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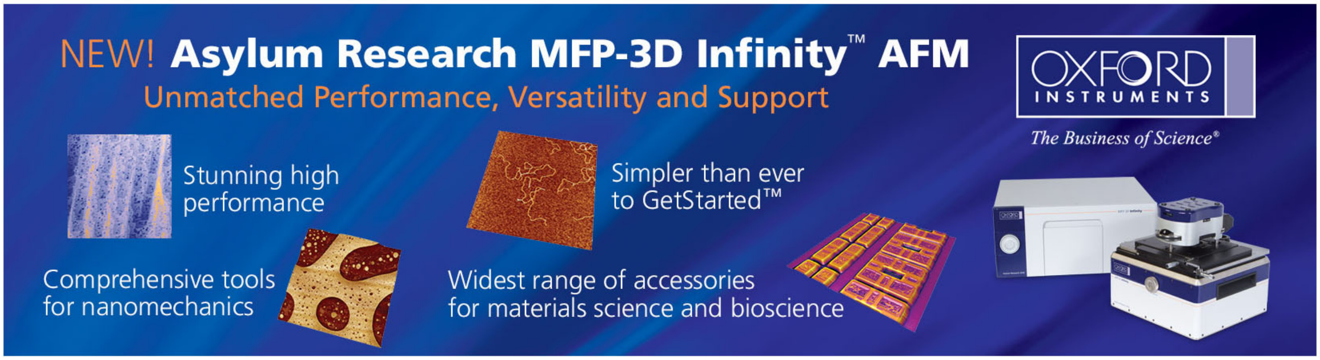

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Isoelectronic As doping effects on the optical characteristics of GaN films grown by metalorganic chemical-vapor deposition

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We have studied the As doping effects on the optical characteristics of GaN films by time-integrated photoluminescence and time-resolved photoluminescence. When As is incorporated into the film, the localized defect levels and donor–acceptor pair transition become less resolved. The recombination lifetime of neutral-donor-bound exciton (I_2) transition in undoped GaN increases with temperature as $T^{1.5}$. However, the I_2 recombination lifetime in As-doped GaN first decreases exponentially from 98 to 41 ps between 12 and 75 K, then increases gradually to 72 ps at 250 K. Such a difference is related to the isoelectronic As impurities in GaN, which generate nearby shallow levels that dominate the recombination process. © *2000 American Institute of Physics.* [S0003-6951(00)01941-0]

Since the advent of commercially available blue light-emitting diodes and laser diodes, the wide-band-gap semiconductor GaN has been recognized as one of the most important optoelectronic materials.[1,2] In the direct-band-gap III–V semiconductors, isoelectronic impurities have been shown to improve the crystalline quality such that the background carrier concentration, deep levels, and dislocation density in GaN can be effectively reduced.[3–5] The electronic and optical properties of As-doped GaN were investigated by Guido *et al.*,[6] and by Li *et al.*[7] It was found that the incorporation of As into a Ga site will act as a deep donor. Because the electronegativity of As is smaller than that of host N atom, it behaves like a hole center and easily traps an electron.[7] However, there are not many reports addressing the issues of isoelectronic doping in GaN. Up to now, very few papers have dealt with the optical transients of As-doped GaN grown by metalorganic chemical vapor deposition (MOCVD). We thus employed time-integrated photoluminescence (TIPL) and time-resolved photoluminescence (TRPL) measurements to investigate the optical properties and dynamic processes of radiative recombination in As-doped GaN.

Undoped and As-doped GaN films were grown on a (0001)-plane sapphire substrate at 1000 °C by MOCVD. The Ga, N, and As precursors were trimethyl gallium (TMGa), ammonia (NH_3), and tertiary butylarsine (TBAs), respectively. To ensure a good film quality, a thin GaN buffer layer of 35 nm was grown at 520 °C before deposition of the As-doped GaN layer. For isoelectronic As doping, TBAs with hydrogen was used at 10 sccm, which gives an equivalent As/Ga+N content ratio less than 0.1%, as determined by secondary ion mass spectrometry.

TIPL and TRPL experiments were carried out with sample held in a cryostat allowing temperature variation from 12 to 250 K, using a Si diode as the temperature sensor. The excitation pulses of several hundred femtoseconds were generated at $\lambda \sim 820$ nm from a mode-locked Ti–sapphire laser, which was synchronously pumped by an Ar^+ laser. Its output was frequency tripled to the UV region (273 nm) with an average power of 1 mW. The laser beam was focused on the sample to a diameter of less than 200 μm. The TIPL and TRPL signals were collected and dispersed through a 0.32 m monochromator (JOBIN-YVON HR320) and detected by a photomultiplier tube (Hamamatsu R-3809U-50). The TRPL spectra were analyzed by a picosecond time analyzer system (EG&G 9308). The overall time resolution of the detection system was about 20 ps.

