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EVIDENCE FOR OXYGEN DX CENTERS IN AlGaN

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ABSTRACT

Experimental and theoretical evidence is presented for oxygen *DX* centers 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, in excellent agreement with first-principles calculations. Unlike oxygen, silicon does not exhibit *DX*-like behavior, in agreement with previous theoretical predictions.

INTRODUCTION

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 [1]. Oxygen is an omnipresent impurity in AlGaN alloys and 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. Experiments [3,4] have verified that oxygen is a prevalent donor in as-grown GaN. $Al_xGa_{1-x}N$ epilayers 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 paper, 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 paper we present experimental evidence that oxygen is a

DX center in $Al_xGa_{1-x}N$ for $x>0.27$, based on Hall effect, persistent photoconductivity, and optical threshold measurements.

EXPERIMENTAL DETAILS

$Al_xGa_{1-x}N$ epilayers were grown to a thickness of 1 μm by metalorganic chemical vapor phase epitaxy (MOCVD) 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 secondary ion mass spectrometry (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 5×10^{14} cm^{-3} and used as calibration standards. Unintentionally doped $Al_xGa_{1-x}N$ shows oxygen and silicon concentrations of approximately 10^{19} cm^{-3} and 10^{18} cm^{-3}, respectively. Intentionally doped $Al_{0.44}Ga_{0.56}N$:Si has a silicon concentration of 8×10^{18} cm^{-3} and an oxygen concentration of 3×10^{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 kGauss.

DX CENTERS IN AlGaN

Hall Effect

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 $n \sim 10^{19}$ cm^{-3}, which is very close to the concentration of silicon atoms measured by SIMS. The temperature independent free-electron concentration suggests 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, 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.

The activation energy E_{DX} was determined by exponential fits to the Hall effect data [13]. 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} . Our results are in qualitative agreement with those of Polyakov *et al* [14].

The increase in E_{DX} is consistent with a deep *DX* level which has a lower energy than the conduction band minimum for $x > 0.27$ (Fig. 2). E_{DX} is interpreted as the energy difference between the conduction band minimum and the *DX* level. Since the *DX* wavefunction is localized in real space, it is extended in *k*-space and its alloy dependence differs from that of the conduction band minimum. To estimate the alloy dependence of the conduction band minimum E_{CBM} , the theoretical $Al_xGa_{1-x}N$ valence band offset of 0.8*x* eV [15,16] is subtracted from the expression for the band gap of $Al_xGa_{1-x}N$ [17], which yields

$$E_{CBM} = 1.45x + 0.53x^2, \quad (3)$$

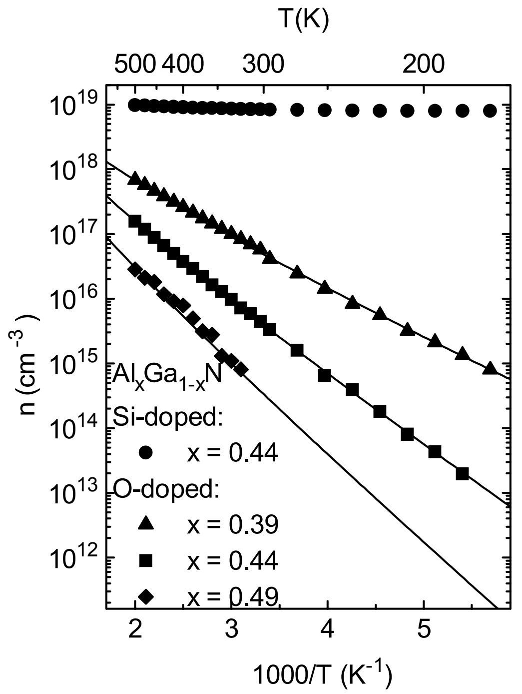

Figure 1. Hall effect measurements of $Al_xGa_{1-x}N$

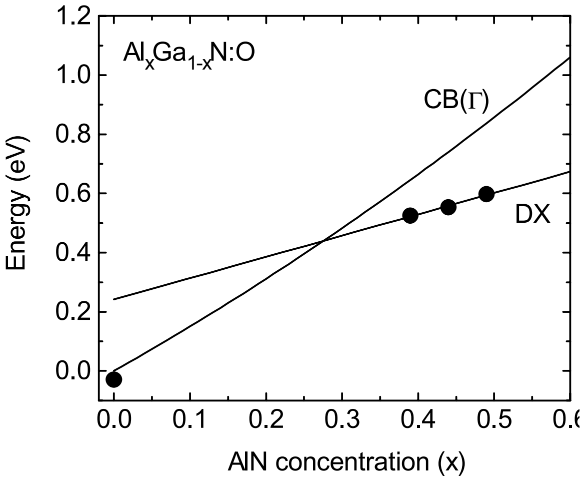

Figure 2. Conduction band (CB) minimum and *DX* level in $Al_xGa_{1-x}N$.

where E_{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 $x = 0.27$. Since the oxygen donor binding energy is nonzero, the point at which the *DX* state intersects the donor level occurs at some point slightly greater than $x = 0.27$. Our results compare favorably with experiments of GaN:O under hydrostatic pressure [7,18]. 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

Persistent photoconductivity 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. As shown in Fig. 3, at a temperature of 100 K and an applied bias of 100 volts, the current through an $Al_{0.39}Ga_{0.61}N$ epilayer increases by over two orders of magnitude after exposure to monochromatic light with a wavelength of 1.1 μm. After the light is turned off, the current decreases as the metastable states transfer back to the *DX* states via electron capture. After 1 hr, the current remains approximately 90 times greater than the dark current.

