CONF-960502--7

SAND96-0784C

EFFECT OF HYDROGEN ON Ca AND Mg ACCEPTORS IN GaN

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The influence of minority carrier injection on the reactivation of hydrogen passivated Mg in GaN at 175°C has been investigated in p-n junction diodes. The dissociation of the neutral MgH complexes is greatly enhanced in the presence of minority carrier and the reactivation process follows second order kinetics. Conventional annealing under zero-bias conditions does not produce Mg-H dissociation until temperatures $\geq$ 450°C. These results provide an explanation for the e-beam induced reactivation of Mg acceptors in hydrogenated GaN. Exposure to a hydrogen plasma at 250°C of p-type GaN (Ca) prepared by either Ca^+ or Ca^+ plus P^+ coimplantation leads to a reduction in sheet carrier density of approximately an order of magnitude ($1.6\times10^{12}cm^{-2}$ to $1.8\times10^{11}cm^{-2}$), and an accompanying increase in hole mobility (6 cm^2/Vs to 18 cm^2/Vs). The passivation process can be reversed by post-hydrogenation annealing at 400-500°C under a N_2 ambient. This reactivation of the acceptors is characteristic of the formation of neutral (Ca-H) complexes in the GaN. The thermal stability of the passivation is similar to that of Mg-H complexes in material prepared in the same manner (implantation) with similar initial doping levels. Hydrogen passivation of acceptor dopants in GaN appears to be a ubiquitous phenomenon, as it is in other p-type semiconductors.

In both Si and GaAs(9-12), 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.(13)

There has recently been a lot of interest in the stability of hydrogen passivated Mg acceptors in GaN. Amano et al.(14) first demonstrated p-type conductivity in GaN (Mg) after an e-beam irradiation process near room temperature and later Nakamura et al.(15) 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.(16) 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.(16) 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 $5 \times 10^{18} cm^{-3}$. Some of the sample were hydrogenated by annealing under NH_3 for 30 mins at 500°C.(15) 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.(11) 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 $1.5x10^{17}cm^{-3}$ to ~6–$7x10^{16}cm^{-3}$. 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.

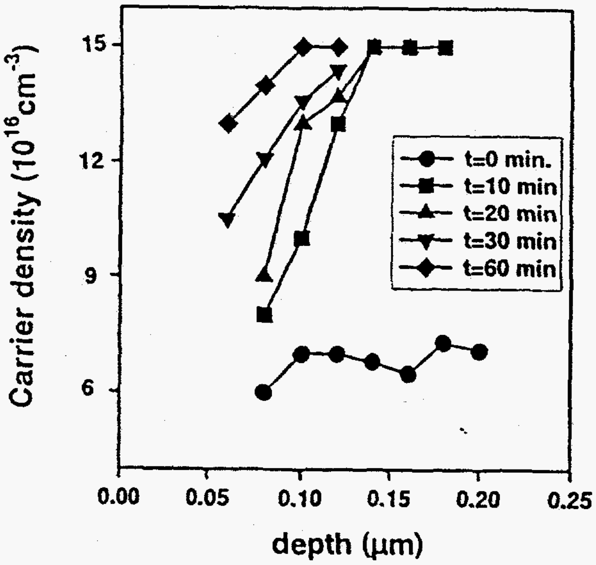

Figure 1. Carrier concentration profiles in hydrogenated GaN (Mg), after annealing for various times at 175°C under forward bias conditions.

DISCLAIMER

Previous experiments on minority carrier enhanced reactivation of hydrogen passivated dopants in Si(5) and GaAs(12) have found that for long annealing times the kinetics can be described by a second-order equation

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

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.

