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Lattice Location of Deuterium in Plasma and Gas Charged Mg Doped GaN

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ABSTRACT

We have used ion channeling to examine the lattice configuration of deuterium in Mg doped GaN grown by MOCVD. The deuterium is introduced both by exposure to deuterium gas and to ECR plasmas. A density functional approach including lattice relaxation, was used to calculate total energies for various locations and charge states of hydrogen in the wurtzite Mg doped GaN lattice. Computer simulations of channeling yields were used to compare results of channeling measurements with calculated yields for various predicted deuterium lattice configurations.

INTRODUCTION

Hydrogen strongly affects the conductivity of p-type GaN grown by MOCVD [1]. P-type GaN grown in the presence of hydrogen has high resistivity due to passivation of acceptors by hydrogen. Low resistivity p-type material required for devices can be obtained through post-growth activation by thermal annealing [2, 3], low energy electron beam irradiation (LEEBI) [4, 5, 6, 7] or minority carrier injection [8, 9]. Mechanisms for these activation treatments are poorly understood but are believed to involve thermal or electronically induced dissociation of hydrogen from acceptors resulting in loss of hydrogen from the material, or a change in atomic configuration or charge state of the hydrogen. We also report preliminary results from first principles total energy calculations for hydrogen at Mg acceptors in wurtzite GaN. The predicted minimum energy configurations are compared with the results from the channeling measurements.

In this study we use ion channeling [10] to examine the lattice location of passivating deuterium in p-type Mg doped GaN. The deuterium is introduced both by exposure to deuterium gas and to ECR plasmas. Results from the channeling measurements are compared with simulated channeling yields for various locations of D in the lattice. These measurements provide a direct test of the location predicted by the first-principles calculations.

EXPERIMENTAL PROCEDURE

Wurtzite GaN:Mg films with (0001) orientation and thickness in the range of 1.4 - 2.3 μm were grown epitaxially by MOCVD on c-oriented sapphire substrates as described elsewhere [11]. The GaN:Mg was doped with Mg at concentrations in the range from 5 to $7 \times 10^{19}/cm^3$ as determined by SIMS.

Samples were passivated by exposure to D_2 gas at 88 kPa and 700° C for four hours. Conductivity measurements showed this treatment yielded high resistivity films indicating passivation [3]. Other samples were exposed to deuterium electron cyclotron resonance (ECR) plasma for one hour. The sample temperature during ECR plasma exposure was chosen to be 600°C based on a previous study [12] which showed deuterium incorporation into p-type GaN at 600°C but not at 400°C from exposure to remote plasma. During ECR plasma exposure the incident D has about 30 eV of kinetic energy which is high enough to penetrate a few lattice spacings but too low to create bulk defects by atomic collisions [13].

DISCLAIMER

Prior to gas or plasma exposures the samples were vacuum annealed at 900°C for one hour to remove hydrogen present from growth. After deuterium exposures, the concentration and depth distribution of deuterium in the films was characterized by $D(^3He,p)\alpha$ nuclear reaction analysis (NRA) and by SIMS. The D concentrations were uniform throughout the Mg doped region of the films and are given in the legends of figures 1 and 2. Although the two plasma charged samples were similar material and were exposed to the same plasma conditions, one had twice as much deuterium as the other. Samples of undoped n-type GaN exposed to the same gas and plasma conditions as the p-type GaN:Mg had much lower D concentrations. In the gas charged sample the D concentration is approximately half the Mg concentration, whereas in the two plasma charged samples the D concentration is higher than the Mg concentration, which suggests that the chemical potential for D from the plasma charging is higher than from the gas charging.

Transmission infrared absorption spectra were also measured in gas and plasma charged samples. In both cases similar absorption peaks were seen at 2320 cm^{-1} (shown in figures 1 and 2) which were not present prior to deuterium exposure. The increase in energy to 3120 cm^{-1} seen for this absorption peak in similar samples exposed to hydrogen shows that the absorption peak is due to stretch vibrations of H or D bound to nitrogen. This is also consistent with our observation that the 2320 cm^{-1} absorption peak disappears when D is removed from the samples by vacuum annealing. The fact that the peak area is similar for the gas and plasma charged samples while the D content is much larger in the plasma charged sample shows that at least in the plasma charged sample much of the D is in an IR inactive state. Similar IR absorption peaks were reported previously for GaN:Mg deuterated with a remote plasma system [14].