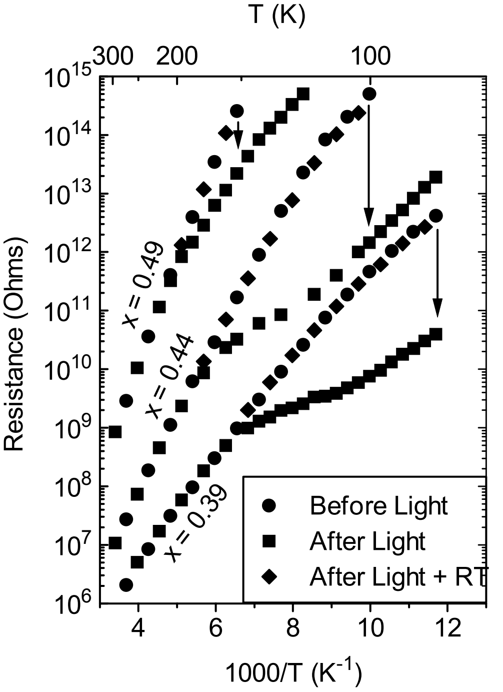

Figure 3. Resistance of $Al_xGa_{1-x}N$ before and after exposure to light.

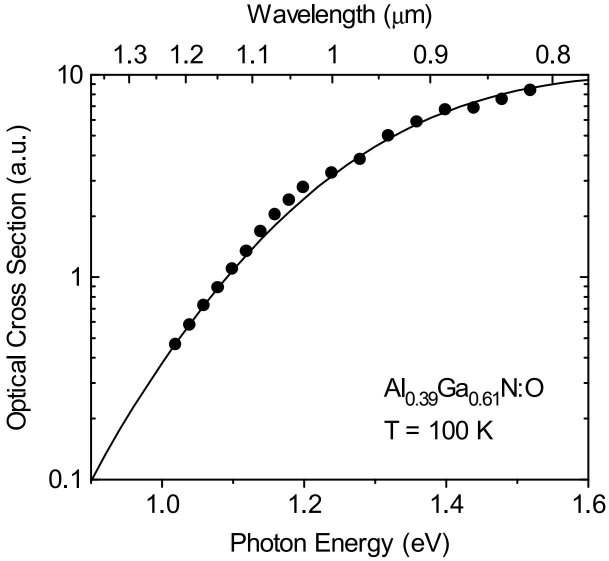

Figure 4. Optical cross section of oxygen *DX* centers in $Al_{0.39}Ga_{0.61}N$.

The temperature dependence of the resistance of $Al_xGa_{1-x}N$ epilayers before and after exposure to light is shown in Fig. 3. The samples were cooled in the dark (circles) to a temperature of 100 K and then exposed to light for 1 hr. The light was then turned off and the system was allowed to relax for 1 hr. The temperature was then raised to room temperature (squares). 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 (diamonds). 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.

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 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.

Optical Absorption Threshold

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, the cross section was assumed to be proportional to the magnitude of the current after a 1 hr exposure to monochromatic light. The data can be fit by a theory [25,26] that describes optical absorption of a deep defect accompanied by significant relaxation. An optical threshold of E_{opt} = 1.3 eV is derived. Although a photon with an energy less than 1.3 eV can excite a transisition from the *DX* to the donor state, such a transition involves a displacement of the oxygen and therefore its probability decreases with decreasing photon energy.

The experimental value of E_{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 subsitutional 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.

CONCLUSIONS

In conclusion, we have discovered evidence for oxygen *DX* centers in $Al_xGa_{1-x}N$. 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.

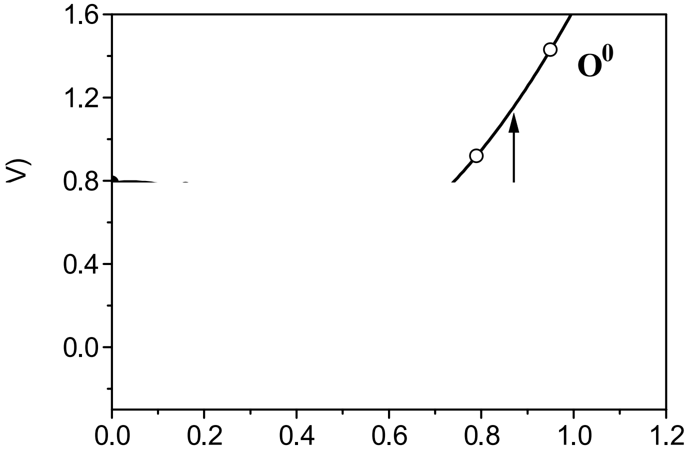

Figure 5. Configuration coordinate diagram for oxygen in AlGaN.

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