To examine the isoelectronic doping effects, we first conducted TIPL measurements on undoped and As-doped GaN at 12 K. As shown in Fig. 1, both spectra are dominated by the neutral-donor-bound exciton (I_2) line at 355.8 nm, and on its shoulder the neutral-acceptor-bound exciton (I_1) line at 358.1 nm can also be recognized. Several groups have reported luminescence lines around 459–477 nm in As-doped or As-implanted GaN.[6–8] However, no additional As-related transition peak was observed in our As-doped samples. We believe that the As concentration was only a trace amount, such that the As-related emission was not clear in our sample. On the low-energy tail of the undoped GaN spectrum, the (I_3) line at 366.8 nm and donor-acceptor pair (DAP) at 376.8 nm are observable. By comparing with the known spectra, the I_3 transition can be assigned to localized defect levels.[9] Note that in the As-doped GaN both the I_3 line and DAP transition are broadened and decreased in intensity so that their features are less resolved. Because isoelectronic As doping in GaN should produce some localized defect levels, they may overlap with DAP transitions, and make transitions broad by combining intrinsic energy levels.

To further investigate the As-doping effects on the dynamic processes of the dominant I_2 line, TRPL measurements were then carried out. Figure 2 shows the typical

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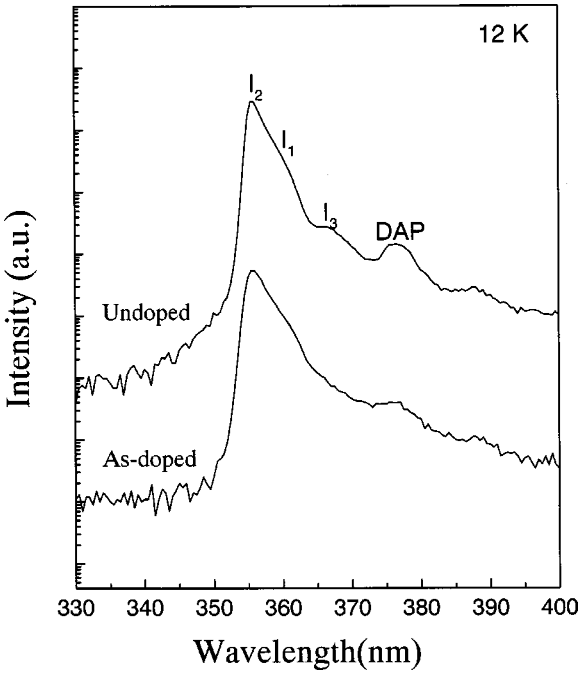

FIG. 1. TIPL spectra of As doping in GaN samples show less-resolved I_3, DAP.

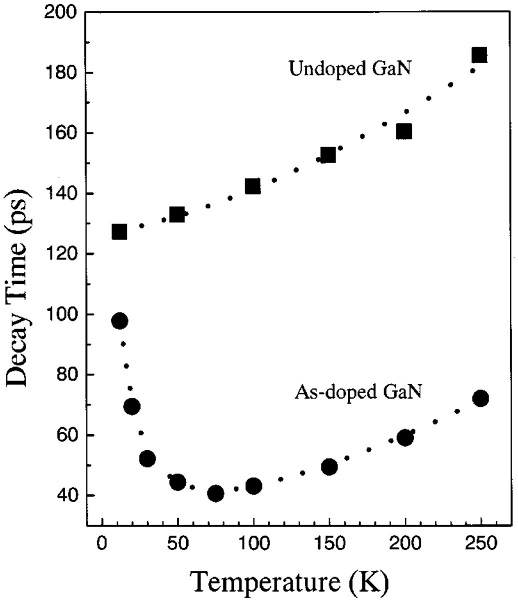

FIG. 3. Recombination lifetimes of undoped and As-doped GaN measured from 12 to 250 K. The dotted lines are the curve fitting of $T^{1.5}$ dependence for the undoped sample and including exponential dependence below 75 K for the As-doped sample.

TRPL spectra of undoped and As-doped samples at 100 K. The TRPL system response is also included in Fig. 2. Obviously, the decay behaviors are different from undoped to doped samples. The undoped GaN has a decay time of 142 ps, whereas the As-doped one ~43 ps. By lowering the cryostat temperature gradually from 250 to 12 K, the lifetime of undoped GaN decreases from 185 to 127 ps (see Fig. 3). More interestingly, an unusual emission process was observed for the As-doped GaN. Its lifetime decreases gradually from 72 to 41 ps between 250 and 75 K, but increases from 41 to 98 ps by further lowering the temperature to 12 K. It is worth noting that this recombination lifetime in As-doped GaN, showing different high- and low-temperature behaviors, is rarely observed in other compound semiconductors.

