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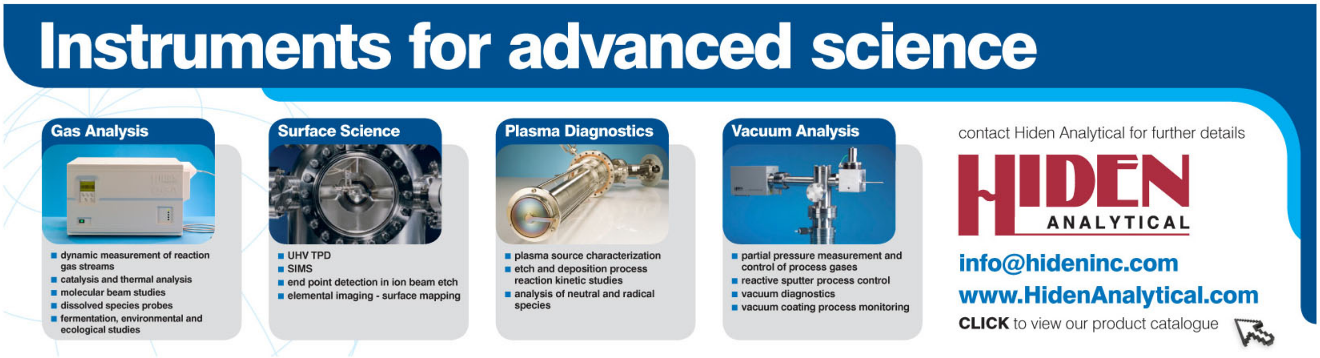

Metastability and persistent photoconductivity in Mg-doped *p*-type GaN

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Electrical properties of Mg-doped *p*-type GaN grown by metalorganic chemical vapor deposition have been investigated by Hall effect and conductivity measurements. Metastability and persistent photoconductivity effects have been observed in GaN. It was found that at low temperatures, it takes several hours for the free hole concentration to reach its equilibrium value in the dark as well as in the photoexcited state, implying a bistable nature of impurities in *p*-type GaN. Temperature dependence of these behaviors have been studied, from which the energy barrier for free hole capture by ionized impurities as well as between the metastable and the stable states of neutral impurities have been obtained. © *1996 American Institute of Physics.* [S0003-6951(96)00913-2]

Recently, group III–V nitride wide band gap semiconductors and their alloys have been intensively studied[1,2] for applications in optical devices that are active in the blue-UV region and electronic devices that are capable of operating at extreme conditions. Despite the many efforts on these materials, understanding and control of impurity properties and *p*-type conduction in these materials remain one of the foremost obstacles hindering device efforts. As is well known, Mg dopant incorporation renders the metalorganic chemical vapor deposition (MOCVD) as-grown GaN highly resistive, and post-growth thermal annealing in a nitrogen ambient is required to activate the Mg dopants in order to obtain *p*-type conduction, possibly due to the dissociation of the H–Mg complex.[3] By incorporating Mg, as deposited *p*-type doping GaN has been achieved only by plasma assisted molecular beam epitaxy (MBE) without post-growth treatment,[4–6] which may be attributed to the absence of H. In all cases, large amounts of Mg are needed in order to achieve *p*-type conduction, and the typical room temperature hole mobilities are lower than 10 cm^2/V s. Thus, there appears to be an urgent need for a better understanding as well as improvement of Mg doping in GaN.

In this letter, we report the observation of the persistent photoconductivity (PPC) effect in Mg-doped GaN. Most strikingly, an anomalously slow thermal equilibrium process for the dark carrier concentration has been observed at low temperatures. These observations suggest that the impurities in *p*-type GaN are of bistable nature. PPC is photoinduced conductivity that persists after the termination of the photoexcitation, which has been observed in many III–V[7,8] and II–VI[9] semiconductors. PPC in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}(x \gg 0.22)$, one of the most common materials used for studying PPC, is believed to be caused by the DX centers that undergo a large lattice relaxation (LLR)[7] and have a negative-U character.[10] Extensive work in this area has led to the conviction that the effect of PPC is strongly correlated to the property of metastability of doped impurities.