In order to quantitatively analyze the reactivation kinetics of the Mg-H complexes in GaN, we measured the inactive acceptor concentration N_A-N(t) at a depth of 0.1μm in the p-GaN layer. Figure 2 shows that there is a linear relationship between $[Na\text{-}N(t)]^{-1}$ and annealing time t, confirming that the reactivation process can be described by a second-order equation with $C=4x10^{-20}cm^3s^{-1}$. This value is consistent with those obtained in Si and GaAs where minority carrier enhanced dopant reactivation has also been reported. In that work, the annealing parameter was found to depend on the injected minority carrier density. Moreover, for short annealing times it was found that the dopant reactivation occurred at a faster rate than predicted by the second-order equation for very short annealing times, and that the annealing process was rate-limited by the formation of stable, electrically inactive diatomic H species. At this point there have not been enough studies of the various states of hydrogen in GaN as determined by infra-red spectroscopy, channeling or secondary ion mass spectrometry for us to conclude anything about the ultimate fate of the atomic hydrogen once it has dissociated from the Mg-H complex, but it is likely that it then reacts with other hydrogen atoms to form diatomic or larger clusters. A strong dependence of reactivation rate on injected minority carrier density would indicate the presence of a charge state for hydrogen and therefore influence the conversion of H^+ into the neutral state and then into the final hydrogen complexes.

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.

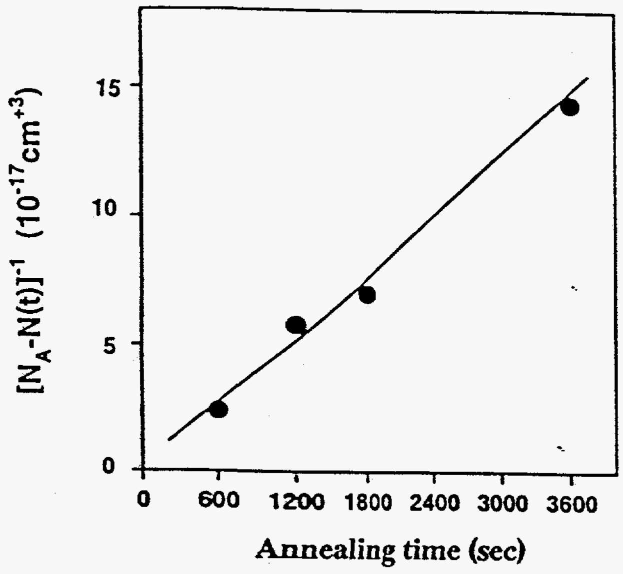

Figure 2. Plot of inverse net inactive Mg concentration determined from Figure 1 at a depth of 0.1μm, as a function of forward bias annealing time.

Theoretical considerations have suggested that Ca might be a shallower acceptor in GaN than Mg.(18) We have recently realized p-type doping of GaN using implantation of Ca^+ alone, or a co-implantation of Ca^+ and P^+, followed by rapid thermal annealing at ¤1100°C.(19) While the activation efficiency of Ca in both implant schemes was ~100%, temperature-dependent Hall measurements showed that the ionization level of Ca was ~169meV similar to that of Mg. An Arrhenius plot of the sheet hole concentration from in Ca-implanted sample annealed at 1150°C shows the activation level to be 169±12meV (Figure 3). The Ca atomic profile was thermally stable to temperatures up to 1125°C. Since Mg has a substantial memory effect in stainless steel epitaxial reactors (or in gas lines leading to quartz chamber systems), Ca may be a useful alternative p-dopant for epitaxial growth of laser diode or heterojuction bipolar transistor structures in which junction placement, and hence control of dopant profiles, is of critical importance.

In considering Ca-doped GaN for device applications it is also necessary to understand the role of hydrogen, since there is always a ready supply of atomic hydrogen available from NH_3, the metalorganic group III source (typically $(CH_3)_3Ga$) of from the gaseous dopant source when using chemical vapor deposition techniques. In this letter we show that Ca acceptors in GaN are also readily passivated by atomic hydrogen at low temperature (250°C), but they can be reactivated by thermal annealing at ≤500°C for 1min in lightly-doped ($3x10^{17}cm^{-3}$) materials. As the carrier density is restored by such annealing treatments there is a corresponding decrease in hole mobility, indicating that there is a true passivation and not just compensation of the Ca acceptors by the hydrogen.

