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Acceptor-bound exciton recombination dynamics in *p*-type GaN

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Dynamics of the neutral-acceptor-bound exciton transition (the I_1 line) in a Mg doped *p*-type GaN epitaxial layer grown by metalorganic chemical vapor deposition (MOCVD) have been studied by time-resolved photoluminescence emission spectroscopy. Two emission lines in the I_1 transition region have been resolved in the time-resolved spectra, possibly due to the existence of two energy states of the Mg impurities after postgrowth thermal annealing. The recombination lifetimes of the acceptor-bound exciton transition have been measured under different conditions including temperature, excitation intensity, and emission energy. From these measurements, a value of about 450 ps for the radiative recombination lifetime has been obtained, which is an important physical quantity for optoelectronic device applications based on GaN. © *1995 American Institute of Physics.*

The group III nitride semiconductors have gained increasing attention in recent years due to potential applications of the well-known wide band gap and outstanding thermal and mechanical properties of these materials. Among them, GaN and $Al_xGa_{1-x}N$ wide band gap semiconductors have been intensively studied[1–4] recently for many applications including blue-UV light emitting diodes (LED) and laser diodes. There has been a considerable amount of research effort directed towards the understanding of the optical properties of GaN and $Al_xGa_{1-x}N$. However, many of their fundamental properties are still not well established. With the recent advances in epitaxial growth, very narrow luminescence emission lines of the free and bound exciton transitions have been reported.[5,6] However, the investigation and understanding of the dynamic processes of fundamental optical transitions are just in their infancy. Important basic quantities such as the recombination lifetimes of these optical transitions, which are crucial to the design of optoelectronic devices, have not yet been established.

In a previous letter, we have reported the dynamical behavior of a band-edge transition in *n*-type GaN.[6] We have demonstrated that time-resolved photoluminescence is a powerful technique that can provide important information and key parameters in group III nitride semiconductors. In the work reported here, we have further employed time-resolved photoluminescence emission spectroscopy to probe the dynamics of acceptor-bound exciton transitions (or the I_1 line) in an Mg-doped *p*-type GaN epitaxial layer. Time-resolved spectra and recombination lifetimes have been measured under different conditions. Temperature and emission energy dependencies of the recombination lifetime of the I_1 transition have been obtained.

The GaN sample used here was grown using a low pressure metalorganic chemical vapor deposition (MOCVD). Triethylgallium, trimethylindium, and ammonia were used as the precursor. Prior to deposition of the GaN layer, a thin 50 nm AlN buffer layer was grown on the sapphire (Al_2O_3) substrate. The substrate temperature during the growth was 1000 °C. The thickness of the GaN epitaxial layer was about 0.2 μm. Mg doping was provided by transporting bismethylcyclopentadienyl magnesium (MCp_2Mg) into the growth chamber with ammonia during the growth. Postgrowth annealing at 750 °C in nitrogen gas ambient at 76 Torr for about 20 min resulted in *p*-type conduction with a hole concentration of about $1.0\times10^{17}/cm^3$ as determined by Hall measurements at room temperature. The excitation light source used in the experiments is a picosecond pulsed laser with a tunable photon energy up to 4.5 eV. More detailed description of the time-resolved spectroscopy system and data analysis procedures can be found elsewhere.[6] For excitation intensity dependence, the laser intensity was controlled by a set of neutral density filter with different values of optical density *D*, and was thus proportional to 10^{-D}.

In Fig. 1 we plot a continuous-wave (cw) photoluminescence spectrum measured at $T=10$ K, which shows two emission lines at 3.402 and 3.459 eV. We assign the emission band at 3.459 eV to the recombination of excitons bound to the neutral Mg acceptor impurities (A_0,X) or the I_1 line in GaN. The I_1 transition line has been observed previously by photoluminescence measurements in Mg-compensated and highly resistive GaN sample with a peak position at about 3.455 eV at 4 K.[7,8] The emission line at 3.402 eV is most likely due to optical interference effects caused by a Fabry–Pérot cavity formed by GaN surface and GaN/AlN interface.

The full width at half maximum of the I_1 line from the cw spectrum is about 23 meV at 10 K. We have also measured cw emission spectra at different temperatures and excitation intensities. The temperature variation of the I_1 peak position follows that of the energy band gap. From the luminescence peak positions of the I_1 line (3.459 eV) observed here and the peak position of the free-exciton emission line (3.484 eV) observed by photoluminescence[9] and photoreflectance[5] measurements, we thus obtain a value of

