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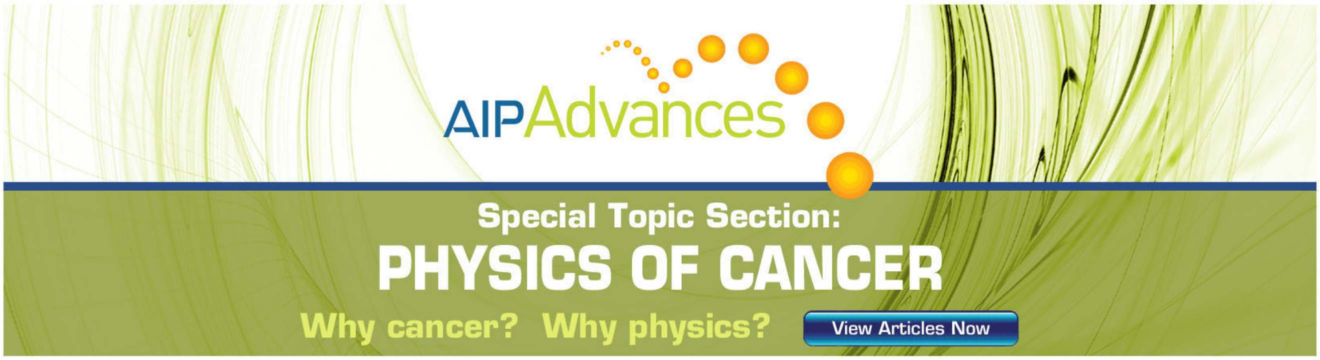

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Mechanism of donor–acceptor pair recombination in Mg-doped GaN epilayers grown on sapphire substrates

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Temperature-dependent photoluminescence (PL) measurements in Mg-doped GaN epitaxial layers grown on sapphire substrates by plasma-assisted molecular beam epitaxy have been performed in order to investigate the process of donor–acceptor pair (DAP) recombination. The PL intensity of the DAP peak decreases below 35 K, and then it increases as the temperature increases in the temperature range between 35 and 100 K. This behavior originates from the interaction between two different Mg-related traps, one shallow and the other deep level. The ionization energies of the shallow trap and the deep level trap determined from the calculations and the PL experiments are 126 and 160 meV, respectively. The DAP recombination process suggests that holes are caught in the shallow trap and that they subsequently transfer, via a tunneling process, from the shallow trap to the deep trap, where recombination with electrons takes place. © *1998 American Institute of Physics.* [S0021-8979(98)06916-3]

I. INTRODUCTION

Rapid advancements in *p*-type doping technologies for GaN epitaxial layers have made possible the fabrication of blue and ultraviolet light-emitting diodes and of high-power laser diodes.[1] The achievement of a *p*-type GaN epitaxial layer using Mg in metalorganic chemical vapor deposition requires thermal treatment[2] or low-energy electron-beam irradiation.[3] Recently, *p*-type Mg-doped GaN epilayers have been grown by using molecular beam epitaxy (MBE) techniques.[4,5] Even though some works concerning Mg-related deep levels in Mg-doped GaN have been performed using several measurement techniques,[6–10] to the best of our knowledge, detailed studies of the temperature-dependent behavior of the donor–acceptor pair (DAP) peak in a Mg-doped GaN epilayer have not yet been conducted.

This article presents data for photoluminescence (PL) measurements on Mg-doped GaN epitaxial layers grown on sapphire substrates by plasma-assisted molecular beam epitaxy (PAMBE). The measurements to determine the dependence of the PL on the temperature were carried out to investigate the optical properties of the shallow Mg level and the deep Mg complexes. The temperature-dependent behavior of the DAP peak in PL from the Mg-doped GaN epilayer is discussed by introducing a model for the interaction between two different Mg-related levels, one shallow and the other deep level. The PL spectra for the Mg-doped GaN epilayer are compared with those for the nominally undoped GaN epilayer.

II. EXPERIMENTAL DETAILS

The GaN epilayers used in this study were grown by PAMBE on (0001) sapphire substrates. An inductively coupled radio frequency nitrogen plasma source with a purity of 99.9999% provided the reactive nitrogen, and the Ga and the Mg were evaporated using conventional effusion cells. The Mg doping concentration was controlled by the temperature of the Mg effusion cell. As soon as the chemical cleaning process was finished, the sapphire wafer was mounted onto a molybdenum susceptor. Prior to GaN growth, the substrate surface was exposed to an activated nitrogen beam for 10 min for complete covering with a nitridated layer. The deposition of the GaN active epilayer on the GaN buffer layer grown at 550 °C was done at a substrate temperature of 750 °C. The thickness of the GaN epilayers was 600 nm, and the Mg cell temperatures for the growth of the GaN epilayers for samples A and B were 270 and 220 °C, respectively.

