489 eV in the PL spectrum of the insulating sample in Fig. 1(a) are due to the recombination of the free-excitons associated with the top two valence bands, or the A- and B-excitons, implying the energy separation between the A- and B-exciton transition lines of about 6 meV. This assignment has been further confirmed by polarization and time-resolved measurements. In some samples, we have observed both the I_2 and the A-exciton transitions simultaneously at the corresponding

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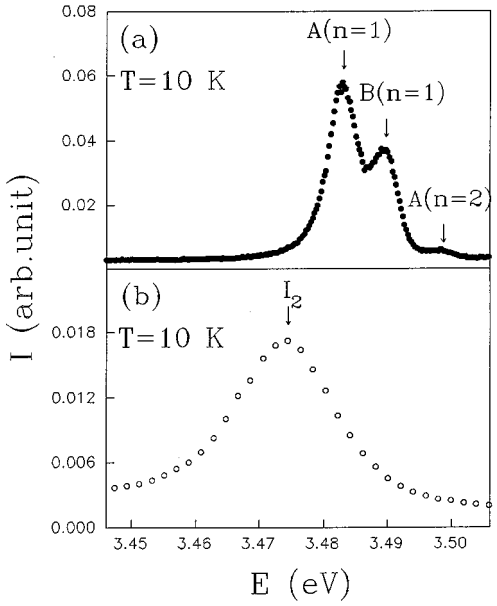

FIG. 1. (a) cw photoluminescence spectrum of an insulating GaN epitaxial layer grown recently by MBE at 10 K. The arrows indicate the transition peaks of the ground states *A*-exciton $A(n=1)$, *B*-exciton $B(n=1)$, and the first excited state of the *A*-exciton $A(n=2)$ at 3.483, 3.489, and 3.498 eV, respectively. (b) cw photoluminescence spectrum of an *n*-type epitaxial layer grown previously by conventional plasma-assisted MBE measured at 10 K. The arrow indicates the peak position of the I_2 line.

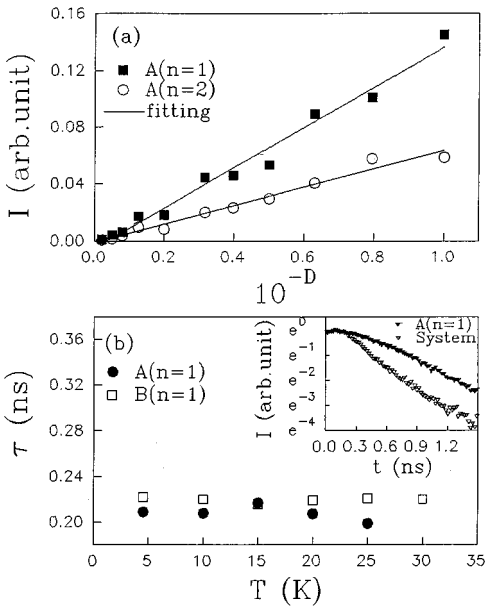

FIG. 2. (a) Photoluminescence emission intensities of the $A(n=1)$ and $A(n=2)$ transitions as functions of excitation intensity. (b) Temperature dependence of the recombination lifetime of the *A*- and *B*-exciton transitions in the insulating sample. The inset in (b) shows an example of the photoluminescence decay of the *A*-exciton $(n=1)$ transition measured at its peak position. The detection system response to the laser pulses (7 ps) is also included in the inset and indicated as ''system''. The lifetimes are obtained by deconvoluting the system response from the photoluminescence data.

energies,[8] which further supports our assignment. From these measurements, we also obtain a value of about 7.5 meV for the binding energy of the neutral-donor-bound exciton. There is also a weak transition line at about 3.498 eV, which is confirmed to be due to the recombination of the first excited state of the *A*-exciton $(n=2)$ by its spectral peak position, emission intensity, and temperature dependence. The *C*-exciton transition is expected to lie about 40 meV above the *A*-exciton line according to a recent photoreflectance measurement on the same MBE grown GaN[9] and calculation based on local-density approximation.[10] From the energy difference between the ground $(n=1)$ and the excited states $(n=2)$ of the *A*-exciton, $E_{12}^{A}(=15$ meV), we obtain a value of about 20 meV for the binding energy of the *A*-exciton. Furthermore, from the peak position of the *A*-exciton shown in Fig. 1(a) (3.483 eV) and the binding energy of the *A*-exciton obtained here (20 meV), we deduce the band gap of GaN at 10 K to be about 3.503 eV, which is about the same as the current accepted value.[11] This further corroborates our assignment for the excited state of the *A*-exciton $A(n=2)$ at 3.498 eV. The binding energy of the *A*-exciton observed here is slightly larger than a value of 18.3 meV observed in a superior quality GaN layer (3.8 μm thickness) grown very recently by metalorganic chemical vapor deposition (MOCVD).[12] Comparing the PL spectra in Figs. 1(a) and 1(b), remarkable features exhibited by the insulating sample include (1) the complete absence of the I_2 emission line, (2) the narrow emission linewidths of about $\sim$3 meV in Fig. 1(a) versus about 13 meV in Fig. 1(b), and (3) the clearly resolved free-excitonic transitions including excited states in a small energy region, all of which indicate that the quality of the insulating sample is superior.

