Optical properties of a high-quality insulating GaN epilayer

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Picosecond time-resolved photoluminescence (PL) spectroscopy has been used to investigate the optical properties of an insulating GaN epilayer grown by metalorganic chemical vapor deposition on a sapphire substrate. Two emission lines at 3.503 and 3.512 eV in the continuous wave (cw) PL spectra observed at 10 K under a low excitation intensity ($\sim$23 W/cm^2) were identified as the band-to-band transitions involving the *A* and *B* valence bands, respectively. A third emission line at 3.491 eV was identified as a band-to-impurity transition involving a shallow donor. The PL decay behavior can be well understood with a model taking into account both the free carriers and impurities. The effective recombination lifetime of the band-to-band transition in GaN was found to be about 3.7 ns. Possible mechanisms for the band-to-band transition being dominant in this high quality insulating GaN epilayer have also been discussed. © *1999 American Institute of Physics.* [S0003-6951(99)04025-5]

Group III–V nitride semiconductors have been recognized as promising materials for many optoelectronic device applications, such as blue/UV light emitting diodes (LEDs), laser diodes (LDs), and high-temperature/high-power electronic devices.[1] There has been a considerable amount of research efforts directed toward the understanding of the optical properties of GaN epilayers. However, most of the previous work was mainly concentrated on *n*-type (doped or undoped) and *p*-type GaN epilayers.[2–6] Little work has been reported for undoped high quality insulating GaN epilayers.[7,8] Understanding the properties of insulating GaN epilayers may provide basic information regarding how to control the properties of GaN epilayers, such as from *n* type to insulating, as well as on how to optimize the doping process and the sample quality. Insulating GaN layers are needed for the design of many III-nitride optoelectronic and electronic devices.

In this letter, we report the optical properties of a high quality insulating GaN epilayer. The nominally undoped high quality wurtzite GaN insulating sample studied here was grown by low pressure (76 Torr) metalorganic chemical vapor deposition (MOCVD) on a sapphire substrate with a 50 nm low temperature AlN buffer layer at a temperature of 1050 °C. It was observed that undoped GaN epilayers show *n*-type conductivity when the ammonia (NH_3) flow rate is 2 standard liters per minutes (slm). However, the conductivity of the as-grown GaN epilayers decreases with the reduction of the NH_3 flow rate during the sample growth. When the NH_3 flow rate was lowered to 1.5–1.8 slm, insulating GaN epilayers were obtained. The thickness of the insulating GaN epilayer studied here was about 0.6 μm. A picosecond laser system with power output of about 20 mW at 290 nm was used for the PL measurement.

cw PL spectra of the GaN sample measured under a low excitation intensity ($I_{exc}\sim$23 W/cm^2) at different temperatures from 8.7 to 50 K are presented in Fig. 1. Three emission lines with peak positions at 3.491, 3.503, and 3.512 eV are clearly resolved. The PL spectra of the MOCVD grown insulating GaN epilayer observed here are quite different from those of as-grown *n*-type GaN epilayers produced by MOCVD or those of as-grown insulating epilayers produced by reactive molecular beam epitaxy (MBE). A typical PL spectrum for a relatively high quality MOCVD grown *n* type or MBE grown insulating GaN epilayer on sapphire shows either I_2 (neutral-donor-bound exciton) transition near 3.478 eV or free *A*- and *B*-exciton transitions around 3.485 and 3.491 eV, respectively.[2–8] It has been pointed out that the free *A*-exciton transition energy can be as high as 3.494 eV due to a higher biaxial strain in the GaN epilayer.[9,10] However, it was never previously observed that the dominant transition peak in a GaN epilayer on sapphire can be as high as 3.503 eV (observed here) at low temperatures. The peak energy at 3.503 eV is exactly the expected value of the fundamental band gap energy (involving the *A*-valence band) of the wurtzite GaN epilayer.[2] We thus assign the transition lines at 3.503 and 3.512 eV for the insulating GaN epilayer

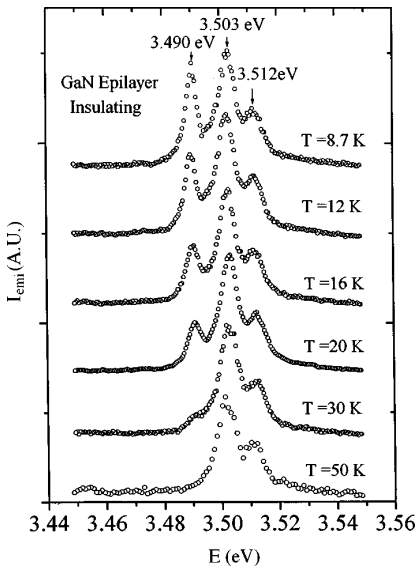

FIG. 1. cw PL spectra of a high quality insulating GaN epilayer measured at different temperatures. The spectra have been shifted vertically for a clear presentation.

