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PROPERTIES OF H, O AND C IN GaN

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ABSTRACT

The electrical properties of the light ion impurities H, O and C in GaN have been examined in both as-grown and implanted material. H is found to efficiently passivate acceptors such as Mg, Ca and C. Reactivation occurs at ≥450°C and is enhanced by minority carrier injection. The hydrogen does not leave the GaN crystal until >800°C, and its diffusivity is relatively high ($\sim 10^{-11} cm^2/s$) even at low temperatures (<200°C) during injection by wet etching, boiling in water or plasma exposure. Oxygen shows a low donor activation efficiency when implanted into GaN, with an ionization level of 30 - 40 meV. It is essentially immobile up to 1100°C. Carbon can produce low p-type levels ($3 \times 10^{17} cm^{-3}$) in GaN during MOMBE, although there is some evidence it may also create n-type conduction in other nitrides.

INTRODUCTION

H, O and C are the most common residual impurities in III-V semiconductors. Hydrogen can form neutral dopant-hydrogen complexes and dramatically reduce carrier levels. Oxygen introduces a deep acceptor level in GaAs and in particular AlGaAs, while carbon is an efficient shallow acceptor in some materials and a donor in others.

In both Si and GaAs[1-4], injection of minority carriers either by forward biasing of a diode structure or illumination with above-bandgap light produces dissociation of neutral acceptor-hydrogen or donor-hydrogen complexes at temperatures at which they are normally thermally stable. While the details of the reactivation process are not clearly established, it is expected that for an acceptor A the reactions likely can be described by

$$(AH)^\circ \leftrightarrow A^- + H^+ \qquad (1)$$

$$H^+ + e^- \leftrightarrow H^\circ \qquad (2)$$

The neutral hydrogen most likely forms diatomic or larger clusters with other neutral or charged hydrogen species.(4)

RESULTS AND DISCUSSION

1. Hydrogen

There has recently been a lot of interest in the stability of hydrogen passivated Mg acceptors in GaN. Amano et al.[5] first demonstrated p-type conductivity in GaN (Mg) after an e-

beam irradiation process near room temperature and later Nakamura et al.(6) showed that simple thermal annealing at ~700°C also reactivated the Mg acceptors. It is clear that atomic hydrogen remaining in the GaN after growth by metal organic chemical vapor deposition (MOCVD) with NH_3 and $(CH_3)_3Ga$ precursors attaches to the Mg, forming neutral complexes. Currently all Mg-doped GaN grown by MOCVD is annealed under N_2 for 20–60mins at ~700°C to achieve the full level of p-type conductivity.[6] The mechanism for acceptor activation during the e-beam irradiation process has not been studied in detail to date. To establish that minority carrier enhanced debonding of Mg-H complexes in GaN is responsible for this phenomenon, we examined the effect of forward biasing in hydrogenated p-n junctions. We find that the reactivation of passivated acceptors obeys second order kinetics and that the dissociation of the Mg-H complex is greatly enhanced under minority carrier injection conditions.

The sample were grown an c-Al_2O_3 by MOCVD using a rotating disk reactor. After chemical cleaning of the substrate in both acids (H_2SO_4) and solvents (methanol, acetone), it was baked at 1100°C under H_2. A thin (≤300Å) GaN buffer was grown at 510°C, before growth of ~1μm undoped material, 0.5μm of GaN(Mg) with a carrier density of $p \sim 1.5 \times 10^{17}$cm^{-3} after 700°C annealing and 0.3μm of GaN (Si) with a carrier density of 5×10^{18}cm^{-3}. Some of the samples were hydrogenated by annealing under NH_3 for 30 mins at 500°C. This produces passivation of the Mg acceptors but has little effect on the Si donors.

Mesa p-n junction diodes were processed by patterning 500μm diameter TiAl ohmic contacts on the n-GaN by lift-off and then performing a self-aligned dry etch with an Electron Cyclotron Resonance BCl_3/Ar plasma to exposure the p-type GaN. E-beam evaporated NiAu was patterned by lift-off to make ohmic contact to the p-type material. The carrier profiles in the p-type layer were obtained from 10kHz capacitance-voltage measurements at room temperature. Anneals were carried out in the dark at 175°C under two different types of condition. In the first, the diode was in the open-circuit configuration. while in the second the junction was forward biased at 9mA to inject electrons into the p-type GaN. After each of these treatments the samples were returned to 300K for re-measurement of the net electrically active acceptor profile in this layer.