To verify the low defect concentration in the insulating sample, we have measured the dependence of the exciton photoluminescence on the excitation intensity at different temperatures and the results for the ground $A(n=1)$ and excited $A(n=2)$ states obtained at $T=5$ K are given in Fig. 2(a). We see that the free-exciton recombination is strictly linear with excitation intensity at $T=5$ K. A similar behavior has been observed up to a temperature $T=60$ K. This is the first time that such a linear behavior for the free-excitonic transitions in GaN has been recorded. This demonstrates that the material is ultrapure and that the recombination is governed by radiative processes below $T=60$ K.[13] Thus, our results clearly demonstrate the superior crystalline quality as well as the ultrahigh purity of the insulating sample.

The dynamic processes of the observed transitions have been studied. The recombination of the I_2 transition in the *n*-type sample grown earlier by conventional plasma-assisted MBE is predominantly determined by the nonradiative processes and its systematic dependence on temperature cannot be measured due to the large nonradiative recombination decay rate. In a sharp contrast, we are able to measure directly the recombination lifetimes of the *A*- and *B*-excitons in the insulating sample by employing time-resolved measurements because of its superior quality. The inset of Fig. 2(b) shows an example of the *A*-exciton decay measured at its spectral peak position at 5 K. The detection system response to the laser pulses is also included and indicated as ''system'', which is about 0.3 ns. With the use of a deconvolution tech-

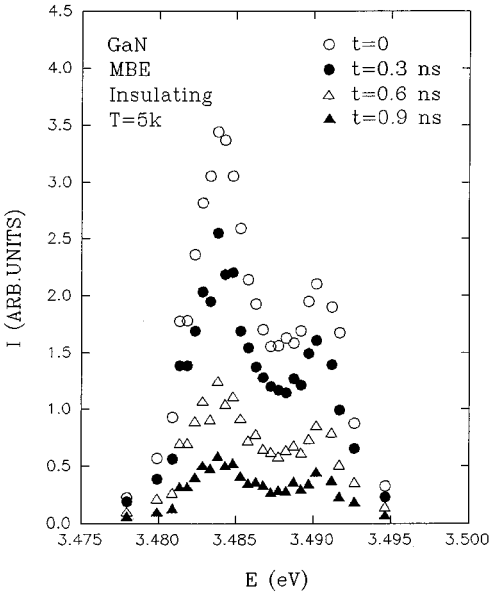

FIG. 3. Time-resolved emission spectra measured at $T=5$ K for several delay times which are measured with respect to the peak positions of the temporal responses.

nique the recombination lifetimes can be measured down to about 40 ps. The free-exciton photoluminescence decays exponentially $I(t)=I_0e^{-t/\tau}$, where τ defines the recombination lifetimes. In Fig. 2(b), we have plotted the temperature dependence of the recombination lifetime of the *A*-exciton ($n=1$) and *B*-exciton ($n=1$) measured at their respective spectral peak positions, which shows several features. First, the measured recombination lifetimes of the *A*- and *B*-exciton transitions are nearly temperature independent, which again indicates that the *radiative* recombination is the dominant process at low temperatures in the insulating sample, consistent with all other observed aspects of this sample. Second, the recombination lifetimes of the *A*- and *B*-excitons are comparable. The free-exciton recombination lifetime remains almost constant of about 0.22 ns in the range of excitation power investigated. On the other hand, we have observed that the free-exciton lifetime decreases monotonically with excitation power in the same excitation power range in the high-quality MOCVD grown layer due to exciton-exciton interactions.[12] There we have deduced from the excitation intensity dependence values of 0.35 and 0.3 ns for the radiative recombination lifetimes for single free *A*- and *B*-excitons, respectively. The slightly shorter radiative recombination lifetimes observed here is, in fact, consistent with the slightly larger exciton binding energies deduced for this sample. We speculate that the MBE grown layers may have different interface properties from the MOCVD grown layer and therefore, a different effect on the exciton properties (including exciton mass, binding energy, and lifetime) as well. The importance of the interface effects (such as strain) has been demonstrated by a significant change in the valence band dispersion on the layer plane and therefore, in the hole and exciton masses seen in GaAs expitaxial layers previously.[14]

In Fig. 3, we present time-resolved emission spectra of the *A*- and *B*-excitons in the insulating layer obtained at 5 K for several representative delay times. The delay times are measured with respect to the peak positions of the luminescence temporal responses such as that shown in the inset of Fig. 2(b). Unlike the band-to-impurity transition observed in a previous grown GaN layer where the spectral peak position shifts towards lower energies as the delay time increases,[4] the spectral peak positions and the line widths of the free-exciton transitions are almost independent of delay time. This again indicates that the exciton recombination is dominated by radiative processes across the entire emission band. An interesting feature observed in the time-resolved spectra is that the *A*-exciton decays slightly faster than the *B*-exciton. This fact can be seen in Fig. 2(b) but shows up much more pronounced in the time-resolved spectra.

In conclusion, time-resolved emission spectroscopy has been employed to study the free-excitonic transitions in GaN at different conditions. Our results have demonstrated that the GaN epitaxial layers recently grown by MBE are of superior crystalline quality as well as ultrahigh purity. Because of this, we have been able to obtain fundamentally important parameters, including the binding energies of the free- and neutral-donor-bound excitons, energy band gap, energy split between the *A*- and *B*-excitons, and the free-exciton recombination lifetimes in MBE grown GaN from photoluminescence measurements for the first time. Our results also suggest that the epitaxial layer interface can modify the optical properties of GaN.

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