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Nature of Mg impurities in GaN

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Mg doped GaN epilayers grown by reactive molecular beam epitaxy (MBE) exhibit clear persistent photoconductivity (PPC) whose manifestation has been used to probe the nature of Mg impurities in GaN. PPC buildup and decay transients and the dependence of the PPC decay time constant on the PPC buildup time have been systematically measured and formulated in the context of lattice relaxed Mg impurities (or *AX* centers). Our results have demonstrated that there is an energy barrier of about 129 meV which prevents free hole capture by ionized Mg impurities and that there is a lattice relaxation associated with Mg impurities in GaN. We also present a detailed comparison for Mg impurities in *p*-type GaN epilayers grown by MBE (hydrogen-free) and metalorganic chemical deposition (hydrogen rich). © *1996 American Institute of Physics.* [S0003-6951(96)01134-5]

GaN based devices offer great potential for applications such as high power electronics, UV-blue lasers, and solar-blind UV detectors.[1,2] An important aspect remains to be understood and improved is the *p*-type doping of GaN. Although *p*-type GaN has been largely obtained with Mg doping, the nature of Mg impurities in GaN are not well understood. Previously, we have observed a slow thermal equilibrium process of the dark conductivity and a weak persistent photoconductivity (PPC) effect in Mg-doped *p*-type GaN grown by metalorganic chemical vapor deposition (MOCVD), implying a metastability associated with impurities in *p*-GaN.[3] However, due to the coexistence of H and Mg impurities in MOCVD grown epitaxial layers, the physical origin of this behavior could not be identified unambiguously. In this letter, we report the observation of a large PPC in reactive molecular beam epitaxy (MBE) grown GaN layers which are largely free from H impurities. The PPC behaviors at different conditions reveal the *AX* nature of Mg impurities in *p*-GaN.

Mg-doped *p*-GaN samples used in this work were grown by reactive MBE on sapphire substrates with 65 nm thick of AlN buffer layers.[4] The dominant photoluminescence emission lines in these samples resulted from the band-to-acceptor recombination.[5] Details of the PPC measurement procedure were similar to those described previously.[3] The dark conductivities of MBE samples behave normally, while the slow thermal equilibrium process of the dark conductivity seen in MOCVD grown samples is absent in MBE samples.

A typical low temperature ($T=30$ K) PPC behavior of a *p*-GaN sample grown by MBE is shown in Fig. 1(a), which shows that the conductivity increases by more than one order of magnitude after exposure to light and that the light-enhanced conductivity persists for a very long period of time. PPC seen here is much larger than that in the MOCVD grown *p*-type epilayers.[3] Light exposure enhances the low temperatures conductivity only by 5% in MOCVD samples. Figure 1(b) shows the dark conductivity as a function of temperature. The bottom curve (filled dots) represents data taken with the sample cooling down in the dark, while the top curve (open triangles) is for data taken with the sample being illuminated at 10 K for about 10 min and then warming up in the dark. Figure 1(b) clearly illustrates that the MBE sample exhibits PPC effect below 310 K. The observed hysteresis of the dark conductivity after light exposure is the hallmark of *DX* centers (or *AX* centers) in semiconductors.[6–8]