The GaN sample used here was grown using a low pressure metalorganic chemical vapor deposition (MOCVD).[11] Ohmic contacts were formed by depositing Au thin film to the four corners of the sample. A Ne lamp was used as the photoexcitation light source. To ensure that each set of data obtained under different conditions has the same initial conditions, the system was always allowed to warm up to room temperature after each measurement, then cooled down in darkness to the desired temperature of measurements. For PPC measurements, because of the metastability behavior of the dark carrier concentration at low temperatures, it was necessary to wait in darkness for more than 7 h before turning on the excitation light source. This was to ensure the true dark current level. The hole concentration and mobility were measured by the standard van der Pauw method and a 1.5 V bias was supplied by a battery for the conductivity measurements. The magnetic field for the measurements was 0.46 T.

In Fig. 1 we present an Arrhenius plot of the dark current of Mg-doped GaN measured from 100 to 600 K. The inset shows the hole mobility, μ_h, as a function of temperature in the range between 150 and 350 K. In the investigated sample, μ_h has a maximum value of about 6 cm^2/V s and a minimum of about 2 cm^2/V s. The small variation in μ_h indicates that the change in the conductivity with temperature is predominantly caused by the change in the hole concentration. A direct measure from the slope of the $\ln(I_d)$ vs $1/T$ plot of Fig. 1 gives a value of 131 meV for the thermal ionization energy of the *activated* Mg acceptor, which is in agreement with previous electrical measurements.[12,13]

The most intriguing observation is the complicated thermal equilibrium process of the dark current seen at low temperatures, as illustrated in Fig. 2. To our knowledge, such a behavior has never been observed in other crystalline semiconductors. It was observed that it is necessary to wait for a very long period of time (typically a few hours) in order for the dark current to reach the equilibrium value. In Fig. 2 we present the dark current as a function of time for four representative temperatures. The starting time $(t=0)$ in Fig. 2 was defined at the moment in which the measurement temperature was attained by the sample, a process that typically takes 10 to 15 min and is short compared with the measuring time. We see that the dark currents are far from their equilibrium values immediately after the sample has reached the desired temperatures. As shown in Fig. 2(a), at temperatures

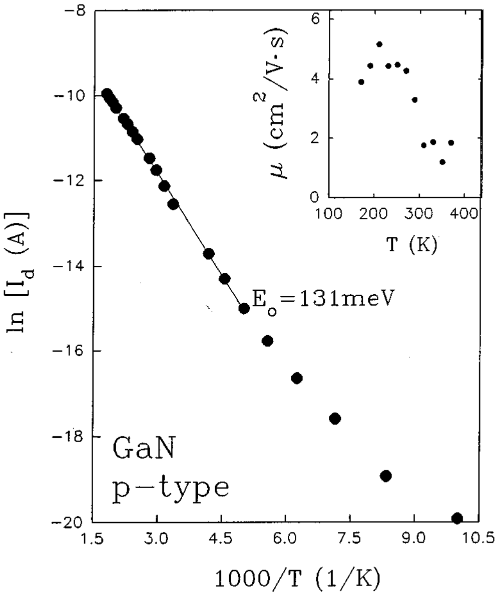

FIG. 1. The Arrhenius plot of the dark current (I_d) for a Mg-doped *p*-GaN sample. The inset shows the hole mobility (μ) as a function of temperature.

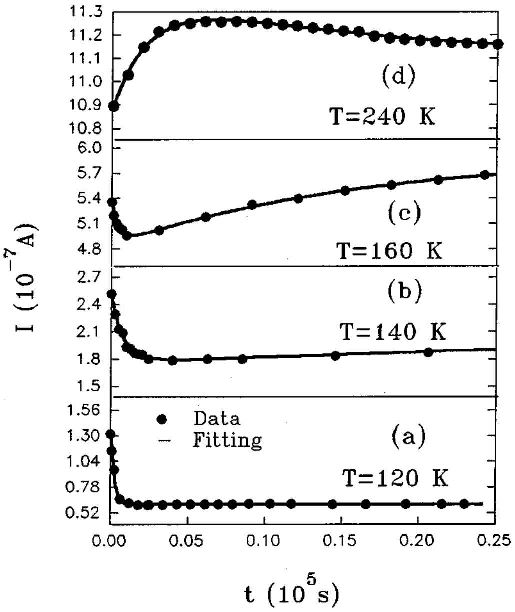

FIG. 2. The dark current as a function of time for four representative temperatures, where $t=0$ is defined as the time when the measuring temperature was attained by the sample. The solid curves are the least-squares fits of data (solid dots) by Eq. (1).