Figure 1 shows a series of acceptor concentration profiles measured on the same p-n junction sample, after annealing at 175°C under forward bias conditions. After the NH_3 hydrogenation treatment the electrically active acceptor density decreased from 1.5×10^{17}cm^{-3} to ~6–7×10^{16}cm^{-3}. If the subsequent annealing was carried in the open-circuit configuration there was no change in the carrier profile for periods up to 20hr at 175°C. By sharp contrast Figure 1 shows that for increasing annealing times under minority carrier injection conditions there is a progressive reactivation of the Mg acceptors with a corresponding increase in the hole concentration. After 1hr, the majority of these acceptors have been reactivated. Clearly therefore, the injection of electrons has a dramatic influence on the stability of the MgH complexes. The Mg reactivation has a strong dependence on depth into the p-type layer, which may result from the diffusion distance of the injected electrons prior to recombination. We rule out heating of the sample during forward biasing as being a factor in the enhanced dissociation of the neutral dopant-hydrogen complexes. The samples were thermally bonded to the stainless steel stage and the junction temperature rise is expected to be minimal (≤10°C). Moreover from separate experiments we found that reactivation of the Mg did not begin until temperatures above ~450°C under zero-bias conditions.

The reactivation kinetics were found to follow second-order kinetics, according to [3]:

$$d[N_A-N(t)]/dt = C[N_A-N(t)]^2 \qquad (3)$$

where N_A is the uniform Mg acceptor concentration in the non-hydrogenated sample, N(t) is the acceptor concentration in the hydrogenated GaN after forward bias annealing for time t and C is a second order annealing parameter. C was found to be $4x10^{-20} cm^3/s$

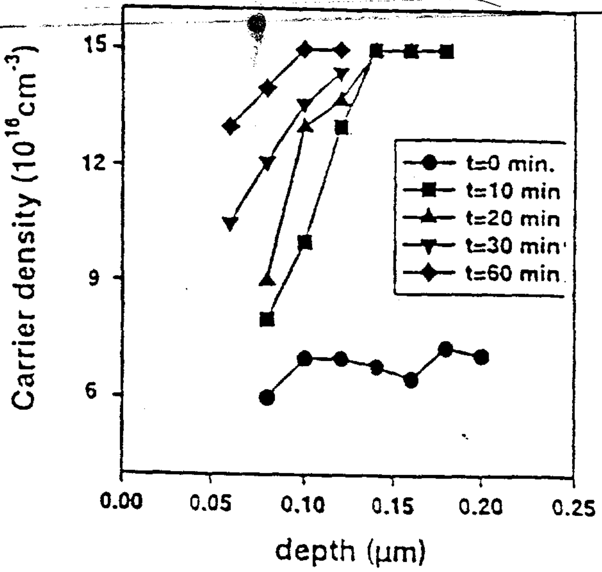

Figure 1. Carrier concentration profiles in hydrogenated GaN (Mg), after annealing for various times at 175°C under forward bias conditions.

The fact that the MgH complexes are unstable against minority carrier injection has implications for several GaN-based devices. Firstly, in a laser structure the high level of carrier injection would rapidly dissociate any remaining Mg-H complexes and thus would be forgiving of incomplete removal of hydrogen during the post-growth annealing treatment. In a heterojunction bipolar transistor the lower level of injected minority carriers would also reactivate passivated Mg in the base layer, leading to an apparent time-dependent decrease in gain as the device was operated.

We also investigated the susceptibility to hydrogen passivation of Ca acceptors in GaN. The Ca was implanted at a dose of $\sim 5x10^{14}cm^{-2}$, and activated by annealing at 1100°C. The ionization level was found to be ~169meV from transport measurements. Samples were hydrogenated for 30 min at 250°C.

The initial H_2 plasma exposure caused a reduction in sheet hole density of approximately an order of magnitude, as shown in Figure 2. No change in electrical properties were observed in the He-plasma treated samples, showing that pure ion bombardment effects are insignificant and the chemical interaction of hydrogen with the Ca acceptors is responsible for the conductivity changes. Post-hydrogenation annealing had no effect on the hole density up to 300°C, while the initial carrier concentration was essentially fully restored at 500°C. Assuming the passivation mechanism is formation of neutral Ca-H complexes, then the hole mobility should increase upon hydrogenation. This was indeed the case. If the carrier reduction were due to introduction of compensating defects or impurities, then the hole mobility would decrease, which was not observed.

