Controlled oxygen doping of GaN using plasma assisted molecular-beam epitaxy

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High-quality (0001) and (000$\bar{1}$)-GaN films were grown by plasma-assisted molecular-beam epitaxy to study the dependence of oxygen incorporation on polarity and oxygen partial pressure. Oxygen incorporates at a rate ten times faster on nitrogen-polar GaN than on the Ga polarity. Oxygen doping is controllable, reproducible, and produces low compensation material up to concentrations of at least 10^{18} cm^{-3} with higher levels showing significant compensation. Layers containing oxygen at levels above 10^{22} cm^{-3} exhibit severe cracking while oxygen concentrations less than 10^{21} cm^{-3} do not introduce significant strain. The oxygen incorporation rate has a weak dependence on Ga overpressure during Ga-stable growth but dramatically increases for conditions approaching N-stable growth. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1403276]

Many groups have studied the role of oxygen in GaN, but most studies have focused on unintentionally doped material with oxygen supplied either by an "uncontrolled" system background or from outdiffusion from the sapphire substrate. Also of importance, and something that has not received the proper attention, is the effect of surface polarity on the incorporation of oxygen. Zywietz *et al.*[1] used first-principles calculations to predict that, for typical Ga-stable growth conditions, the Ga-polar surface would adsorb lower amounts of oxygen than the N-polar surface. A secondary ion mass spectrometry (SIMS) study of Ga- and N-polar GaN grown by metalorganic chemical vapor deposition (MOCVD) by Sumiya *et al.*[2] found about 170 times more oxygen for N-polar growth. However, N-polar material grown by MOCVD is typically of poor quality, raising the uncertainty that poor structure could be the cause of the increased incorporation. It is also not clear this result is directly applicable to the molecular-beam epitaxy (MBE) growth of GaN. In this letter, we present the results of a controlled study of oxygen incorporation in GaN using MBE.

The oxygen doped GaN layers were grown at West Virginia University (WVU) by rf plasma-assisted MBE using procedures described in prior studies.[3] Ultrahigh purity oxygen gas (99.998%) was introduced through a tube directed at the substrate using an ultrahigh vacuum leak valve and monitored using a residual gas analyzer. N-polarity GaN was obtained by nucleating GaN buffer layers directly on sapphire under heavily Ga-rich conditions.[4] Incorporation in Ga-polarity GaN was studied by growth on semi-insulating MOCVD GaN templates on A-plane sapphire substrates grown at the Naval Research Laboratory. Transmission electron microscopy studies on similar layers grown under identical conditions at WVU indicated that our growth procedure produces N-polar and Ga-polar layers of comparable quality, with typical dislocation densities in the low 10^9 cm^{-3}.[5]

Temperature-dependent Hall effect measurements were performed using indium to form ohmic contacts with the standard van der Pauw geometry. Measurements routinely included several current levels at each temperature to ensure contact resistance was not an issue, particularly for the lower doped samples. The use of semi-insulating MOCVD templates resolved the difficulties encountered in measuring low carrier concentration material when using conducting templates. Room temperature Raman spectroscopy was performed using a Jobin–Yvon Ramanor U-1000 micro-Raman system excited by 476 nm laser light. SIMS measurements at Evans Analytical Group, Charles Evans and Associates (Sunnyvale, CA) determined the concentration of oxygen in the films using a Cameca ion microprobe.

Figure 1 shows a SIMS measurement of oxygen incorporation for a N-polar step-doped sample. During growth, the doped regions were created through adjusting the leak valve to attain the proper oxygen partial pressure. Approximately 0.25 μm of doped material was grown in each step followed by closing the oxygen valve to grow a 0.5 μm thick undoped spacer. A clear dependence of the concentration of oxygen, [O], is seen with increasing oxygen partial pressure. The steps are very sharp (less than 8 nm decade) for N-polarity growth. Similar Ga-polar structures grown on MOCVD templates exhibited the same trend for incorporation with oxygen partial pressure, but the steps were not as abrupt (approximately 88 nm/decade).