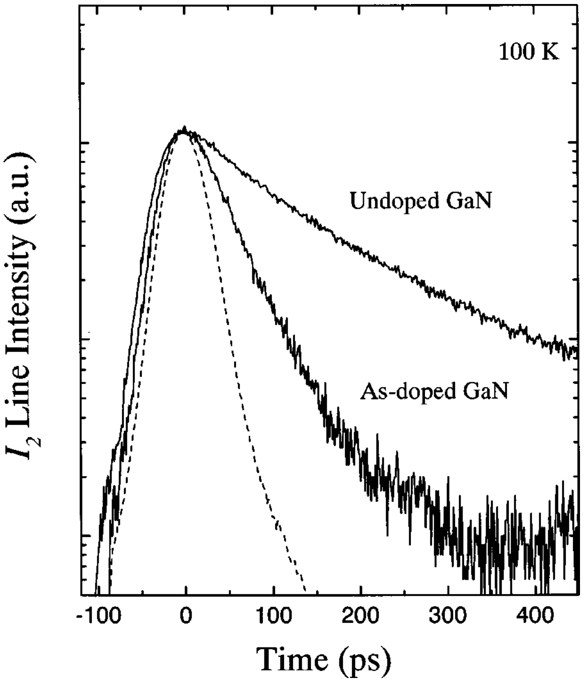

FIG. 2. Temporal evolution of the I_2 emission for both undoped and As-doped GaN. The dotted line is the system response.

In general, the recombination lifetime ($\tau_{\rm PL}$) for the salient I_2 line transition combines the radiative lifetime of the I_2 transition (τ_{I_2}) itself and other decay processes (τ') associated with shallow donor levels.[10–13] It is recognized that the theoretical value of τ_{I_2} for GaN is about 400 ps that does not change much with temperature.[14] Thus, the measured $\tau_{\rm PL}$ represents virtually τ'. For the undoped GaN film, its recombination behavior can be described well by using the Shockley–Read–Hall model (SRH), in which τ' can be expressed by the following equation:[5,10,13]

$$\tau=\frac{1}{\sigma v_{\rm th}N_t}, \tag{1}$$

where σ, $v_{\rm th}$, and N_t are the capture cross section, electron thermal velocity, and trap concentration due to impurities, respectively. From the scattering theory, the cross section σ has a T^{-2} temperature dependence.[15] Because the thermal velocity $v_{\rm th}$ is proportional to $T^{0.5}$, a $T^{1.5}$ dependence for the lifetime τ is thus obtained.[5] As shown by the top dotted line in Fig. 3, the fitting to measured recombination lifetimes is very good for the undoped GaN film. Since GaN material usually contains a high density of defects, one would expect a large SRH recombination rate that causes a significant drop in τ_{I_2} from 400 to 185 ps. The same trend is also observed in our recent studies of other GaN films.

As far as isoelectronic As doping in GaN is concerned, As substitution on the N site can form hole traps because its electronegativity is smaller than that of the host N atoms.[16–18] Therefore, the electronically neutral As atom should trap a hole first and then bind to an electron. By introducing the As atom into the reactor, the incorporation effect of As on the N site is believed to become more conspicuous. Thus, the substitution of As for N creates many shallow-acceptor-like recombination centers which could eventually dominate the transition processes.

Compared with the undoped sample, As-doped GaN has a similar $T^{1.5}$ dependence decay behavior above 75 K. However, the recombination lifetime decreases rapidly from 12 to 75 K, as illustrated in Fig. 3. We have attempted to describe this low temperature behavior due to As doping by another raised SRH recombination rate as follows. Generally, the intrinsic trap density N_t is independent of temperature, but As incorporation creates many shallow-acceptor-like levels whose occupation is temperature dependent.[18] If the number of these shallow-acceptor-like levels is larger than that of the holes, the effective trap density can be assumed as the product of the effective hole concentration ($N_v \propto T^{1.5}$) and the probability of holes occupying those levels, which is expressed by,[19]

$$N_t = N_v \exp\left(\frac{-\Delta E}{kT}\right), \tag{2}$$

where ΔE is the energy difference between the trap level and the valence-band extremes. At low temperature, τ_{As} may be approximated by the following equation:[10]

$$\tau_{\mathrm{As}} \propto \exp\left(\frac{\Delta E}{kT}\right), \tag{3}$$

as shown by the lower dotted curve in Fig. 3. The cause for the specific temperature of 75 K is yet unknown, the fitting value of $\Delta E = 0.13$ meV is so small that it cannot be resolved in the PL spectrum. However, for temperatures above 75 K, the original nonradiative decay rate (the exponential part) appears saturated and the recombination is dominated by the common SRH relaxation processes. Obviously, there is a temperature-dependent competition between the SRH recombination processes of intrinsic impurities and As-doping-induced shallow-acceptor-like levels. It is associated with the redistribution of internal energy levels due to As incorporation and accounts for the lifetime shortening in the As-doped sample. We should add that the understanding of the isoelectronic doping effects in GaN is still in the preliminary stage; more investigations are needed.

In summary, we have studied the TRPL of neutral-donor-bound exciton recombination dynamics in undoped and As-doped GaN. It is observed that As doping has changed the spectral and temporal behaviors of the I_2 transition. In particular, the recombination lifetimes show a drastically different temperature dependence that can be described by the SRH model.

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