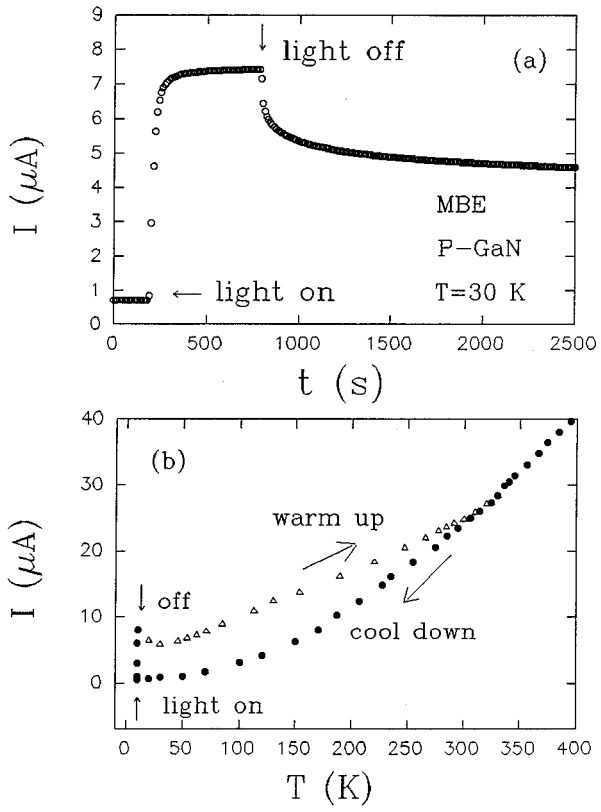

FIG. 1. (a) A typical behavior of persistent photoconductivity (PPC) in Mg-doped *p*-GaN grown by reactive MBE. (b) The dark conductivity as a function of temperature. The bottom curve (solid dots) represents data taken with the sample cooling down in the dark, while the top curve (open triangles) is for data taken with the sample illuminated at 10 K for about 10 min and then warming up in the dark.

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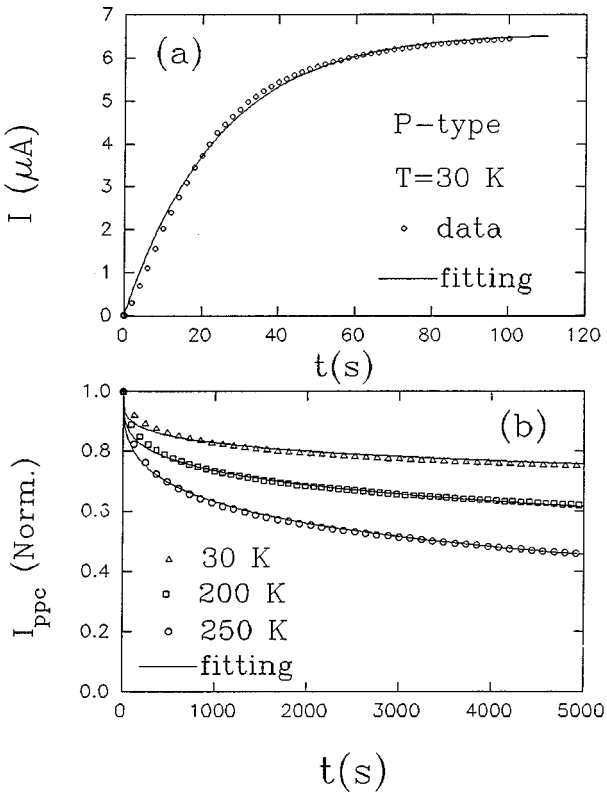

FIG. 2. (a) PPC buildup transient recorded for the first 100 s at 30 K. The solid curve is the least squares fit of data by Eq. (1). (b) PPC decay obtained at three representative temperatures for relatively low buildup levels. Each decay curve is normalized to a unity at $t=0$, the moment at which the light excitation is terminated, and dark level has been subtracted. The solid curves are the least squares fit of data by stretched-exponential functions of Eq. (4).

A crucial feature which further reveals the *AX* nature of Mg impurities in GaN is the kinetics of PPC buildup and decay shown in Fig. 2. As illustrated in Fig. 2(a), the PPC buildup transients can be well described by

$$I_{\mathrm{PPC}}(t)=I_{\max}(1-e^{-\alpha t}), \tag{1}$$

where α is a constant and $I_{\max}$ is the saturation level. Such a PPC buildup behavior has been observed experimentally and formulated theoretically for *DX* centers in AlGaAs.[9] By adopting the picture which has been worked out for AlGaAs, the hole concentration (p) in the valence bands during the illumination is described by

$$dp/dt=g(N_{\mathrm{AX}}-p)-\omega p. \tag{2}$$

Here g is the optical generation rate of the free hole concentration, ω is the hole decay rate in the PPC buildup process, and N_{AX} is concentration of *AX* centers. From Eq. (2) we thus have

$$p(t)=p_{\max}(1-e^{-\alpha t}), \tag{3}$$

where $\alpha=(g+\omega)$ and $p_{\max}=gN_{\mathrm{AX}}/(g+\omega)$. Under the assumption that the hole mobility (μ) is independent of p, Eq. (3) immediately leads to Eq. (1). The solid curve in Fig. 2(a) is the least squares fit of PPC buildup data at 30 K with Eq. (1) and the fitted value of α^{-1} is 23.5 s.