If the dissociation of the Ca-H species is a first-order process then the reactivation energy from the data in Figure 2 is ~2.2eV assuming a typical attempt frequency of $10^{14}s^{-1}$ for bond breaking processes. This is similar to the thermal stability of Mg-H complexes in GaN which we prepared in the same manner (implantation) with similar doping levels. In thicker, more heavily doped samples, the apparent thermal stability of hydrogen passivation is much higher because of the increased probability of retrapping of hydrogen at other acceptor sites. This is why for thick, heavily doped ($p>10^{18}cm^{-3}$) GaN(Mg), a post-growth anneal of at least 700°C for 60min is employed to ensure complete dehydrogenation of the Mg. True reactivation energies can only be determined in reverse-biased diode samples where the strong electric fields present sweep the charged hydrogen out of the depletion region and minimize retrapping at the acceptors.

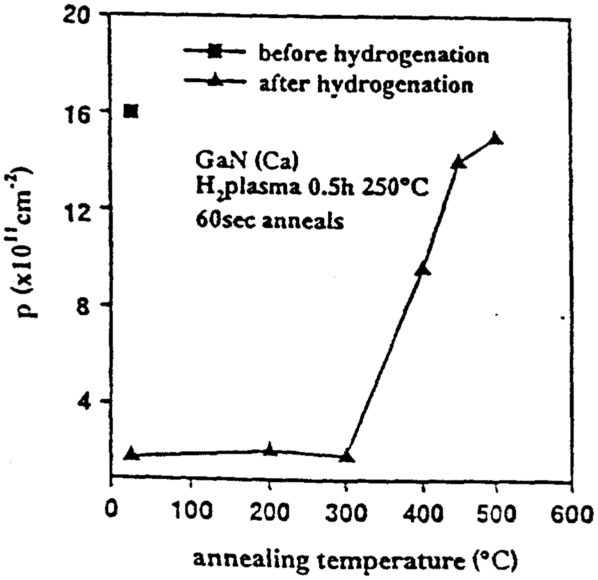

Figure 4. Sheet hole density at 300K in hydrogenated GaN(Ca) as a function of subsequent annealing temperature.

2. Oxygen

Oxygen is often assumed to be responsible for the background n-type doping in thin film GaN, although in bulk GaN it is more likely that nitrogen vacancies are responsible.[8]

Figure 3 is an Arrenhius plot of the resistance/temperature product of O-implanted GaN annealed at 1050°C along with data for an unimplanted and annealed (1100°C) GaN sample. For n-type conduction, an Arrhenius plot of the resistance/temperature product is thought to be more appropriate to account for the potential presence of two band conduction in GaN. O is seen to have an ionization level of 28.7meV. Using this value, the activation efficiency can be estimated to be only 3.6% for O ($n_S=5.9x10^{12}cm^{-2}$) assuming $n_S \propto n_0 exp(Ea/kT)$. The low activation of O may be the result of the lighter O-ion not creating sufficient lattice damage, and therefore N-vacancies, for the O to occupy a substitutional N-site. This situation may be improved in the future by using a co-implantation scheme.[9] The low apparent O activation may also be explained by the existence of a second deep level for O in GaN that is associated with an oxygen complex. If this were the case, the electrons in the deep level would remain unionized at room temperature and not contribute to the measured electron density. Note that the unimplanted and annealed material has an activation energy for conduction of 335eV. The diffusivity of O in GaN was estimated to be $<2.7x10^{-13}cm^2/sec$ at 1125°C from SIMS measurements.

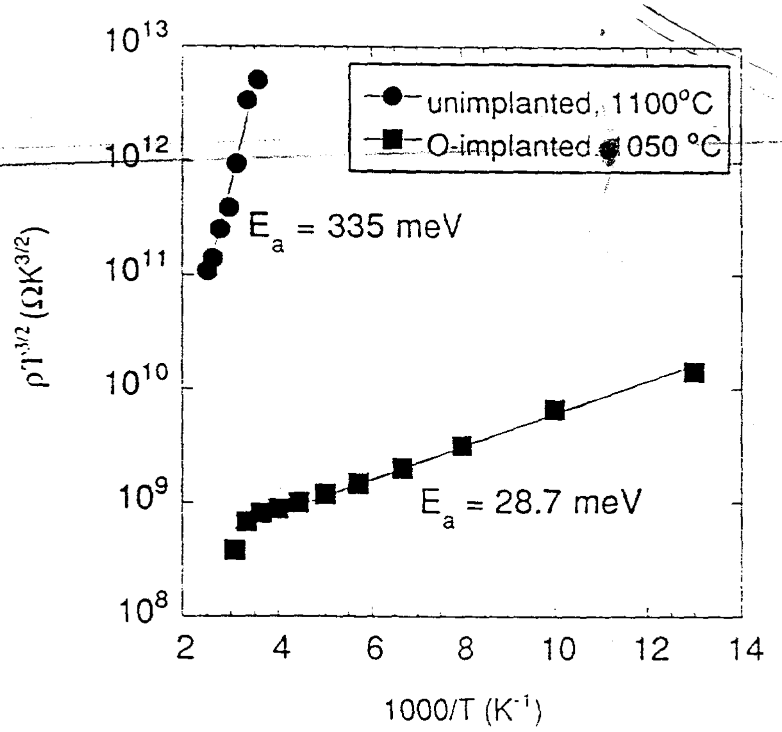

Figure 3. Arrhenius plot of resistance-temperature product for unimplanted GaN annealed at 1100°C and O-implanted GaN annealed at 1050°C.