During the growth, the crystalline quality of the GaN epitaxial layers was monitored *in situ* by reflection high energy electron diffraction (RHEED). Van der Pauw Hall-effect measurements were carried out at room temperature in a magnetic field of 0.5 T by using a Keithley 181 nanovoltmeter. The PL measurements were performed using a 75 cm monochromator equipped with a GaAs photomultiplier tube. The excitation source was the 3250 Å line of a He–Cd laser, and the sample temperature was controlled between 10 and 300 K by using a He displex system.

III. RESULTS AND DISCUSSION

Figure 1 shows the PL spectra at 11 K for the nominally undoped GaN epilayer and the Mg-doped GaN epilayers of

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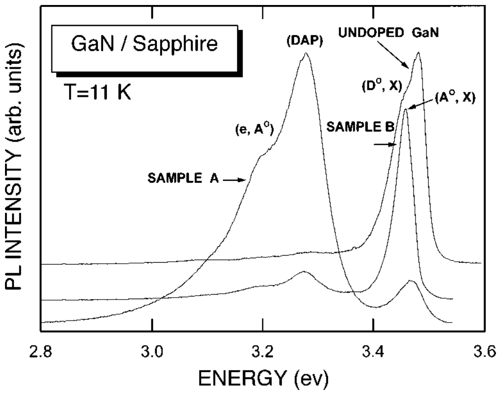

FIG. 1. PL spectra measured at 11 K for the nominally undoped GaN epilayer and for the Mg-doped GaN epilayers of samples A and B.

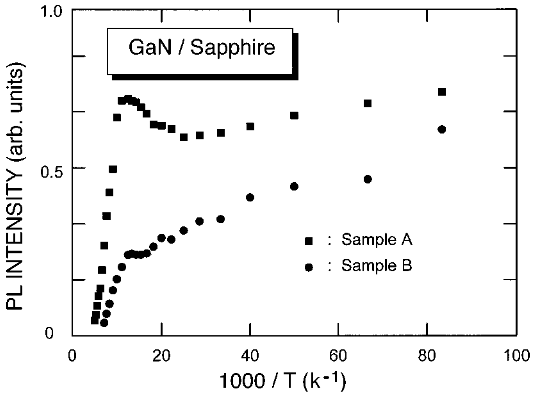

FIG. 2. PL intensities of the donor–acceptor pair recombination at 3.27 eV of samples A and B as a function of the reciprocal of the measurement temperature.

samples A and B. The RHEED patterns show streaky and sharp (1×1) structures for the 0.75-μm-thick GaN films, which implies that a uniform two-dimensional growth has been reconstructed. The carrier concentrations of samples A and B, as determined from the Hall-effect measurements at 300 K, are 2×10^{17} and 1×10^{16} cm^{-3}, respectively, and the carrier types of the two samples are *p* type. The chemical concentrations of samples A and B determined from the secondary-ion mass spectroscopy (SIMS) measurements are 2.1×10^{19} and 1×10^{18} cm^{-3}, respectively. The peak at 3.46 eV for the Mg-doped GaN epilayers is considered to be from excitons bound to shallow neutral acceptors (A^0,X), and the peak at 3.27 eV is attributed to DAP recombination together with phonon replicas.[11] The shoulder at 3.197 eV for the Mg-doped GaN epilayers is considered to be a free to a neutral bound acceptor exciton (e,A^0).[10] The peak at 3.455 eV appearing in the PL spectrum for the nominally undoped GaN epilayer is related to the neutral donor-bound exciton (D^0,X); the DAP recombination peak does not appear in the PL spectrum of the undoped epilayer. Since the DAP emission was not observed in the undoped GaN films, the (A^0,X) appearing in the Mg-doped epilayers must have been caused by Mg. While the dominant emission line is associated with (A^0,X) in the Mg-doped GaN epilayer of sample B with a smaller carrier concentration, the DAP recombination peak is more dominant in sample A with higher carrier concentration. These results indicate that the DAP peaks in the PL spectra are strongly dependent on the Mg doping concentration.