$T<120$ K, the dark current decreases initially and freezes into a lower value throughout the investigated period of time, implying that the process of hole capture by ionized impurities takes about 500 s. As illustrated in Figs. 2(b) and 2(c), two relaxation processes occur at higher temperatures (e.g., 140 and 160 K) i.e., an initial decrease in dark current is followed by a slow increase with a typical time constant of several hours. Notice that the true dark equilibrium level at 160 K is even higher than the initial dark level. On the contrary, an initial increase in dark current is followed by a slow decrease at temperatures above 240 K, which is shown in Fig. 2(d). These results conclusively speak for a bistable nature of impurities in *p*-type GaN.

An effect that complements the metastability behavior of the dark level is the PPC effect seen in the same sample. Figure 3 shows such an effect for two representative temperatures $T=200$ and 240 K. Since the observed PPC decays nonexponentially, the decay constant τ_{PPC} is defined at a time when PPC decays to 30% of its initial level. We find that τ_{PPC} increases with a decrease of temperature as shown in Fig. 4 (open circles) and is thermally activated. Since μ_h does not change with time at a fixed temperature, what we observed is the capture of the photoexcited free holes by the ionized impurity centers.

Our experimental results clearly indicate that there is an energy barrier that prevents the immediate capture of free holes by ionized impurity centers both in the dark and photoexcited states, similar to the properties of *DX* centers in AlGaAs. However, a similar metastable dark current behavior was never observed for *DX* centers in AlGaAs, implying that carrier relaxation processes in *p*-type GaN are more complicated. Based on our observation, we propose the following: (a) Neutral impurities in *p*-type GaN have two different states, a metastable and a stable state. These two states probably correspond to two different local configurations of neutral impurities and neutral impurities are in their metastable state immediately after capturing free holes. (b) There is a potential barrier between the metastable and the stable states of neutral impurities. After capturing a free hole, a neutral impurity will relax from its metastable to stable state with a rate depending on temperature. At this stage, the physical origin of the impurities that are responsible for the observed behaviors is not clear. The observed behavior could be associated with isolated Mg acceptors. Recent low temperature photoluminescence measurements suggest an optical ionization energy of about 300 meV for the shallow Mg acceptors in GaN,[14,15] which is larger than the thermal ionization energy (130–160 meV as determined by electrical measurements) and implies a possible lattice relaxation associated with Mg impurities. Our time-resolved photoluminescence result has also suggested that there may be two neutral acceptor states in *p*-type GaN.[11] However, the observed behavior could be associated with the presence of isolated H impurities or Mg-H complexes. As is well known, the presence of H can lead to a metastability behavior in the dark carrier concentration in polycrystalline Si semiconductors.[16] There is also theoretical evidence that hydrogen and hydrogen complexes in GaN have a negative-*U* character, similar to the *DX* centers in AlGaAs,[17] which could lead to metastability and PPC effects. Comparison experiments on MBE grown *p*-type GaN samples free from hydrogen are underway that will further elucidate the physical origin of the bistable impurities in *p*-type GaN.

In the context of our proposal, at 120 K, free holes are captured by the ionized impurities and are freezed in the metastable state due to the fact that the thermal energy is too low to overcome the potential barrier between the metastable and the stable states. At temperatures of 140 and 160 K, in addition to an increased rate of hole capture by ionized impurities, the increased thermal energy also allows the neutral impurities to relax from their metastable state to stable state. At $T=240$ K, the rate for the neutral impurities to relax from