Ion channeling studies of D were done by counting protons from the $D(^3He,p)\alpha$ nuclear reaction using an incident analysis beam of 0.85 MeV $^3He^+$ ions. This gives counts from D to depths of about 1 μm. The analysis beam size was 1 mm square and the angular divergence was 0.05 degree. Channeling measurements were done with the samples at room temperature. The proton yield was measured as a function of angle between the analyzing ion beam and the crystallographic c-axis of the samples. The proton yield is proportional to the local flux of ^3He at the location of the D in the GaN lattice. For angles of incidence far from major crystallographic axes or planes the flux of ^3He is nearly the same at all locations in the lattice. However, when the analysis beam is aligned along the c-axis, channeling reduces the flux near the rows of host atoms and increases the flux near the center of the open channels relative to fluxes with off-axis alignment. This flux redistribution causes a dip in the NRA yield if the D is near the host atom rows, or conversely, to a peak in the NRA yield if the D is near the center of the channel. The absence of a peak or dip would indicate that the D is randomly located relative to the lattice.

Figure 1 shows the measured NRA yield normalized to the off-axis or random yield versus the angle between the analysis beam direction and the c-axis for the gas charged sample. The solid circles show measurements taken beginning on axis and stepping progressively farther from the axis, using an analysis ion beam dose of 1 microcoulomb at each angular position. The open circles show a repeat angular scan at the same location on the sample. The first scan shows a dip with halfwidth almost 1 degree and a small narrow central peak. In the second scan the dip is gone but a peak remains. The result that the on-axis yield is higher for the second scan than for the first

scan shows that the analysis beam used for the first angular scan has caused a change in lattice location of some of the deuterium.

Figure 2 shows the NRA channeling yield for the two plasma charged samples. The plasma charged sample with lower D concentration showed a broad dip similar to the gas charged sample whereas the plasma charged sample with more deuterium showed little variation of yield with angle. These measurements were made using 0.5 and 0.25 microcoulomb at each angular position for the low-D and high-D samples respectively. Repeat angular scans at the same location as the first scan were also done on the plasma charged samples to test for effects of analysis beam dose on channeling. These repeat scans showed little variation in yield with angle, i.e. the broad dip seen in the first scan on the low-D plasma charged sample was no longer present. Based on measurements of yield versus analysis beam dose at fixed on-axis angular position on the low-D plasma charged sample, we infer that the on-axis yield for the first scan was not significantly influenced by the analysis beam. The results described above were reproduced in measurements at different locations on each of the samples.

EFFECTS OF ANALYSIS ION BEAM

Next we discuss possible causes of the change in channeling yield induced by the analysis ion beam and implications of this effect on conclusions regarding the D lattice location from the channeling results. Collisions with lattice atoms produce vacancies and interstitial defects. Using the TRIM Monte Carlo particle transport code [15] we estimate the number of displacements produced by one microcoulomb of 850 keV He^3 on an area of 1 mm^2 to be ~ 10^{20} displacements/cm^3. This is comparable to the concentrations of Mg and D in the samples. If the D or the defects are mobile at room temperature, D-defect complexes might form which would change the lattice location of the D. However, when the analysis beam is aligned along the c-axis, channeling reduces the ion beam flux at the GaN lattice sites, and thus also the number of displacement events by about two orders of magnitude. Therefore we expect that with the beam near the c-axis on a fresh spot the number of displacements produced by the first few microcoulombs should be small compared to the concentration of D and Mg in the sample and is therefore not likely to have a large effect on the location of the D in the lattice.

Free electrons and holes produced by the analysis ion beam might also cause a change in lattice location of hydrogen which could change the channeling yield. Mg acceptors in GaN passivated by hydrogen are observed to be activated by electron beam irradiation [5, 7]. While mechanisms for this activation are not known, a change in lattice location of hydrogen initially bound at the acceptor site, induced by a change in charge state, could be involved. Acceptor activation by electron-hole production should be similar for ion and electron irradiation. The energy deposition required to activate Mg acceptors in GaN by 15 keV electron irradiation is about 10^{21} eV/cm^3 [6, 7] which will produce about 10^{20} /cm^3 electron-hole pairs in GaN [16]. The channeling analysis ion beam dose required to generate this number of electron- hole pairs is estimated, using the known stopping power of helium ions [15], to be 0.3 nanocoulomb onto the analyzed area of 1mm^2. Since this dose is much less than the dose used for our channeling measurements we expect that acceptor activation by electron-hole production is likely to occur very early in the channeling measurement. We therefore interpret our channeling results to represent material in which some or all of the Mg acceptors are not passivated or compensated by deuterium. The He stopping power and hence also electron-hole

production is only slightly affected by channeling and will therefore not be very different for on versus off-axis alignment.