The decay kinetics of PPC seen here are also identical to those of *DX* centers in AlGaAs and follow stretched-exponential functions,[9]

$$I_{\mathrm{PPC}}(t)=I_{\mathrm{PPC}}(0)\exp[-(t/\tau)^{\beta}],\ \ (\beta<1), \tag{4}$$

where $I_{\mathrm{PPC}}(0)$ here is defined as the PPC buildup level at the moment of light excitation being removed, τ is the PPC decay time constant, and β is the decay exponent. Figure 2(b) shows PPC decay for three representative temperatures for relatively low buildup levels. The solid curves are the least squares fit of data with Eq. (4). The fitted values of β are between 0.16 to 0.18. According to the lattice relaxation model for *AX* centers, the temperature dependence of τ can be described by,[9]

$$\tau \propto \exp(E_C/kT),\quad \text{(nondegenerate)} \tag{5a}$$

$$\tau \propto \exp[(E_C-E_F)/kT],\quad \text{(degenerate)}, \tag{5b}$$

where E_C denotes the hole capture barrier of the *AX* centers (Mg acceptors) measured from the valence-band edge, E_F is the hole quasi-Fermi level, and hence (E_C-E_F) is the effective hole capture barrier in the degenerate case. Figure 3(a) presents an Arrhenuis plot of τ ($\ln\tau$ vs $1/T$) for low PPC buildup levels [corresponding to nondegenerate case of Eq. (5a)]. The data in the higher temperature region give a value of 129 meV for the capture barrier (E_C).

In the context of the *AX* center picture, it is expected from Eq. (5b) that, at a fixed temperature, the PPC decay time constant τ would decrease with an increase of hole quasi-Fermi level E_F. Usually hole concentration and hence quasi-Fermi level are varied with dopant level. With PPC the free hole concentration at a fixed temperature can be conveniently varied in a single sample with excitation photon dose (product of excitation intensity and light exposure time). By utilizing this unique feature of PPC, we have obtained a systematic dependence of the PPC decay time constant (τ) on the PPC buildup time (t_b) at a fixed excitation intensity. The experimental result is shown in Fig. 3(b) for 30 K (solid dots). The dependence of τ on t_b can also be derived theoretically from Eq. (5b). If we choose the energy (E) to be positive in the valence band and zero at the valence band edge, then the free hole concentration (p) is related to the Fermi distribution function, $f(T,E_F)=\{1+\exp[(E-E_F)/kT]\}^{-1}$ and the density of states in the valence bands, $g(E)=[(2m_h^*)^{3/2}/2\pi^2\hbar^3]E^{1/2}=CE^{1/2}$, by

$$p=\int_0^{\infty} f(T,E_F)g(E)dE=C(kT)^{3/2}\int_0^{\infty}\frac{y^{1/2}}{(e^{y-\nu}+1)}dy, \tag{6}$$

where $\nu=E_F/kT$. Eq. (6) can be written as,

$$p=C(kT)^{3/2}\Gamma(3/2)J(\nu),\quad \Big[\text{where}\ \ \Gamma(3/2)=\pi^{1/2}/2\ \ \text{and}$$

$$J(v)=\frac{1}{\Gamma(3/2)}\int_0^{\infty}\frac{y^{1/2}}{(e^{y-\nu}+1)}dy.\Big]. \tag{7}$$

Equation (7) gives p in terms of E_F. However, what we need is E_F in terms of p. Such a mapping task has been accomplished previously,[10] where a very accurate expression has been obtained for $\nu[=\nu(J)]$ from $J[=J(\nu)]$, which is,

$$\nu=\ \log J+K_1\ \log(K_2J+K_3)+K_4J+K_5. \tag{8}$$

In Eq. (8), $K_1=4.897$, $K_2=3.311$, $K_3=73.626$, $K_4=0.133$, and $K_5=-21.051$. From Eqs. (5b) and (8), we have

