Reactivation of acceptors and trapping of hydrogen in GaN/InGaN double heterostructures

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The apparent thermal stability of hydrogen passivated Mg acceptors in GaN is a function of the annealing ambient employed, with H_2 leading to a reactivation temperature approximately 150 °C higher than N_2. The dissociation of Mg–H complexes and the loss of hydrogen from GaN are sequential processes, with reactivation occurring at ≤ 700 °C for annealing under N_2, while significant concentrations of hydrogen remain in the crystal even at 900 °C in implanted samples. The hydrogen is gettered to regions of highest defect density such as the InGaN layer in GaN/InGaN double heterostructure. © *1996 American Institute of Physics*. [S0003-6951(96)00739-5]

Hydrogen plays an important role in GaN and related alloys, since it is part of the growth environment for metal organic chemical vapor deposition (MOCVD), which employs $(CH_3)_3Ga$ and NH_3 as its standard precursors.[1] Hydrogen remaining in Mg-doped GaN layers has been identified as the cause of the high resistivity of these films, since it appears that the hydrogen forms stable neutral complexes $(Mg–H)^0$, with the Mg acceptors.[1] Postgrowth annealing at ~ 700 °C,[1,2] or exposure to a low energy electron beam[3] reactivates the Mg acceptors and produces conductivities five to six orders of magnitude higher than in the as-grown material. Hydrogen has been shown to be injected into GaN during a number of processing steps, including dry etching in CH_4/H_2 plasma chemistries, boiling in water, wet etching in KOH solutions, and chemical vapor deposition of dielectrics using SiH_4.[4]

The behavior of hydrogen in device structures is likely to be more complicated. For example, light-emitting diodes or laser diodes contain both *n*- and *p*-type GaN cladding layers with one or more InGaN active regions. The first laser diode reported by Nakamura *et al.*[5] contained 26 InGaN quantum wells. In other III–V semiconductors, the diffusivity of atomic hydrogen is a strong function of conductivity type and doping level since trapping by acceptors is usually more thermally stable and more efficient than trapping of hydrogen by donor impurities.[6–14] Moreover, hydrogen is attracted to any region of strain within multilayer structures and has been shown to pile up at heterointerfaces in the GaAs/Si,[15,16] GaAs/InP,[14,15] and GaAs/AlAs (Ref. 6) materials systems. Therefore, it is of interest to investigate the reactivation of acceptors and trapping of hydrogen in double heterostructure GaN/InGaN samples, since these are the basis for optical emitters. We find that the reactivation of passivated Mg acceptors also depends on the annealing ambient,

with an apparently higher stability for annealing under H_2 rather than N_2. Hydrogen is found to redistribute to the regions of highest defect within the structure.

The sample was grown by MOCVD in a rotating disk reactor on *c*-plane Al_2O_3.[2] The sapphire substrate was rinsed in H_2SO_4, methanol, and acetone prior to loading into the growth chamber, where it was first baked at 1100 °C under H_2. A low temperature (~ 510 °C) GaN buffer (~ 300 Å thick) was followed by 3×3 μm of n^+ GaN ($n = 10^{18}$ cm^{-3}, Si doped), 0×1 μm InGaN (undoped), and 0×5 μm thick p^+ GaN ($p = 3\times 10^{17}$ cm^{-3}, Mg doped). The growth temperature was 1040 °C for the GaN and ~ 800 °C for the InGaN. Cross-sectional transmission electron microscope (XTEM) analysis was carried out on the MOCVD grown InGaN/GaN double heterostructure. A XTEM bright-field image, obtained using two-beam diffraction conditions with $\mathbf{g}=(2\underline{11}0)$ along the $[0\underline{1}10]_{GaN}$ zone axis of the double heterostructure light-emitting diode (DH-LED) structure is shown in Fig. 1 (top). The interface between the various layers appears to be abrupt with no indication of interfacial phases. Selected-area-diffraction and high resolution electron microscopy revealed that the entire DH-LED structure grew epitaxially on the substrate.