H CONFIGURATION PREDICTED BY DENSITY FUNCTIONAL THEORY

A density functional approach including lattice relaxation, was used to calculate total energies for various locations and charge states of hydrogen in the wurtzite GaN lattice. The minimum energy configuration and energy barrier for diffusion depend on the H charge state. In the undoped lattice the most stable sites for H^0 and H^- are near the center of the trigonal channel along the c-axis whereas H^+ prefers sites nearer the nitrogen [17]. In wurtzite GaN there are two types of antibonding (AB) and bond-centered (BC) sites which we refer to as $AB_{N\parallel}$ and $BC_{N\parallel}$, when the N-H^+ direction is parallel to the c axis, and $AB_{N\perp}$ and $BC_{N\perp}$ when the N-H^+ direction is roughly perpendicular to the c axis. In undoped GaN the lowest energy sites for H^+ are the $AB_{N\perp}$ and $BC_{N\parallel}$ sites which have the same formation energy. H^- at the $AB_{N\perp}$ site is 0.063 nm from the center of the trigonal channel and H^+ at the $BC_{N\parallel}$ site is in-line with the rows of host atoms as viewed along the c axis.

The energies of H^+ and H^- depend on the Fermi level. In p-type material the H^+ charge state has the lowest energy so one might expect most of the H to occupy $AB_{N\perp}$ sites since there are three of these for each $BC_{N\parallel}$ site. However, several additional effects may influence the location of H in p-type GaN. First, the energy of H^+ is lower when it is near a Mg atom. The minimum energy site for H^+ near the Mg is the $AB_{Mg\text{-}N\perp}$ site of nitrogen atoms neighboring the Mg atom, which is 0.056 nm from the center of the trigonal channel. Thus, a neutral complex Mg^- - H^+ forms which has a binding energy of about 0.7 eV relative to H^+ far from the Mg. Formation and dissociation of this complex is believed to be the mechanism involved in passivation and activation of Mg acceptors by H. The energy for H^+ at other sites near Mg, including, $AB_{Mg\text{-}N\parallel}$ and $BC_{Mg\text{-}N\parallel}$ and $BC_{Mg\text{-}N\perp}$ sites between Mg and neighboring N, were found to be 0.2 eV or more higher in energy than the $AB_{Mg\text{-}N\perp}$ site.

If the H concentration exceeds the Mg concentration, or if the Mg is fully passivated, the Fermi level may be near the middle of the bandgap. Density functional theory predicts that under these conditions interstitial H_2 is energetically favored [17]. The minimum energy configuration for H_2 is at the center of the trigonal channel with the H-H bond parallel to the c axis. In our experiments, the high D concentrations in the plasma charged samples could lead formation of interstitial D_2. Electronically induced dissociation of Mg^- - H^+ complexes, for example through capture of an electron, could lead to release of mobile H^0 which could then react to form intersititial H_2 or other metastable neutral complexes. Such a process might be involved in Mg activation by LEEBI and minority carrier injection.

SIMULATED CHANNELING YIELDS FOR VARIOUS LATTICE LOCATIONS

We have carried out computer simulations of the yield versus angle for various D locations in the GaN lattice. These simulations were done using a statistical equilibrium continuum (SEC) model [18] modified for the case of channeling along the c axis in wurtzite GaN. Our calculations use Doyle Turner potentials [19] for the GaN lattice with 24 rows. The model includes dechanneling due to thermal vibration of the host atoms. RMS vibrational amplitudes of 0.00735 nm for Ga and 0.00806 nm for N were used [20]. The SEC model gave good agreement with the observed channeling dip for 2 MeV ^{4}He backscattered from host lattice Ga as shown in figure 3, providing an important validation

of the model. Figure 3 shows the NRA yield predicted by the SEC model for various locations of D in the channel as indicated in the inset diagram. Curve C is for D at the channel center, curve S is for D in-line with the host atom rows which includes $BC_{N\parallel}$ sites. Curve AB is for D 0.056 nm from the channel center, corresponding to the $AB_{Mg\text{-}N\perp}$ site. Also shown is the yield for D midway between the Ga and N atoms at the channel edge. D vibrational amplitudes used in the simulations (0.026 nm for $BC_{N\parallel}$ and 0.018 nm for $AB_{N\perp}$ and other sites) were estimated assuming a harmonic oscillator model with vibrational frequencies from the density functional calculations. The vibrational amplitude is mainly due to the low frequency bending modes. Except for the S site, changes in D vibrational amplitude by factors of 2 do not significantly change the calculated yield curves. The channeling simulations show that D near the channel center (which includes $AB_{N\perp}$ sites) gives a peak in the channeling yield and D along the host atom rows gives a broad dip. D at the channel edge midway between host atom rows gives a dip which is narrower and shallower.