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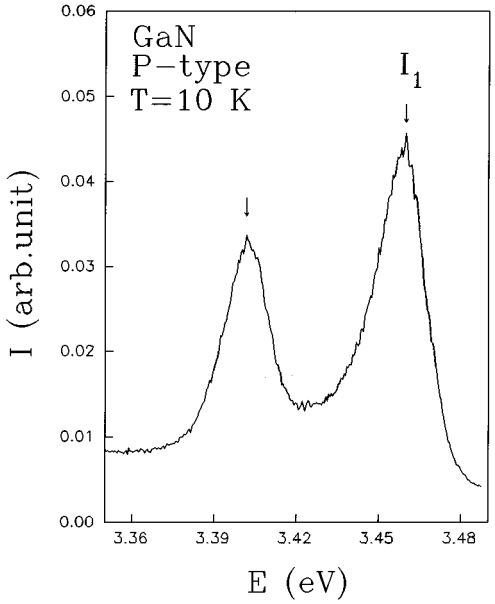

FIG. 1. Continuous-wave (cw) photoluminescence spectrum of an Mg-doped *p*-type GaN measured at $T=10$ K. The emission line with the peak position at 3.459 eV is due to the recombination of excitons bound to neutral Mg acceptor impurities (I_1).

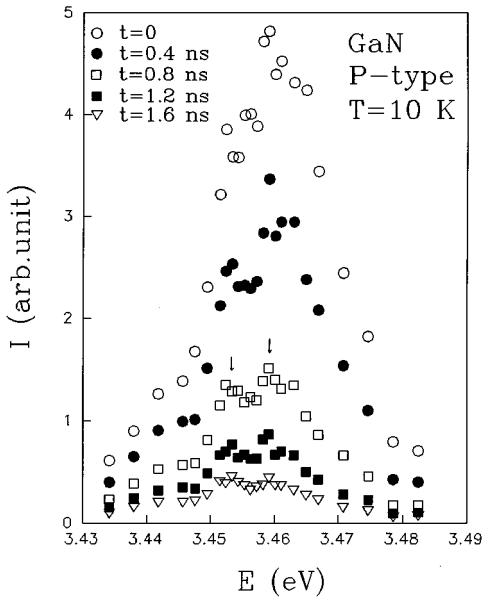

FIG. 2. Low temperature (10 K) time-resolved photoluminescence spectra of the I_1 transition measured at several representative delay times. Two arrows at 3.453 and 3.459 eV in the 0.8 ns spectrum indicate the peak positions of two emission bands resolvable only in spectra of later delay times.

about 25 meV of the binding energy of the acceptor-bound exciton, E_{bx}. This value is in a rough agreement with Haynes' rule; the binding energy of the exciton-neutron-impurity complex is about 10% of the impurity binding energy if we neglect the central cell correction, since the Mg binding energy is about 160 meV in *p*-type GaN.[10]

Figure 2 shows the time-resolved emission spectra in the energy region of the I_1 transition line at several representative delay times at $T=10$ K. At delay time $t=0$, we obtain an emission spectrum that is almost identical to the cw spectrum shown in Fig. 1. However, an additional emission line that is absent in the cw spectrum has been resolved in the time-resolved spectra at later delay times. As indicated by two arrows in the $t=0.8$ ns spectrum, two emission lines at 3.453 and 3.459 eV can be seen clearly. In fact, the intensity ratio of these two emission bands evolves with delay time. At a delay time $t=1.6$ ns, the intensity of the 3.453 eV emission band is even higher than that of the 3.459 eV emission band, although the former one is hardly observable in the spectrum of $t=0$ or in the cw spectrum. The 3.453 eV emission line may be related to acceptor-bound exciton transitions associated with acceptors other than the activated Mg acceptor impurities. If this is the case, the binding energy of this bound exciton is about 30 meV, which corresponds roughly to an acceptor binding energy of about 300 meV by applying Haynes' rule, although such an estimation becomes even less accurate for deeper impurities. As is well know at the present, Mg dopant incorporation renders the MOCVD as-grown GaN highly resistive, when the inactivated Mg impurities have an activation energy of about 250 meV[11] and post-growth thermal annealing is required to activate the Mg dopants in order to obtain *p*-type conduction, possibly due to the dissociation of H–Mg complex.[12–14] The activation energy of the activated Mg acceptors in *p*-type GaN is about 160 meV as determined by Hall measurements.[10] These previous results imply that there may be two energy states associated with Mg impurities, a deep and a shallow one. We speculate from the time-resolved photoluminescence emission spectra that the Mg impurities in the sample investigated here are not completely activated. The 3.459 eV emission line is due to the recombination of the acceptor-bound excitons associated with the activated Mg impurities, while the 3.453 eV line may be due to the recombination of the acceptor-bound excitons associated with inactivated Mg impurities. This speculation is supported by the fact that the 3.453 eV line observed here is the peak position of the I_1 emission peak observed previously in highly resistive sample,[8] considering the temperature difference here. The time evolution of the luminescence intensities of these two emission bands is caused by the emission energy dependence of the recombination lifetime, to be discussed later. To our knowledge, this is the first time that more than one transition line has been resolved in GaN in such a narrow energy range near the I_1 transition peak from the photoluminescence measurements, which demonstrates the power of time-resolved luminescence spectroscopy.