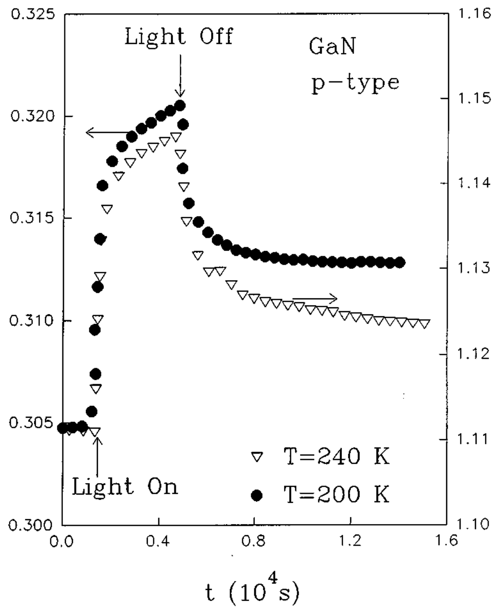

FIG. 3. Build-up and decay of PPC in *p*-type GaN measured at two representative temperatures $T=200$ and 240 K. The arrows indicate the moments at which the excitation light was turned on and off.

their metastable state to stable state is apparently larger than that of the free hole capture by the ionized impurities. Thus, an initial increase followed by a gradual decrease is seen for the dark current at 240 K. The free hole concentration in the dark state or the dark current $I_d(t)$ as a function of time can be described by

$$I_d(t)=I_i-I_1[1-\exp(-t/\tau_1)]+I_2[1-\exp(-t/\tau_2)], \qquad (1)$$

where I_i is the initial dark current at $t=0$, τ_1 is the time constant of free hole capture by ionized impurities, and τ_2 is the relaxation time constants of neutral impurities from their metastable state to stable state. Equation (1) fits dark current data very well for all temperatures, as shown by the solid curves in Fig. 2. From the fit we can also get $I_\infty=I_i-I_1+I_2$, the true equilibrium dark current at different temperatures. We want to point out that although the starting time ($t=0$) is somewhat arbitrarily chosen, the values of τ_1 and τ_2 are unaffected by this arbitrary choice because the relaxation processes are exponential. In Fig. 4 we presented the Arrhenius plot of τ_2 (filled circles) which is also thermally activated as indicated by the straight line. Both τ_{PPC} and τ_2 can be described by

$$\tau_i=\tau_0\ \exp(E_i/kT)\quad(\tau_i=\tau_{\mathrm{ppc}},\tau_2,\ E_i=E_c,E_t), \qquad (2)$$

where E_c is the capture barrier for the photoexcited free holes and E_t is the potential barrier between the metastable and the stable states of the neutral impurities. From Fig. 4 we obtained $E_c=55$ meV and $E_t=68$ meV, respectively. τ_1 describes the capture of free holes in the dark state and is not thermally activated. It increases slightly as temperature increases from 100 to 160 K and then decreases as temperature increases further. Nonthermal activation behavior of τ_1 is consistent with the nonexponential decay behavior of PPC.

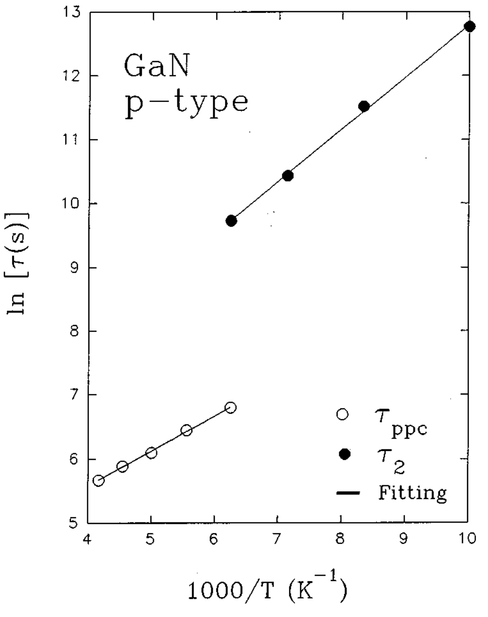

FIG. 4. The Arrhenius plots of the PPC relaxation time constants, τ_{PPC} (open circles) and τ_2 (solid circles). The solid lines are the least squares fits of data with a thermal activation behavior described by Eq. (2).

In conclusion, metastability behavior and persistent photoconductivity effects have been observed in Mg-doped *p*-type GaN grown by MOCVD. Our results clearly demonstrate the bistable nature of impurities of *p*-type GaN. The energy barriers for free hole capture by ionized impurities and between the metastable and stable states of neutral impurities have been obtained.

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