Oxygen doping to produce *n*-type material was controllable and reproducible under Ga-stable growth conditions us-
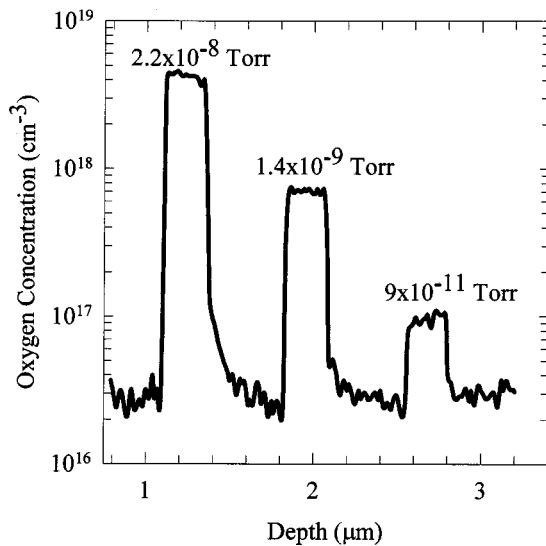
FIG. 1. SIMS measurement showing oxygen incorporation in a N-polar step-doped sample is presented. The partial pressure of oxygen used for each step is indicated.
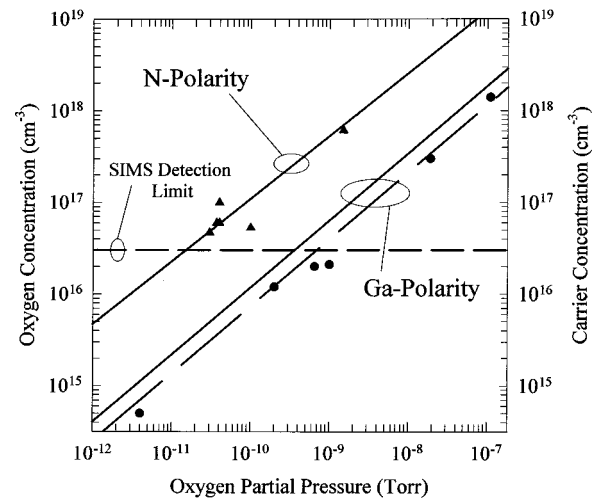

FIG. 2. SIMS measurement of oxygen concentration (lines) and room temperature Hall carrier concentrations (points) vs oxygen partial pressure is shown. The lines represent a least-squares fit to SIMS oxygen concentration for constant Ga-overpressure (solid: 1.6×10^{-6} Torr BEP and dashed: 1.0×10^{-6} Torr BEP). N-polar Hall results were for layers grown under a Ga overpressure of 1.6×10^{-6} Torr BEP while Ga-polar Hall results were for a Ga-overpressure of 1.0×10^{-6} Torr BEP.

ing O_2 as the dopant source for concentrations up to 10^{18} cm^{-3}. Figure 2 compares the least-squares fit to the oxygen concentrations as determined by SIMS from the step-doped layers to room-temperature Hall effect measurements of carrier concentration from uniformly doped layers. The lines representing the SIMS data have been extrapolated below the SIMS detection limit. N-polar GaN incorporates about one out of every fifty available oxygen atoms into the growing layer based on measured partial pressures. Incorporation in Ga-polar GaN is less effective by about an order of magnitude. The two oxygen incorporation trend lines for Ga-polar growth indicated in Fig. 2 were generated for different Ga overpressures.

The room temperature carrier concentrations determined by Hall effect measurements are consistent with oxygen acting as a shallow donor that appears uncompensated up to concentrations of $\sim 10^{18}$ cm^{-3}. The oxygen incorporation predicted from the SIMS calibration and the measured carrier concentration were in good agreement for both polarities, with all measurements agreeing to within a factor of two. Interestingly, measured carrier concentrations from our unintentionally doped Ga-polar material correlates nicely with the extrapolated oxygen concentration predicted by the SIMS calibration based on the residual background partial pressure of oxygen in our system during growth (approximately $4-5 \times 10^{-12}$ Torr). This strongly suggests that our residual n-type carrier background is primarily due to oxygen. The SIMS and Hall effect results provide consistent evidence of the influence of polarity on the incorporation of oxygen.