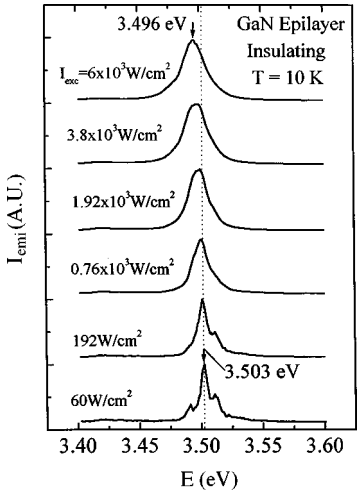

FIG. 2. Low temperature ($T=10$ K) cw PL spectra of the high quality insulating GaN epilayer measured at different excitation intensities, I_{exc}.

to the band-to-band transitions involving the *A*- and *B*-valence bands, respectively. The 9 meV difference between the *A*- and *B*-valence bands observed here is slightly larger than a value of 6 meV difference observed previously in undoped *n*-type epilayers produced by MOCVD or insulating epilayers produced by reactive MBE.[7,8]

The assignment of the band-to-band transition lines at 3.503 and 3.512 eV is further supported by the excitation intensity dependence of the PL peak positions. In Fig. 2, we plotted the PL spectra of the insulating GaN epilayer measured at different I_{exc} from 60 to 6000 W/cm^2. The dominant emission line redshifts from 3.503 to 3.496 eV as I_{exc} increases from 60 to 6000 W/cm^2. In Fig. 3(a), we have plotted the spectral peak position of the dominant emission line, E_p, as a function of $I_{\mathrm{exc}}^{1/3}$, which clearly shows a linear dependence. This is a direct evidence of the band-to-band transition.[6,11] The solid line in Fig. 3(a) is the least-squares fit of data with equation

$$E_p = E_g(n\rightarrow 0) - \gamma I_{\mathrm{exc}}^{1/3}, \tag{1}$$

where $E_g(n\rightarrow 0)$ is the energy gap of the GaN epilayer as free carrier concentration approaches zero (the fundamental energy band gap) and γ is a proportionality constant. The relation described by Eq. (1) for the band-to-band transitions is expected from the enhanced many-body and screening effects at higher free carrier densities.[11] Figure 3(b) is a logarithmic plot of the PL emission intensity (I_{emi}) of the dominant emission line versus I_{exc}, i.e., $L_n(I_{\mathrm{emi}})$ vs $L_n(I_{\mathrm{exc}})$, which shows $I_{\mathrm{emi}}\propto I_{\mathrm{exc}}^{\eta}$ with η (=1.9) being very close to 2. The emission intensity of a band-to-band transition is expected to be proportional to the product of the photoexcited electron (n) and hole (p) concentrations and is thus proportional to I_{exc}^2 since $n\propto I_{\mathrm{exc}}$ and $p\propto I_{\mathrm{exc}}$. Thus the result shown in Fig. 3(b) again support the band-to-band transition assignment for the dominant emission line.

The intensity of the emission line at 3.491 eV has a strong temperature dependence and it diminishes at $T=50$ K as shown in Fig. 1. Figure 3(c) is the Arrhenius plot of the emission intensity (I_{emi}) of the 3.491 eV transition line, i.e., $L_n(I_{\mathrm{emi}})$ vs $1/T$. The solid line in Fig. 3(c) is the least-squares fit of the experimental data (open squares) with equation $I_{\mathrm{emi}}=I_0/(1+C^*T^{3/2}e^{-E_0/kT})$, from which a thermal activation energy of $E_0=10.3$ meV is obtained. This activation energy is close to the 12 meV energy difference between the 3.491 and 3.503 eV emission lines measured at $T=8.7$ K. The possibility of the 3.491 eV emission line being a free exciton transition can be precluded because the free exciton binding energy is around 20 meV.[2–8] We thus assign the 3.491 eV line to a band-to-impurity transition involving a shallow donor.