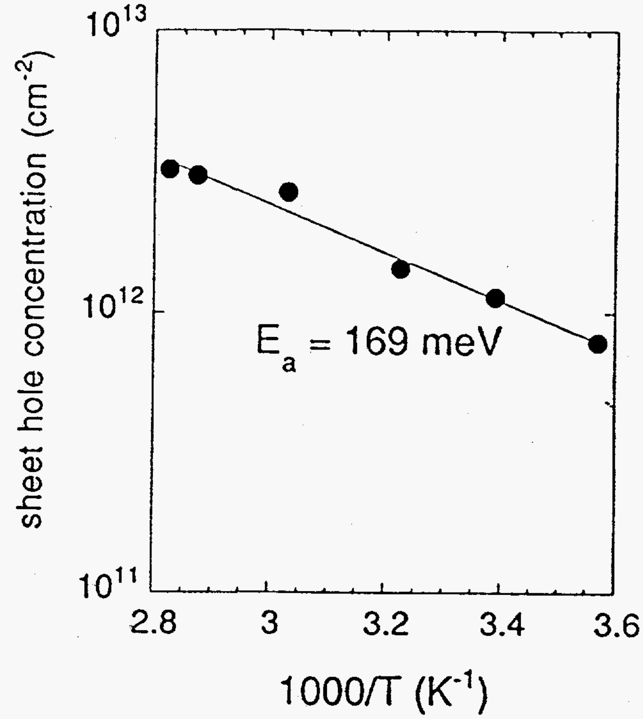

Figure 3. Arrhenius plot of sheet hole density in Ca-implanted GaN. The acivation energy is 169±12 meV

Nominally undoped ($n<3x10^{16}cm^{-3}$) GaN was grown on double-side polished c-Al_2O_3 substrates prepared initially by $HCl/HNO_3/H_2O$ cleaning and an in-situ H_2 bake at 1070°C.(20) A GaN buffer ≤300Å thick was then grown at ~500°C and crystallized by ramping the temperature to 1040°C where trimethylgallium and ammonia are again used to grow the 2µm thick epitaxial layer. The materials properties have been discussed in detail earlier,(20,21) but in brief the double crystal x-ray full width at half maxima are ~300 arc·sec and the total defect density (threading dislocations, stacking faults) apparent in plan view transmission electron microscopy was typically 2-$4x10^9cm^{-2}$. The as-grown films are featureless, transparent and have strong bandedge (3.47eV) luminescence.

^{40}Ca ions were implanted at 180keV and a dose of $5x10^{14}cm^{-2}$. In some cases, a co-implant of P^+ to the same dose at an energy of 130keV was performed to try to enhance the substitutional fraction of Ca upon subsequent annealing in analogy to the case of Mg implantation in GaN.(22) For the case of Ca we found there was little additional activation as a result of the W-implant. After rapid annealing at 1150°C for 15 secs under N_2 in a face-to-face geometry we measured sheet carrier densities of $p \sim 1.6x10^{12}cm^{-2}$ with a mobility at 300K of $6cm^2/Vs$. Arrhenius plots of the hole density showed an ionization level of 16g meV for the Ca in GaN. Samples with alloyed HgIn ohmic contacts were exposed to an Electron Cyclotron Resonance (ECR) H_2 or H_2 plasma (2.45GHz) with 850W forward power and a pressure of 10mTorr. The exposure time was 30min at 250°C, and the temperature was lowered to room temperature with the plasma on the sheet carrier density and hole mobility at 300K were obtained from Van der Pauw geometry Hall measurements. Post hydrogenation annealing was performed between 100-500°C for 60 sec under flowing N_2 with the ohmic contacts already in place.

The initial H_2 plasma exposure caused a reduction in sheet hole density of approximately an order of magnitude, as shown in Figure 4. 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 is indeed the case, as-shown in Figure 5. Note that the mobility decreases to its initial value with post-hydrogenation annealing. If the carrier reduction were due to introduction of compensating defects or impurities, then the hole mobility would decrease, which is not observed.

