# Metastability of Oxygen Donors in AlGaN

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Experimental and theoretical evidence is presented for the metastability of oxygen donors in $Al_xGa_{1-x}N$. As the aluminum content increases, Hall effect measurements reveal an increase in the electron activation energy, consistent with the emergence of a deep *DX* level from the conduction band. Persistent photoconductivity is observed in $Al_{0.39}Ga_{0.61}N$:O at temperatures below 150 K after exposure to light, with an optical threshold energy of 1.3 eV. A configuration coordinate diagram is obtained from first-principles calculations and yields values for the capture barrier, emission barrier, and optical threshold which are in good agreement with the experimental results. [S0031-9007(98)05950-X]

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In the race to develop blue laser diodes, GaN-based devices have emerged as the current leaders, with projected lifetimes of up to 10 000 hours [1]. An understanding of the role of dopants in group-III-nitride semiconductors is essential for the realization of high-performance optoelectronic devices. In addition to laser diodes, doping issues in AlGaN alloys have important implications for the fabrication of wide band-gap devices such as ultraviolet detectors and high-temperature, high-power transistors.

Oxygen is an omnipresent impurity in the AlGaInN materials system; it is at least partly responsible for the background *n*-type conductivity in nominally undoped as-grown GaN. First-principles theoretical calculations [2] predicted that oxygen can occupy a substitutional nitrogen site ($O_N$) and act as a shallow donor, with a low formation energy under typical growth conditions. Results from secondary ion mass spectrometry (SIMS) [3,4] have shown that in unintentionally doped GaN the concentration of free electrons is approximately equal to the concentration of oxygen present in the material, consistent with the hypothesis that oxygen is a prevalent donor. Layers of heteroepitaxially grown $Al_xGa_{1-x}N$ also exhibit *n*-type conductivity for $x < 0.4$ [5]. For $x > 0.4$, however, undoped $Al_xGa_{1-x}N$ is semi-insulating at room temperature [5]. The freeze-out of carriers has also been observed in GaN under hydrostatic pressures greater than 20 GPa [6,7]. In this Letter, we present evidence that the low concentration of free electrons in Al-rich AlGaN is due to the formation of oxygen *DX* centers.

*DX* centers have been intensively studied for over two decades [8]. In $Al_xGa_{1-x}As$ alloys with $x > 0.22$, the *DX* center is the lowest-energy state of silicon donors. Chadi and Chang [9,10] proposed a model for the negatively charged *DX* center in which the Si atom is displaced into an interstitial position. Recent first-principles calculations [11,12] have predicted that oxygen forms *DX* centers in wurtzite AlN, with the oxygen atom relaxed along a [0001] direction. While Park and Chadi [12] predict that silicon can form *DX* centers in AlGaN, Van de Walle [11] has concluded that silicon is a shallow donor for the entire alloy range.

In this Letter, we present experimental evidence that oxygen is a *DX* center in $Al_xGa_{1-x}N$ for $x > 0.27$, based on the Hall effect, persistent photoconductivity, and optical threshold measurements. The results of first-principles calculations for oxygen in $Al_xGa_{1-x}N$ are also presented and compared with the experimental data.

$Al_xGa_{1-x}N$ epilayers were grown to a thickness of 1 $\mu$m by metalorganic chemical vapor phase epitaxy on *c*-plane sapphire substrates. The Al concentrations were determined by x-ray diffraction (XRD), by assuming relaxed layers and Vegard's law. The concentrations of silicon and oxygen impurities were measured by SIMS. $Al_{0.4}Ga_{0.6}N$ and $Al_{0.5}Ga_{0.5}N$ epilayers were implanted with $^{18}O$ and $^{29}Si$ ions at respective doses of $5 \times 10^{14}$ cm$^{-3}$ and used as calibration standards. Unintentionally doped $Al_xGa_{1-x}N$ shows oxygen and silicon concentrations of approximately $10^{19}$ and $10^{18}$ cm$^{-3}$, respectively. Intentionally doped $Al_{0.44}Ga_{0.56}N$:Si has a silicon concentration of $8 \times 10^{18}$ cm$^{-3}$ and an oxygen concentration of $3 \times 10^{18}$ cm$^{-3}$.