Figure 2 shows the PL intensities of the DAP recombination at 3.27 eV for samples A and B as a function of the reciprocal of the measurement temperature. Akasaki *et al.*[12] reported that the quenching phenomena of the DAP emission above 100 K are due to thermal activation with an Mg acceptor energy of approximately 160 meV. However, above 35 K, as the temperature of sample A increases, the PL intensity of the DAP emission increases; it decreases above 100 K. This behavior is very different from the results obtained from Akasaki *et al.* for Mg-doped *p*-type GaN.[12] As shown in Fig. 2, the thermal dynamic process of the PL intensities does not vary exponentially.

In order to explore the physical origin of the observed emission lines, their dynamical behaviors have been studied. The conduction band, the valence band, and the impurity levels are related to the luminescence process. Excess carriers play an important role in the PL process. Optical transition processes in Mg-doped *p*-type GaN are dominated by the distribution of the excess holes occupying each state. The distribution of the nonequilibrium holes at each state in the photoexcitation process at a constant temperature is determined from the Boltzmann distribution function. The DAP recombination probability is determined partly by the number of neutral donors and the number of neutral acceptors. Under the same power optical excitation conditions, excess holes may be captured by the acceptor level *A*; the PL intensity of the DAP emission is related to this process. The excess holes captured in the trap center A' may cause a decrease in the PL intensity of the DAP recombination. The holes trapped in level A' have some probability of tunneling back to the acceptor level *A*, and this process increases the PL intensity of the DAP recombination. Since the capture probabilities and the tunneling processes are dependent on the temperature, they affect the temperature-dependent PL intensity of the DAP emission.

The distribution of the holes occupying the *A* and the A' states is dependent on the temperature. When the capture cross section of level *A* is large enough to catch all the holes that tunnel from level A', the increase in the number of neutral acceptors is determined from the number of the holes that tunnel to level *A*. Since the carrier concentrations of the Mg acceptors obtained from the Hall-effect measurements are much less than their chemical concentrations determined from the SIMS measurements, the number of holes transferred from *A* to A' can also be ignored. The variance of the number of holes occupying the level *A* (Δp) as a function of temperature (T) is given by

$$\begin{aligned}\Delta p = {} & N_{A'}C_p[1-\exp(-E_{A'}/k_BT)] \\ & -N_{A'}P_T[1-\exp(-E_{A'}/k_BT)], \qquad (1)\end{aligned}$$

where $N_{A'}$ is the carrier concentration of the trap level A', C_p is the capture coefficient of the trap level *A*, $E_{A'}$ is the ionization energy of the trap level A', k_B is the Boltzmann's constant, and P_T is the tunneling probability. P_T as a function of energy (E) can be written as[13]

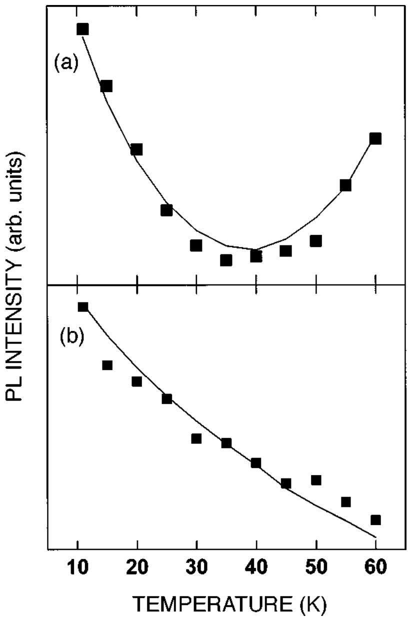

FIG. 3. PL intensities of the donor–acceptor pair recombination as a function of the temperature for (a) sample A and (b) sample B in the temperature range between 10 and 60 K. The solid lines represent a least-squares fittings of the data.

$$P_T = \exp\left(-4\pi(2m^*/h^2)^{1/2} \int [E(x)-E]^{1/2}\, dx \right), \qquad (2)$$

where $E(x)$ is the potential barrier height, h is Planck's constant, and m^* is the hole effective mass. When $E(x)$ is the same as the ionization energy of the trap level A', E is replaced by $\frac{3}{2}k_BT$. x is the distance between levels A and A' in real space, and it can be replaced by the average distance (x_0) between the two levels. Thus, Δp as a function of the temperature has the following expression:

$$\Delta p = N_{A'}[1-\exp(-E_{A'}/k_BT)] \cdot \{\sigma_h(3k_BT/m^*)^{1/2} - \exp[-4\pi(2m^*/h^2)^{1/2}(E_{A'}-\tfrac{3}{2}k_BT)^{1/2}x_0]\}, \qquad (3)$$