In the immediate vicinity of the *n*-GaN/Al_2O_3 interface, the defect density was high but was reduced with increasing film thickness. However, after the growth of the active layer (InGaN) the defect density of the threading dislocations increased as shown at the bottom of Fig. 1. A possible reason could be due to the different growth conditions used for growing the active layer and the GaN layers. The growth mechanism for *p* GaN on InGaN in the DH-LED structure could be similar to that proposed by Hiramatsu.[17] During the growth of the subsequent *p*-GaN layer the underlying active layer may be undergoing solid-phase epitaxy. Hence, the quality of *p* GaN grown on top of the active layer depends on the amount of epitaxy undergone by the active layer, and
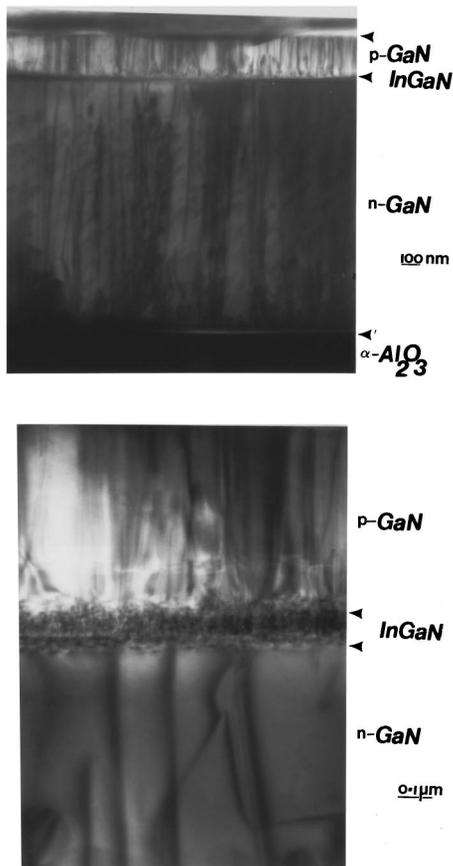
FIG. 1. (Top) Bright-field XTEM image showing the defect distribution along the device obtained using two-beam diffraction condition with $\mathbf{g}$ $=(2\bar{1}10)$ along $[01\bar{1}0]_{GaN}$ zone axis. (Bottom) Bright-field XTEM image of the top region of the device including the double-heterostructure active region showing the increase in threading dislocation density after the growth of the active layer. The image was obtained using two-beam condition with $\mathbf{g}=(2\bar{1}10)$ along the $[01\bar{1}0]_{GaN}$ zone axis.

FIG. 2. Formation of passivated Mg acceptors remaining in hydrogenated p-type GaN after annealing for 20 min at various temperatures in either N_2 or H_2 ambients.

in this structure the thermal degradation of the InGaN upon raising the growth temperature for the p GaN leads to a higher defect density in this overlayer.

XTEM of the DH-LED showed dislocations as dark lines propagating in the direction normal to the substrate. Most of the dislocations appeared to traverse the entire double heterostructure, while some appeared to bend and follow the interface for a short distance before threading out to the surface. The nature of the threading dislocations was studied by conventional XTEM using the $\mathbf{g}\cdot\mathbf{b}=0$ criteria. The dislocation will be invisible when $\mathbf{b}$ lies in the reflecting plane.

Some of the dislocations were invisible both in $\mathbf{g}2$ $=(0002)$ and $\mathbf{g}5=(1\bar{1}01)$ and, because $\mathbf{b}$ was common to both reflections, $\mathbf{b}$ was found to be $1/3[11\bar{2}0]$. Assuming that the growth is the same as the translation vector of the dislocation, these defects would be pure edge type in nature. The average threading dislocation density was also found along the plane normal to the growth direction. The dislocation density was found to be $\sim 8\times10^{10}/cm^2$.

The double-heterostructure sample was exposed to an electron cyclotron resonance plasma (500 W of microwave power, 10 mTorr pressure) for 30 min at 200 °C. The hole concentration in the p-GaN layer was reduced from 3
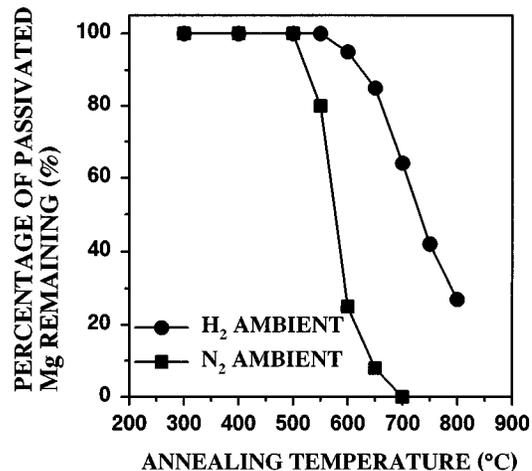
$\times10^{17}$ cm^{-3} to $\sim2\times10^{16}$ cm^{-3} by this treatment, as measured by capacitance voltage $(C-V)$ at 300 K. Sections from this material were then annealed for 20 min at temperatures from 500 to 900 °C under an ambient of either N_2 or H_2 in a Heatpulse 410T furnace. Figure 2 shows the percentage of passivated Mg remaining after annealing at different temperatures in these two ambients. In the case of N_2 ambients the Mg–H complexes show a lower apparent thermal stability (by ~150 °C) than with H_2 ambients. This has been reported previously for Si donors in InGaP and AlInP, and Be and Zn acceptors in InGaP and AlInP, respectively,[18] and most likely is due to indiffusion of hydrogen from the H_2 ambients, causing a competition between passivation and reactivation. Therefore, an inert atmosphere is clearly preferred for the postgrowth reactivation anneal of p GaN to avoid any ambiguity as to when the acceptors are completely active. Previous experimental results by Brandt et al.[19] and total energy calculations by Neugebauer and Van de Walle[20] suggest that considerable diffusion of hydrogen in GaN might be expected at ≤600 °C.