To determine the electron activation energies, variable-temperature Hall effect measurements were performed in the van der Pauw geometry with a magnetic field of 17 kG. Arrhenius plots of electron concentration as a function of inverse temperature for several $Al_xGa_{1-x}N$ samples are shown in Fig. 1. The free-electron concentration of the $Al_{0.44}Ga_{0.56}N$:Si epilayer is $n = 1 \times 10^{19}$ cm$^{-3}$, which is very close to the concentration of silicon atoms measured by SIMS. The fact that the free-electron concentration is independent of temperature indicates that the silicon donors have a small binding energy such that the donor level is degenerate with the conduction band. In the unintentionally oxygen-doped material,

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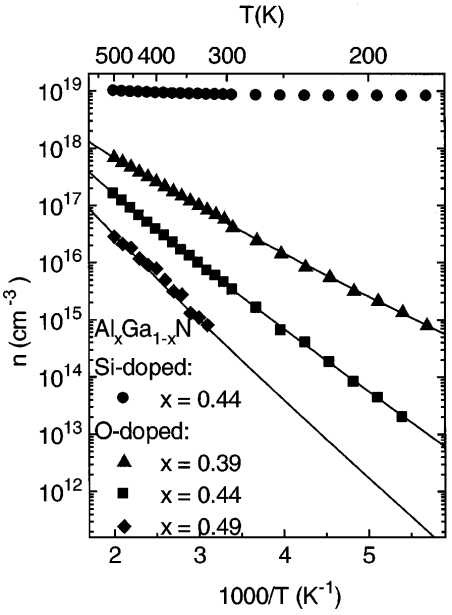


FIG. 1. Free-electron concentration as a function of inverse temperature for silicon- and oxygen-doped $Al_xGa_{1-x}N$.

however, the free electrons freeze out with decreasing temperature. The electron activation energies increase with increasing AlN concentration, which results in freeze-out curves with progressively steeper slopes.

To quantitatively model these results, we derived an expression for the free-electron concentration as a function of temperature. The oxygen is assumed to have three stable charge states: a negatively charged $DX$ state, a neutral donor state, and a positive donor state. With the additional assumption of charge neutrality [13], in the regime where $n \ll N_D - N_A$, the free-electron concentration is given by

$$n \approx N_c \left[ \frac{N_D - N_A}{N_D + N_A} \right]^{1/2} \exp(S/k_B) \exp(-E_{DX}/k_B T), \tag{1}$$

where $n$, $N_D$, and $N_A$ are the free-electron, donor, and acceptor concentrations, respectively; $S$ is the difference in entropy between the donor and $DX$ configurations; $k_B$ is Boltzmann's constant; $E_{DX}$ is the energy difference between the conduction band minimum and the $DX$ level; and $T$ is the temperature in Kelvin. $N_c$ is the conduction band effective density of states, given by

$$N_c = 2 \left( \frac{2\pi m^* k_B T}{h^2} \right)^{3/2}, \tag{2}$$

where $m^* = 0.2 m_e$ is the electron effective mass.

The activation energy $E_{DX}$ was determined by least-square fits of Eq. (1) to the Hall effect data. As shown in Fig. 1, the decrease in the free-electron concentration with increasing AlN content can be explained by an increase in $E_{DX}$. These results are in qualitative agreement with those of Polyakov *et al.* [14]. For $x > 0.5$, the resistivity was such that reliable Hall voltages could not be obtained.

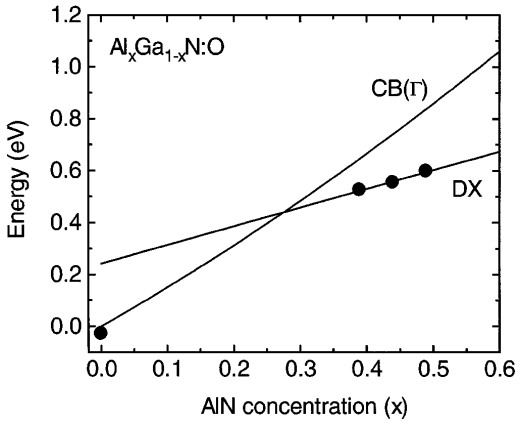


FIG. 2. Dependence of the $DX$ energy level on AlN concentration in $Al_xGa_{1-x}N$:O. The $DX$ level is extrapolated to intersect the conduction band (CB) minimum at an Al concentration of $x = 0.27$.

The increase in the donor binding energy is consistent with a deep $DX$ level which has a lower energy than the conduction band minimum for $x > 0.27$ (Fig. 2). Since the $DX$ wave function is localized in real space, it is extended in $k$ space and is not pinned to the conduction band minimum. To estimate the alloy dependence of the conduction band minimum $E_{\mathrm{CBM}}$, the theoretical $Al_xGa_{1-x}N$ valence band offset of $0.8x$ eV [15,16] is subtracted from the expression for the band gap of $Al_xGa_{1-x}N$ [17], which yields

$$E_{\mathrm{CBM}} = 1.45x + 0.53x^2, \tag{3}$$

where $E_{\mathrm{CBM}}$ is in units of eV and is arbitrarily set to zero for GaN. By linear extrapolation, the $DX$ level intersects the conduction band minimum at $x = 0.27$. This value is significantly lower than the value of $x = 0.4$ predicted by Wetzel *et al.* [7,18] from Raman scattering experiments of GaN:O under hydrostatic pressure. That prediction, however, assumed that the pressure dependence of the valence band is negligible. A more realistic approach is to consider the pressure dependence of the band gap. The band gap of GaN at the critical pressure (20 GPa) is approximately 0.8 eV higher than at ambient pressure [19]. This value corresponds to an Al concentration of $x \sim 0.3$, in good agreement with our results.