We have also measured (a) emission energy, (b) temperature, and (c) excitation intensity dependencies of the recombination lifetime of the I_1 transition line, as shown in Fig. 3. The recombination kinetics of the I_1 transition observed at different conditions can be well described by a single exponential function, $I(t)=I_0e^{-t/\tau}$, where τ defines the recombination lifetimes. Figure 3(a) shows that at 10 K, the recombination lifetime decreases monotonically from 0.56 to 0.30 ns with increasing emission energy, while a

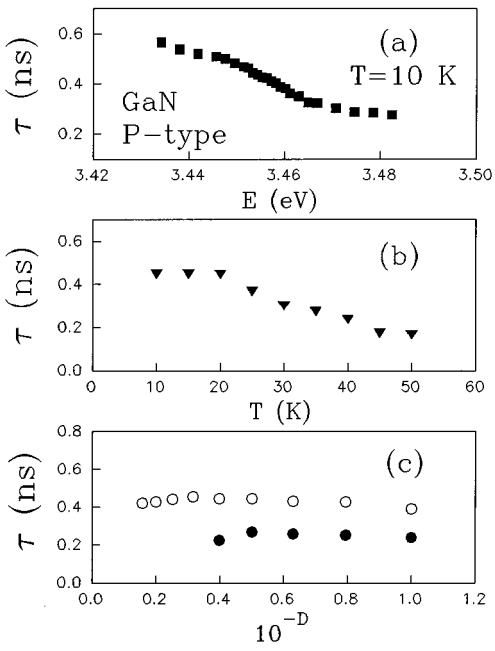

FIG. 3. (a) Emission energy, (b) temperature, and (c) excitation intensity dependencies of the recombination lifetime of the I_1 transition measured (a) around the I_1 spectral peak at $T=10$ K, (b) at the I_1 spectral peak positions, and (c) at two representative temperatures $T=10$ (○) and 35 K (●).

large change in τ is observed in the energy region between 3.445 and 3.465 eV. The observed emission energy dependence of the recombination lifetime in Fig. 3(a) can be explained by a well-known theory for bound excitons, which indicates that the radiative recombination lifetime of an impurity bound exciton increases with its binding energy, E_{bx}.[15] This theory has been confirmed experimentally in many materials. On the other hand, E_{bx} can be written as $E_{bx}=E_g-E_x-h\nu$ where E_g, E_x, and $h\nu$ are the energy gap, binding energy of the free-exciton, and emission energy, respectively. Therefore the recombination lifetime decreases with an increase of emission energy ($h\nu$). The observed behavior suggests the existence of a distribution of E_{bx} due to the imperfection of the current *p*-type sample, which is also consistent with the fact that the spectra linewidth of the I_1 transition is much broader than the value of about a few meV for the donor-bound exciton transition (I_2) observed in *n*-type GaN samples grown by the same technique.[9] The low mobilities observed in current *p*-type GaN samples also corroborate this point. The time evolution of the luminescence intensities of the two emission lines shown in Fig. 2 is related to the fact that the 3.453 eV line decays slower than the 3.459 eV line.

The temperature dependence of the recombination lifetime of the I_1 transition measured at its spectra peak positions is plotted in Fig. 3(b). τ is independent of temperature below 20 K and decreases with increasing temperature above 20 K. This behavior is most likely due to the increased recombination rate of the nonradiative processes at higher temperatures, processes such as the bound exciton dissociation to become neutral acceptors and free excitons and subsequent transformation into other recombination channels. The temperature dependence of the recombination lifetime τ shown in Fig. 3(b) also explains the rapid luminescence intensity quenching of the I_1 emission line at higher temperatures. The radiative recombination lifetime of the I_1 transition should be close to the value measured at low temperatures and is about 0.45 ns. This value is a little shorter than the radiative recombination lifetime of I_1 in well-studied CdS materials, which is 0.65 ns.[16]

Figure 3(c) plots the excitation intensity dependence of the recombination lifetime of the I_1 transition measured at its spectral peak position for two representative temperatures $T=10$ K (○) and 35 K (●). The excitation intensity is proportional to 10^{-D}. A very weak excitation intensity dependence has been observed at both of these two temperatures. At $T=35$ K, τ can only be measured for relative excitation intensities greater than 0.4 due to weaker luminescence signals at this temperature compared with those at 10 K. Figure 3(c) indicates that the exciton bound to neutral Mg acceptor complexes are isolated even under the excitation of the highest intensity available here. Therefore, the measured recombination lifetimes accurately represent the recombination lifetimes of isolated acceptor-bound excitons.

In conclusion, the dynamics of the acceptor-bound exciton transitions in an Mg-doped *p*-type GaN has been probed for the first time by time-resolved photoluminescence emission spectroscopy. Two emission lines in the I_1 transition region have been resolved in the time-resolved spectra, possibly due to the existence of two energy states of the Mg impurities after postgrowth thermal annealing. Recombination lifetimes at different conditions have been measured, from which a value of 0.45 ns for the radiative recombination lifetime of the I_1 transition has been deduced.

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