The temperature-dependent Hall effect data for a Ga polar sample shown in Fig. 3 indicates a room temperature mobility of ~ 500 cm^2/V s and a peak mobility at low temperature of ~ 1500 cm^2/V s. Importantly, carrier concentration data obtained for O-doped layers such as that shown in Fig. 3 is consistent with a single donor in relatively uncompensated material. While care must be taken in interpreting fits to the full charge-balance equation, this result is again consistent with the close correlation between Hall and SIMS results indicated in Fig. 1. Direct analysis of the data shown

in Fig. 3 indicates a thermal activation energy of 30 meV for this oxygen doped sample. When carrier screening is taken into account,[6] a donor energy of 35 meV is indicated. Analyses of all temperature-dependent Hall measurements to date on layers with carrier concentrations between 10^{16} and 10^{18} cm^{-3} are consistent with oxygen forming an uncompensated shallow donor with a donor energy level between 35 and 39 meV. Similar Hall activation energies were observed for oxygen doping on both polarities of GaN. The maximum room temperature mobilities measured were around 500 cm^2/V s and occurred at doping levels of about 10^{16} cm^{-3}. Mobility values dropped to 90 cm^2/V s for the lowest carrier concentration measured, $\sim 5 \times 10^{14}$ cm^{-3}, consistent with predictions of dislocation scattering for an estimated dislocation density in the low 10^9 cm^{-2}.[7] The mobility also steadily decreased with increasing oxygen concentration above 10^{16} cm^{-3}, consistent with increased carrier scattering, with resulting mobilities slightly lower than the corresponding results for equivalent Si-doping in GaN.[8]

During Ga-stable growth, oxygen incorporation exhibited only a small dependence on Ga overpressure. Incorporation increased about a factor of two upon changing the Ga beam-equivalent pressure (BEP) from 1.0 to 1.6×10^{-6} Torr. In contrast, oxygen incorporation was found to increase by up to four orders of magnitude for growth approaching N-stable conditions (approximately 5.0×10^{-7} Torr Ga BEP). The dramatic increase in [O] for a given partial pressure as growth approaches N-stable conditions is indicated by the data contained in Table I. The sharp increase with decreasing Ga flux makes oxygen incorporation difficult to control under these conditions, unlike Ga-stable growth.

Significant compensation occurs for concentrations above 10^{21} cm^{-3} as seen by comparing the oxygen incorporation and the carrier density in Table I. The samples with the highest [O] also exhibited significant cracking. Similar cracking is observed for heavy Si doping due to tensile stress
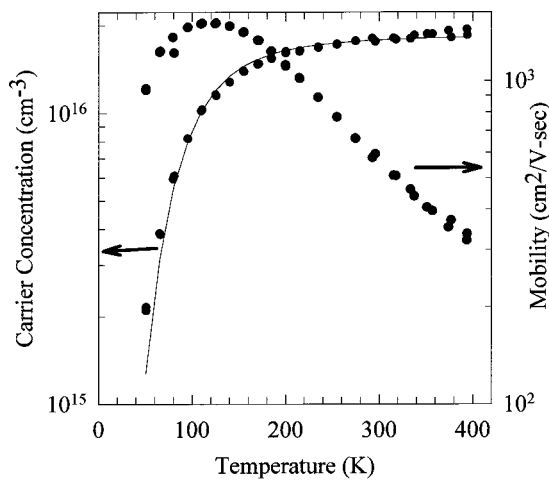
FIG. 3. Temperature-dependent Hall effect measurement of an oxygen doped Ga-polar sample is shown. The line is the fit to the full charge-balance equation assuming a single donor with a potential compensating acceptor with results indicating the sample is reasonably uncompensated.

TABLE I. Growth conditions and results for oxygen doped layers are shown.