3. Carbon

We have reported light ($p=3x10^{17}cm^{-3}$) p-type doping of GaN with CCl_4 doping during MOMBE growth.[10] We have also observed that $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ films are invariably strongly n-type.[11] One reason could be nitrogen vacancies. Another possible explanation for the electrical behavior is the presence of unintentionally incorporated carbon. Though carbon has been shown capable of producing p-type GaN, the hole concentrations obtained have been limited to low $\sim10^{17}cm^{-3}$ even though carbon levels are measured to be $10^{20}cm^{-3}$ or higher. It has been found in other III-V materials that the maximum hole concentration which can be obtained using carbon is related to the difference in bond strength between the group III-carbon case and group V-carbon sites. In the case of InP, the carbon actually sits on the group III site and acts as a donor resulting in n-type material. Based on this simple model, it is expected that carbon will be a donor in InN and high In concentration alloys (see Figure 4).[12] Thus at least some of the conduction observed in these ternary films may be due to carbon. Further, as the composition is reduced in In, the tendency for carbon to act as an acceptor rather than a donor increases, thus possibly explaining the reduction in electron concentration observed with increasing Ga or Al concentration. Clearly more work is needed in this area in order for the role of carbon to be fully understood.

We also implanted C into GaN and annealed at temperatures up to 1100°C, but did not obtain p-type conductivity. Based on the results to date we find that C probably displays amphoteric behavior in the nitrides, with acceptor formation under some conditions (MOMBE-grown GaN) and possible donor action in other cases (implantation in GaN; growth of In-containing alloys).

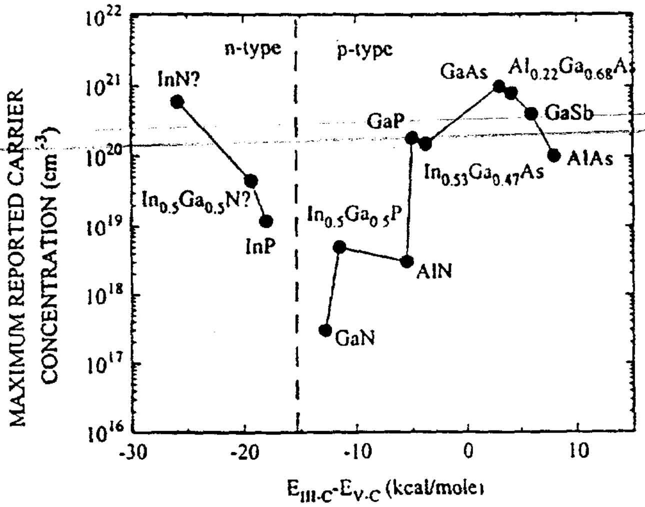

Figure 4. Maximum reported carrier concentrations for materials with various group III-carbon and group V-carbon bond strengths as a function of the difference between the two bonds.

CONCLUSIONS

In summary, we have shown that hydrogen passivated Mg acceptors in GaN may be reactivated at 175°C by annealing under minority carrier injection conditions. The reactivation follows a second order kinetics process in which the $(MgH)^0$ complexes are stable to ≥450°C in thin, highly-doped GaN layers. In thicker, more heavily doped layers where retrapping of hydrogen at the Mg acceptors is more prevalent, the apparent thermal stability of the passivation is higher and annealing temperatures up to 700°C may be required to achieve full activation of the Mg. Our results suggest the mechanism for Mg activation in e-beam irradiated GaN is minority-carrier enhanced debonding of the hydrogen. Hydrogen passivation of acceptors in GaN occurs for several different dopant impurities and that post-growth annealing will also be required to achieve full electrical activity in Ca-doped material prepared by gas-phase deposition techniques. The thermal stability of the passivation is similar for Ca-H and Mg-H complexes, with apparent reactivation energies of ~2.2eV in lightly-doped (~$10^{17}cm^{-3}$) material. O behaves as an inefficient shallow donor when implanted in GaN, whereas C may play a significant role in the conductivity of ternary alloys.

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