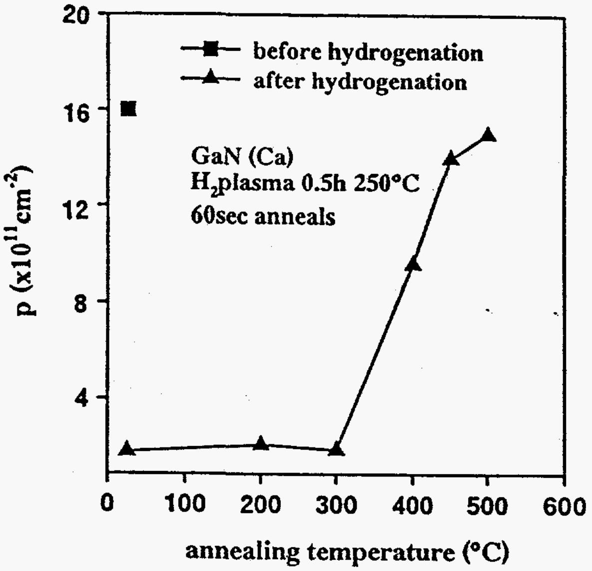

Figure 4. Sheet hole density at 300K in hydrogenated GaN(Ca) as a function of subsequent annealing temperature.

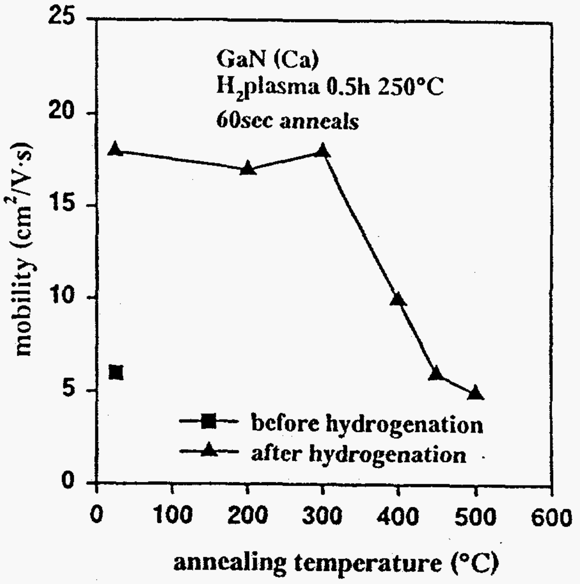

Figure 5. Hole mobility at 300K is hydrogenated GaN(Ca) as a function of subsequent a nnealing temperature.

In other p-type III-V semiconductors it is generally accepted that atomic hydrogen is predominantly in a positive charge state with the donor level being around midgap. If a similar mechanism exists in GaN then the initial Coulombic attraction between ionized acceptor and hydrogen leads to formation of a neutral close pair, i.e.

$$Ca^{-}+H^{+}\leftrightarrow(Ca\text{-}H)^{0} \qquad (4)$$

The existence of the neutral complex should be verified by observation of a vibrational band,(23) but to obtain the sensitivity needed for such a measurement will require a relatively thick epitaxial layer of Ca-doped GaN. Our present implanted samples do not have a sufficient Ca density-times-thickness product to be suitable for infra-red spectroscopy.

If the dissociation of the Ca-H species is a first-order process then the reactivation energy from the data in Figure 4 is ~2.2eV(24) 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.(24) 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.(21,25) 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 minimizes retrapping at the acceptors.(26)

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)° 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 ($\sim 10^{17} cm^{-3}$) material.

ACKNOWLEDGMENTS

The work at UF is partially supported by an NSF grant (DMR-9421109) and an ONR URI (N00014-92-3-1895). The work at Sandia is supported by DOE contract DE-AC04-94AL85000, while that at EMCORE is partially supported by a grant from BMDO administered through ONR (M. Yoder).

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