CONCLUSIONS

Conductivity measurements show that the deuterium gas and plasma exposures passivate the Mg acceptors. Theory predicts that the passivating D occupies the $AB_{Mg\text{-}N\perp}$ site. The ion beam used for the channeling experiments creates electrons and holes which are likely to activate the acceptors similar to acceptor activation produced by electron irradiation. Atomic processes involved in activating acceptors are poorly understood, but conversion of D^+ at the Mg to a neutral state is likely to be involved and this conversion is likely to produce a change in lattice configuration of the D. Prior to significant lattice damage by the analysis ion beam but after creation of electron hole pairs sufficient to activate the Mg acceptors, broad dips in NRA channeling yield are observed in the gas charged sample and one of the plasma charged samples. These dips imply that approximately a third of the D occupies sites near the host atom rows (as viewed along the c axis). In addition, a narrow peak is seen in the gas-charged sample which indicates that a fraction of the D (10-20%) occupies sites near the center of the trigonal channel. The peak was not present in the plasma charged sample.

We conclude that D causing the broad dip seen in both gas and plasma charged material, is not D^- passivating or compensating the acceptors, since theory predicts that D^+ should occupy nitrogen antibonding sites which would give a narrow peak in the channeling yield. Neutral states examined by density functional theory (D^0, D_2) are also predicted to occupy sites near the channel center, so we conclude that these are also not the states giving rise to the broad dip. Thus, much of the D occupies a state which is presently undetermined. The narrow peak seen in the gas charged sample could be due to D^+, which might be present if Mg activation by the ion beam is incomplete, or to D_2 states which might be a metastable product of electronically induced Mg activation.

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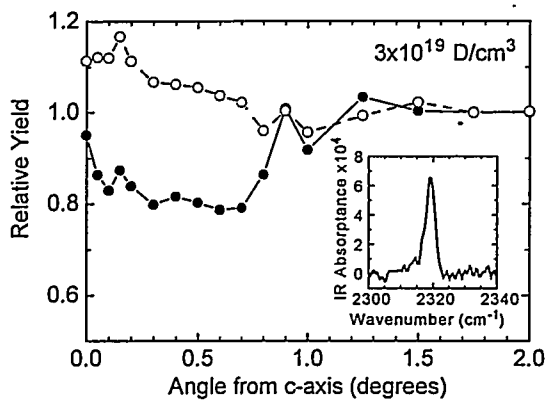

Figure 1 Effect of channeling on NRA yield for a GaN:Mg sample after exposure to deuterium gas. Open circles show the change resulting from exposure to the analysis ion beam. Inset shows IR absorption peak due to N-D stretch local vibration.

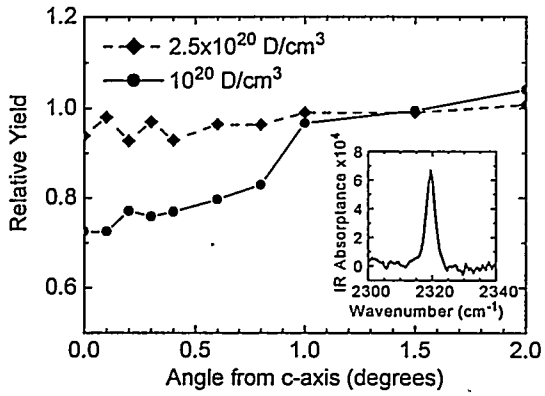

Figure 2 Effect of channeling on NRA yield for two GaN:Mg samples after exposure to deuterium ECR plasma. Inset shows IR absorption peak due to N-D stretch local vibration.

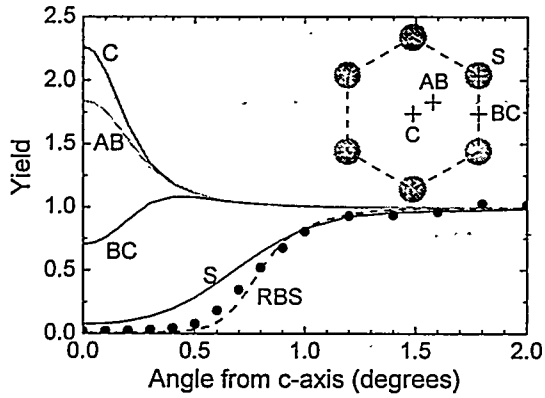

Figure 3 Solid curves show simulated NRA channeling yields for the various D lattice locations indicated in the inset. The dots and dashed curve show measured and simulated yields for 2MeV He^4 scattered from host Ga atoms.