Persistent photoconductivity, a more direct manifestation of metastability, is observed in $Al_xGa_{1-x}N$ epilayers for $x \geq 0.39$ at temperatures below 150 K. The persistent photoconductivity of $DX$ centers is attributed to the photoinduced transfer of the $DX$ state into a metastable state. The metastable state has a lower binding energy than the $DX$ state and therefore is more likely to contribute an electron to the conduction band for a given temperature. As shown in Fig. 3, at a temperature of 100 K and an applied bias of 100 V, the current through an $Al_{0.39}Ga_{0.61}N$ epilayer increases by over 2 orders of magnitude after exposure to monochromatic light with a wavelength of 1.1 $\mu$m. After the light is turned off, the current decreases as the

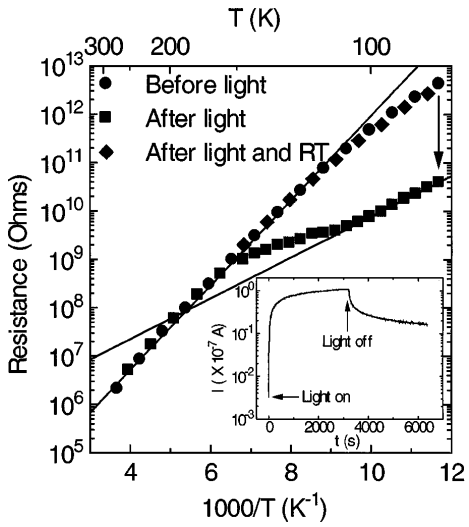


FIG. 3. Resistance of $Al_{0.39}Ga_{0.61}N$:O as a function of temperature. The material was cooled in the dark (circles), exposed to light (squares), and warmed to room temperature. To check the reproducibility of the measurements, the temperature was again lowered (diamonds). The transient current at a temperature of 100 K and an applied bias of 100 V after exposure to infrared light with a wavelength of 1.1 $\mu$m is shown in the inset.

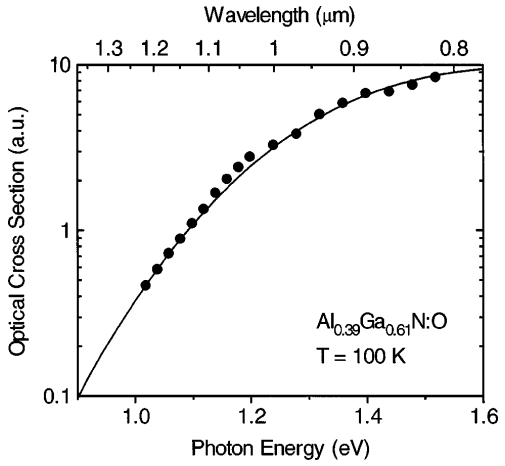


FIG. 4. Optical cross section of oxygen *DX* centers in $Al_{0.39}Ga_{0.61}N$ as a function of wavelength at 100 K. The optical threshold $E_{opt}$ is approximately 1.3 eV.

metastable states transfer back to the *DX* states via electron capture. After 1 h, the current remains approximately 90 times greater than the dark current.

The temperature dependence of the resistance of the $Al_{0.39}Ga_{0.61}N$ before and after exposure to light is shown in Fig. 3. The samples were cooled in the dark to a temperature of 100 K and then exposed to light for a duration of 1 h. The light was then turned off, and the system was allowed to relax for 1 h (inset). The temperature was then raised to room temperature. The resistance was determined by measuring current as a function of voltage at each point. Finally, to check the reproducibility of the measurements, the sample was again cooled in the dark. From the relative slopes of the solid lines in Fig. 3, it is apparent that the binding energy of the metastable state is indeed lower than that of the *DX* state. Since Hall effect measurements were not possible at these low temperatures, however, we were not able to quantitatively determine the binding energy of the metastable state. As shown in Fig. 3, the oxygen centers return to the deep state from the shallow state at temperatures around 120 to 150 K. Given the assumptions of first-order kinetics and an attempt frequency of $10^{13}$ Hz, this temperature range corresponds to a capture barrier of 0.4 to 0.5 eV, in good agreement with our calculations (Fig. 5).