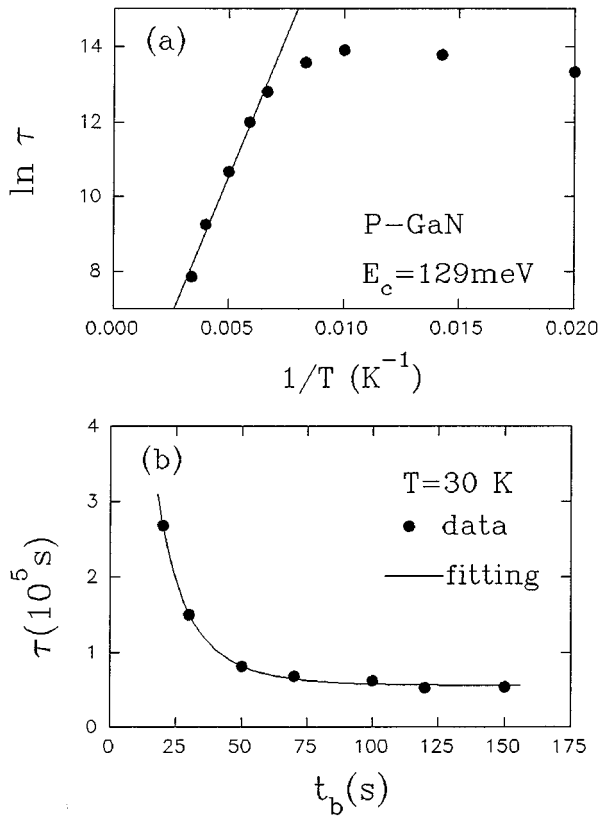

FIG. 3. (a) The Arrhenius plot of the PPC decay time constant τ ($\ln \tau$ vs $1/T$). (b) PPC decay time constant τ as a function of PPC buildup time t_b. The solid curve is the least squares fit of data with Eqs. (9) and (10).

$$\tau = \frac{\tau_0 \exp(E_C/kT)}{J(K_2 J + K_3)^{K_1} \exp(K_4 J + K_5)}. \tag{9}$$

Equations (7) and (3) also give

$$J = \frac{p}{C(kT)^{3/2}\Gamma(3/2)}$$

$$= \frac{p_{\max}}{C(kT)^{3/2}\Gamma(3/2)}[1 - \exp(-\alpha t_b)]. \tag{10}$$

τ as a function of the PPC buildup time (t_b) is described by Eqs. (9) and (10) together, which have been used to fit experimental data. An example is shown in Fig. 3(b) for 30 K data, where the solid curve is the least squares fit of Eqs. (9) and (10) to the experimental data and a perfect agreement has been obtained. Note that by using the experimental value of α, e.g., $\alpha^{-1} = 23.5$ s at 30 K as obtained from Fig. 2(a), there are only two fitting parameters in Eqs. (9) and (10).

Our results demonstrate that there is a lattice relaxation associated with Mg impurities as well as an energy barrier for photoexcited hole capture in Mg-doped GaN. Recent low temperature photoluminescence and Hall measurements suggest that the optical ionization energy of the Mg acceptor (~300 meV) is larger than its thermal ionization energy (~130 meV), implying also a possible lattice relaxation of Mg impurities.[3,5] Such a feature has been theoretically predicted for dopants in various materials.[11] *AX* centers have also been experimentally observed in the other class of blue laser semiconductor materials, namely II–VI wide bandgap semiconductors.[12] The observation of *AX* centers in GaN here seems to suggest that lattice relaxation is a rather common phenomenon of dopants in wide bandgap semiconductors. Our systematic investigations also allow us to draw a detailed comparison between MOCVD and MBE grown epilayers, which is presented in Table I. Our results suggest that Mg impurities are responsible for the PPC effect observed in *p*-GaN grown by both methods and that H passivation may be responsible for the nonequilibrium process of the dark conductivity in MOCVD grown *p*-GaN.

TABLE I. Comparison between Mg impurities in *p*-type GaN grown by MOCVD and MBE.

	MOCVD	MBE
Hydrogen	rich	largely free
Impurities	Mg, H	Mg
Complexes	Mg–H	largely free
Dark conductivity	nonequilibrium	normal
PPC	small	large
Capture barrier (meV)	55	129
Implications	lattice relaxation about Mg (or Mg–H)	lattice relaxation about Mg

In conclusion, the nature of Mg impurities in GaN has been studied by PPC in epilayers grown by reactive MBE. Our results demonstrate the *AX* nature of the Mg acceptors in GaN. Given the fact that a significant advancement of our understanding of impurity properties in semiconductors has been achieved through the studies of *DX* centers and PPC effect in AlGaAs, we expect that the results presented here will shed some light on our understanding of Mg and other impurities in GaN.

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