where σ_h is the hole capture cross section of trap A'. Both the capture and the tunneling probabilities increase with increasing temperature. While the dominant process at low temperatures is hole trapping, that at relatively high temperatures is the tunneling process, as shown in Eq. (3). Equation (3) indicates that the tunneling probability decreases exponentially as x_0 increases. Since the tunneling probability of sample B is very small, the PL intensity of the DAP emission decreases monotonously as the temperature increases, as shown in Fig. 3(b). Therefore, the discussion of the optical process is focused on Fig. 3(a). The solid line represents a least-squares of the data, and fits the best fitting values of x_0, σ_h, and $E_{A'}$ obtained from the solid line in Fig. 3(a) are 3.9 nm, 3.45×10^{-18} cm^2, and 126 meV, respectively. The value of $E_{A'}$ is in good agreement with that obtained from the frequency-dependent capacitance and admittance spectroscopy measurements[8] and from the Hall-effect measurements.[14] The level obtained from the Hall-effect measurements[14] is a hole trap level related to the neutral Mg deep level; this level originates from the capture of holes from the valence band. An additional localized state in the energy band gap can be introduced to trap other holes. A process similar to that of the two levels in the Mg-doped GaN epilayer was observed in HgCdTe alloys.[15] The Mg chemical concentration in sample A, as obtained from the x_0 value, is 1.68×10^{19} cm^{-3}, which is in reasonable agreement with that determined from the SIMS measurements.

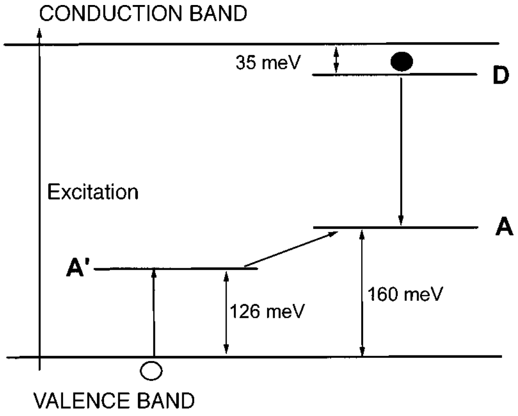

FIG. 4. A schematic energy level diagram and the main transition processes of the holes in a Mg-doped GaN epilayer. *D* and *A* represent the shallow donor energy level formed by the native defects and the acceptor energy level related to the Mg dopants, respectively, and A' is the Mg trap level related to the hole capture.

To clarify the thermal dynamic behaviors of the PL intensities as a function of temperature, a new model for the optical process related to the DAP recombination in the Mg-doped *p*-type GaN epilayer can be suggested. Three energy levels are introduced to explain the dependence of the PL intensity of the emission on the temperature in the low-temperature range. One donor energy level denoted by *D* in Fig. 4 is related to the native defects due to the N vacancy in the GaN epilayer, and its ionization energy is 35 meV.[16] Another level is an acceptor energy level denoted by *A*, which is formed by the Mg dopant; its ionization energy is 160 meV.[12,17] The other energy level can be introduced as a hole trap level and is denoted by A'; its ionization energy, as determined from Fig. 3(a), is 126 meV. Since Mg dopants in the GaN epilayers form several kinds of trap levels,[6–10] A' is also attributed to the Mg deep level acting as a hole trap in the Mg-doped GaN epilayer. The A' level captures nonequilibrium holes from the valence band during the optical excitation process, and it competes with the *A* level for obtaining excess holes. The holes captured by the A' level tunnel to the *A* level due to their thermal energy, and this process affects the PL intensity of the DAP peak. A schematic energy diagram and the main transition processes of the holes are shown in Fig. 4. Since the ionization energies of levels *A* and *D* in GaN are larger than the thermal energy, the carrier transitions from the *A* level to the valence band and from the *D* level to the conduction band can be neglected. Since almost all of the Mg dopants at low temperature occupy the trap levels in Mg-doped *p*-GaN epilayers,[9] the processes shown in Fig. 4 are dominant in the Mg-doped *p*-GaN.

IV. SUMMARY AND CONCLUSIONS

The results of the temperature-dependent PL measurements on Mg-doped GaN epitaxial layers grown on sapphire substrates by PAMBE show that the PL intensity of the DAP recombination decreases below 35 K and increases in the temperature range between 35 and 100 K. This behavior was discussed by introducing an interaction between two kinds of Mg-related levels, which are a shallow acceptor level and a trap level. The interaction between the Mg acceptor and the Mg-related trap center is charge transfer through tunneling. The results of the PL measurement are in reasonable agreement with those obtained from the theoretical analyses.

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