Polarity	Ga BEP (Torr)	P_{O_2} (Torr)	[O][a] (cm^{-3})	n[b] (cm^{-3})
N	1.6×10^{-6}	1×10^{-10}		5.4×10^{16}
N	8.3×10^{-7}	1×10^{-10}		6.3×10^{17}
N	1.8×10^{-6}	3.0×10^{-7}		3.2×10^{18}
N	9.2×10^{-7}	1.8×10^{-7}		9.0×10^{19}
N	5.0×10^{-7}	1.7×10^{-7}		6.8×10^{19}
Ga	5.0×10^{-7}	6×10^{-8}	1.5×10^{20}	
Ga	1.6×10^{-6}	6×10^{-8}	1.6×10^{18}	
Ga	1.0×10^{-6}	6×10^{-8}	8.5×10^{17}	
Ga	9.5×10^{-7}	1.0×10^{-7}		1.4×10^{18}
Ga	4.8×10^{-7}	5.0×10^{-8}	2.6×10^{21}	4.0×10^{19}
Ga	4.9×10^{-7}	2.0×10^{-7}	1.5×10^{22}	8.4×10^{19}
Ga	4.9×10^{-7}	1.5×10^{-7}	2.5×10^{22}	3.0×10^{20}

[a]Measured by SIMS.
[b]Measured by Hall effect at 300 K.

occurring for Si levels above 2×10^{19} cm^{-3}.[9] Raman spectroscopy can be used to measure stress in GaN (Ref. 9) by monitoring shifts in the E_2 Raman peak energy (at ~569 cm^{-1}). For most Ga-polar layers, the E_2 peak was measured for the MOCVD template prior to growth for comparison with that measured for the composite system of 1 μm doped MBE on about 2 μm of MOCVD GaN. For N-polar layers, comparison was made between undoped and oxygen doped layers of the same thickness. Interestingly, no evidence of increased strain was measured for either polarity for [O] up to $\sim3\times10^{21}$ cm^{-3}. This result is consistent with calculations indicating the tensile strain observed in highly n-type Si-doped GaN is not due to electronic effects[9] or else a similar large strain would also be observed in these highly doped layers. Some drastic effect does occur, however, for [O] above this level as all layers with [O] higher than 10^{22} cm^{-3} exhibit significant cracking.

Oxygen incorporation trends are consistent with the prediction that the formation energy of substitutional oxygen should decrease with an increasing III/V ratio for Ga-stable conditions.[10] As discussed, the incorporation of oxygen shows a dramatic increase, by up to four orders of magnitude, upon approaching N-stable growth conditions. Unlike most semiconductors, the growing GaN surface does not relax by forming dimers or other complex structures to reduce surface dangling bonds. Instead, these bonds are saturated by the formation of one or more Ga adlayers.[11] Thus, the surface becomes highly reactive under growth conditions hindering formation of the Ga adlayer. The resulting surface dangling bonds strongly increase the adsorption of oxygen, explaining the increased oxygen affinity[1] as N-stable conditions are approached. Indeed, for lower Ga coverage and lower O$_2$ flux, both polarities are predicted to be equally reactive to oxygen incorporation.[1] It is the presence of the Ga adlayer that significantly reduces the adsorption and incorporation of oxygen, with a more pronounced effect on the Ga-polarity sur-face. Therefore, it is important to grow high-quality GaN under sufficiently Ga-stable conditions to minimize the incorporation of background impurities such as oxygen.

In summary, a controlled study of oxygen incorporation in high-quality GaN grown by plasma-assisted MBE shows distinct surface polarity dependence, with the $(000\bar{1})$ polarity incorporating about an order of magnitude more oxygen than the (0001) polarity. Oxygen can be an effective and controllable donor impurity. Low compensation, unstrained material with carrier concentrations up to 10^{18} cm^{-3} has been obtained although significant strain and electrical compensation do occur at higher levels. Oxygen shows an incorporation dependence on Ga overpressure during growth with a drastic incorporation increase when approaching N-stable conditions likely due to the elimination of the Ga adlayers that exist on the surface during Ga-stable growth.

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