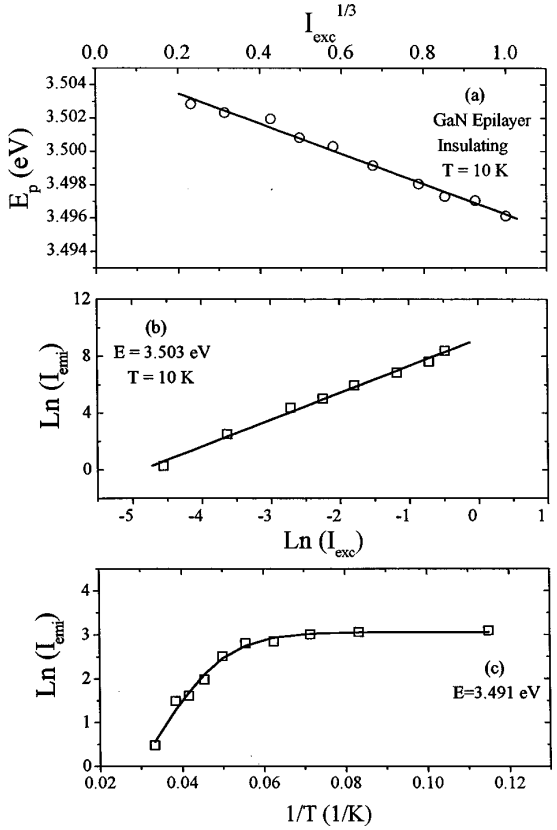

FIG. 3. (a) The emission peak position, E_p, as a function of $I_{\mathrm{exc}}^{1/3}$; (b) the logarithmic plot of the I_{exc} dependence of the emission intensity I_{emi} of the 3.503 eV emission line; (c) the Arrhenius plot of the emission intensity for the 3.491 eV emission line. The solid line is the least-squares fit of the experimental data (open squares) with equation $I_{\mathrm{emi}}=I_0/(1+C^*T^{3/2}e^{-E_0/KT})$ with a fitted value of activation energy $E_0=10.3$ meV.

The low temperature (10 K) PL decay kinetics of the high quality insulating GaN epilayer have also been measured under different pumping intensities from 23 to 73 W/cm^2. Figure 4 shows the PL temporal responses measured at $E=3.491$ and 3.503 eV for two different I_{exc}. The PL decay measured at $E=3.491$ eV can be approximated by a single exponential with a decay lifetime being close to 0.4 ns. However, the PL decay measured at $E=3.503$ or 3.512 eV cannot be described by a one or two exponential decay, nor can it be described by a bimolecular decay which is expected for a pure band-to-band transition.[12] By considering the fact that the band-to-band transitions are under the influence of the band-to-impurity transition, we can model the PL decay by using the following equation:[13,14]

$$dp/dt = -\beta(N_D p + N_A n + pn) - p/\tau_{nr}, \tag{2}$$

where $p(n)$ and $N_D(N_A)$ are the photoexcited hole (electron) and unintentionally doped donor (acceptor) concentration, respectively, τ_{nr} represents the total nonradiative recombination decay lifetime (including both the bulk and interface