It is important to note that persistent photoconductivity has been reported in *p*-type [20,21] and *n*-type [21–24] GaN and has been attributed to the photoionization of deep levels in the band gap. In all of these cases, photoconductivity is observed at room temperature. In the present study, however, photoconductivity is not observed at temperatures higher than 150 K, beyond which point the *DX* and shallow donor levels are in thermal equilibrium. In addition, while the optical absorption threshold energy in *n*-type GaN is greater than 2 eV, as discussed in the next paragraph the threshold energy for oxygen *DX* centers in AlGaN is approximately 1.3 eV.

To estimate the optical cross section of absorption for the DX centers, the photocurrent was measured for photon energies from 1.0 to 1.5 eV. Since the current does not display simple exponential behavior (Fig. 3), the cross section was assumed to be proportional to the magnitude of the current after a 1 h exposure to monochromatic light. The data can be fit by the following expression [25,26], which describes optical absorption of a deep defect accompanied by significant lattice relaxation:

$$\sigma(h\nu) \propto \frac{1}{h\nu}\int_0^\infty E^{1/2}\,dE\left[\frac{(1-\eta)\sqrt{E}}{E_{\rm opt}+E}+\frac{(1+\eta)\sqrt{E_F}}{E_{\rm opt}-E-(E_g+E_A)/2}\right]^2(\Delta E)^{-1}\exp[-(h\nu-E_{\rm opt}-E)^2/(\Delta E)^2], \tag{4}$$

where $h\nu$ is the photon energy, $E_F = 20$ eV is the free-electron Fermi energy, $E_g = 4.2$ eV is the measured band gap of $Al_{0.39}Ga_{0.61}N$, $E_A = 7$ eV is the Penn gap, and $\eta \equiv \exp(-2E/E_A)$. The adjustable parameters are $E_{opt}$ (the optical absorption threshold) and $\Delta E$, a term which accounts for the broadening of the optical absorption peak due to the emission of multiple phonons. As shown in Fig. 4, a good fit to the data is obtained for $E_{opt} = 1.3$ eV

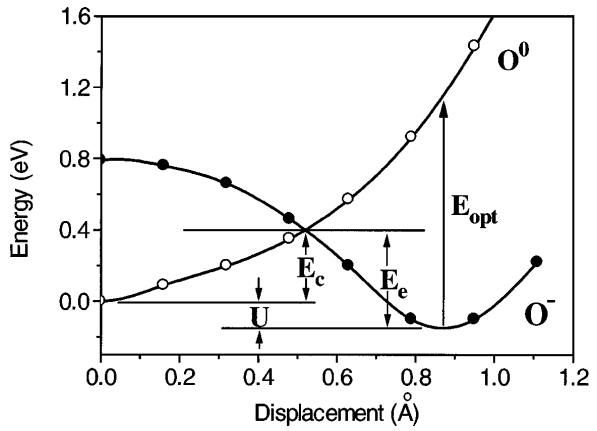


FIG. 5. Configuration coordinate diagram for oxygen displacements along [0001] in AlGaN, based on first-principles calculations for GaN:O and AlN:O. $E_{\text{opt}}$ is the optical ionization energy; $E_c$ and $E_e$ are the capture and emission barriers.

and $\Delta E = 0.25$ eV. The value of $E_{\text{opt}}$ is comparable to that of Si *DX* centers in AlGaAs, which is estimated to lie between 1.3 to 1.6 eV [8].

The experimental value of $E_{\text{opt}}$ is in excellent agreement with theory. Figure 5 shows a configuration coordinate diagram for oxygen displacements along [0001] in AlGaN. The data points are obtained from first-principles calculations for oxygen in GaN and in AlN, based on an interpolation for the case where the *DX* configuration is 0.1 eV lower in energy than the substitutional donor (i.e., $U \sim -0.1$ eV). Details of those calculations, based on density-functional-pseudopotential theory, are described in Ref. [11]. The calculated capture and emission barriers are 0.4 and 0.5 eV, respectively. The calculated optical ionization energy is 1.3 eV, which agrees with the experimental value.

In conclusion, we have discovered a metastability in $Al_xGa_{1-x}N$ that can be ascribed to oxygen donors. The increase in the donor binding energy with $x$ is consistent with a localized *DX* state which intersects the conduction band at $x = 0.27$. In $Al_{0.44}Ga_{0.56}N$ intentionally doped with Si, no evidence was observed for donor metastability, in agreement with theoretical calculations which predict that silicon does not form *DX* centers in AlGaN [11]. These results also concur with measurements of GaN under hydrostatic pressures of ~20 GPa [7] which indicate that oxygen forms a deep level while silicon remains a shallow donor.

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