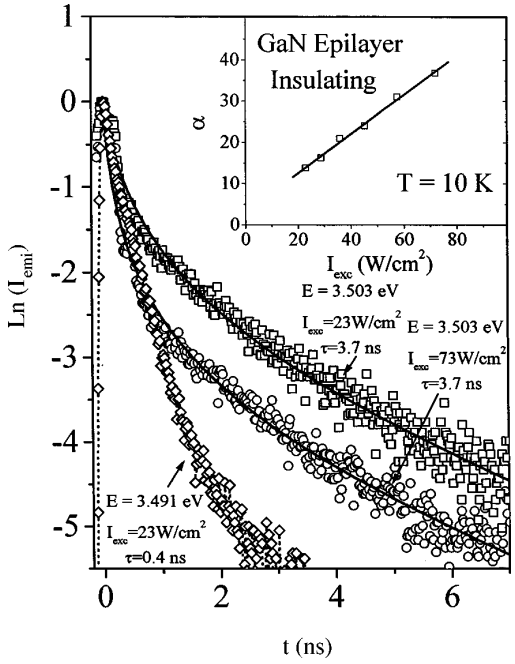

FIG. 4. The PL temporal responses of the 3.491 eV emission line measured at $I_{exc}=23$ W/cm^2 ($\diamond$) and the 3.503 eV emission line measured at $I_{exc}=23$ W/cm^2 ($\square$) and 73 W/cm^2 ($\bigcirc$) at 10 K. The solid lines are the least-squares fits of the experimental data with Eq. (3). The fitted values of α (open squares) for the 3.503 eV emission line under different I_{exc} and a linear fit (solid line) of α vs I_{exc} are plotted in the inset.

nonradiative recombination),[13] and β is the radiative recombination coefficient. We obtain from Eq. (2)[13]

$$p(t)=\frac{p_0 e^{-t/\tau}}{[1+\alpha(1-e^{-t/\tau})]}, \tag{3}$$

where p_0 is the photoexcited hole concentration at delay time $t=0$, $\alpha=p_0/[(N_D+N_A)+1/(\beta\tau_{nr})]$, and $\tau=\{1/[1/\tau_{nr}+\beta(N_D+N_A)]\}$ is the total decay lifetime determined by the total impurity concentration (N_D+N_A), β, and τ_{nr}.

The PL decay measured at 3.503 or 3.512 eV can all be well described by Eq. (3), as shown by the solid fitting curves in Fig. 4 for two representative excitation intensities $I_{exc}=23$ and 73 W/cm^2. The fitted value of α under different I_{exc} is plotted in the inset of Fig. 4, which shows that α increases linearly with I_{exc}, as we expected since $\alpha\propto p_0$ and $p_0\propto I_{exc}$. Here, p_0 is estimated to range from 1.76 to 5.55 $\times10^{17}$/cm^3 as I_{exc} varied from 23 to 73 W/cm^2. The fitted value of α varies from 13.8 to 38.8, which implies $p_0/\alpha=(N_D+N_A)+1/(\beta\tau_{nr})\approx1.27\times10^{16}$/cm^3. The upper-limit value of the total impurity concentration (N_D+N_A) is thus estimated to be smaller than 1.27×10^{16}/cm^3, which is consistent with the fact that the GaN epilayer studied here is insulating. The fitted value of τ is about 3.7 ns for both the 3.503 and 3.512 eV emission lines independent of I_{exc}, which is expected from the relation $\tau=1/[1/\tau_{nr}+\beta(N_D+N_A)]$. From α and τ, we obtain a value of $\beta=\alpha/(p_0\tau)\approx1.96\times10^{-8}$ cm^3/s for the radiative recombination coefficient in this insulating GaN epilayer.

Many important issues remain to be understood concerning the optical properties of insulating GaN epilayers, including (a) why the GaN epilayer becomes insulating under the growth conditions described here, and (b) why the band-to-band transitions are dominant in these MOCVD grown insulating GaN epilayers? The concentration of nitrogen vacancies is expected to increase with a decrease of the ammonia flow rate. Thus one would expect that the GaN epilayers become more heavily *n* type. However, our results are contrary to this expectation. One possibility is that more Ga atoms may occupy *N* sites as the ammonia flow rate is reduced, resulting in more impurities. These impurities behave as compensation centers and make the GaN epilayers more resistive. These impurities may also play the role as scattering centers that prevent the formation of excitons even at low temperatures. As a consequence, the band-to-band transitions are the dominant optical transitions in the insulating layers studied here. A full understanding of the mechanism as well as the procedure for obtaining high quality insulating GaN epilayers is very important for many III nitride device applications such as heterostructure field effect transistors (HFETs), *p-i-n* detectors, etc.

In summary, a high quality insulating GaN epilayer grown by MOCVD has been studied by picosecond time-resolved PL spectroscopy. The band-to-band transitions involving both the *A*- and *B*-valence bands were dominant even at 10 K under low excitation intensities. A donor level with a binding energy of 12 meV was also identified in the insulating GaN epilayer. The PL decay was analyzed by a model that considered the photoexcited free carriers under the influence of impurities. The band-to-band transition decay lifetime τ was found to be about 3.7 ns and the total impurity concentration (N_D+N_A) was found to be smaller than 1.27×10^{16}/cm^3 in the insulating GaN epilayer studied here.

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