Other sections of the double-heterostructure material were implanted with $^2H^+$ ions (50 keV, 2×10^{15} cm^{-2}) through a SiN_x cap in order to place the peak of the implant distribution within the p^+GaN layer. Some of these samples were annealed at 900 °C for 20 min under N_2. As shown in the secondary ion mass spectrometry (SIMS) profiles of Fig. 3, the ^2H diffuses out of the p^+ GaN layer and piles up in the defective InGaN layer, which we saw from the TEM results, suffers from thermal degradation during growth of the p^+GaN. Note that there is still sufficient ^2H in the p^+GaN ($\sim10^{19}$ cm^{-3}) to passivate all of the acceptors present, but electrical measurements show that the p-doping level was at its maximum value of $\sim3\times10^{17}$ cm^{-3}. These results confirm that as in other III–V semiconductors, hydrogen can exist in a number of different states, including being bound at dopant atoms or in an electrically inactive form that is quite thermally stable. We expect that after annealing above 700 °C all of the Mg–H complexes have dissociated, and the electrical measurements show that they have not reformed.
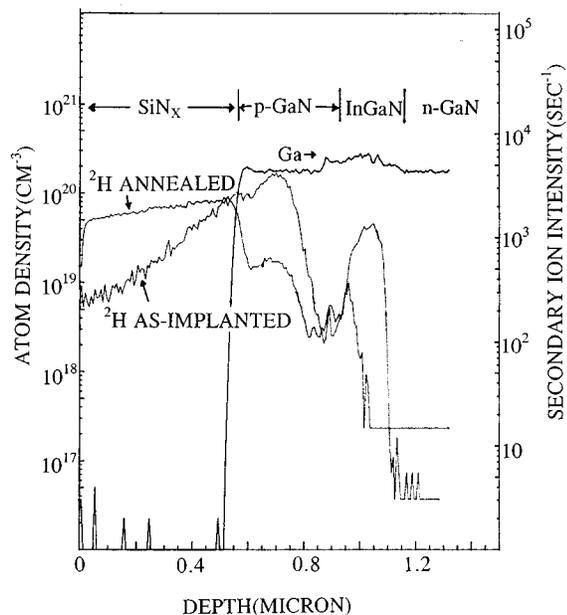
FIG. 3. SIMS profiles of ^{2}H in an implanted (50 keV, 2×10^{15} cm^{-2} through a SiN$_x$ cap) double-heterostructure sample, before and after annealing at 900 °C for 20 min.

In other III–Vs the hydrogen in p-type material is in a bond centered position forming a strong bond with a nearby N atom, leaving the acceptor threefold coordinated.[18] Annealing breaks this bond and allows the hydrogen to make a short-range diffusion away from the acceptor, where it probably meets up with other hydrogen atoms, forming molecules or larger clusters that are relatively immobile and electrically inactive. This seems like a plausible explanation for the results of Figs. 2 and 3, where the Mg electrical activity is restored by 700 °C, but hydrogen is still present in the layer at 900 °C. In material hydrogenated by implantation, there is almost certainly a contribution to the apparently high thermal stability by the hydrogen being trapped at residual implant damage as is evident by the fact that the ^{2}H profile retains a Pearson IV type distribution even after 900 °C annealing. The other important point from Fig. 3 is that as in other defective crystal systems, hydrogen is attracted to regions of strain, in this case the InGaN sandwiched between the adjoining GaN layers.

In conclusion, the apparent thermal stability of hydrogen-passivated Mg acceptors in p GaN is dependent on the annealing ambient, as it is in other compound semiconductors. While the acceptors are reactivated at $\leqslant700$ °C for annealing under N$_2$, hydrogen remains in the material until much higher temperatures and can accumulate in defective regions of double-heterostructure samples grown on Al$_2$O$_3$. It will be interesting to compare the redistribution and thermal stability of hydrogen in homoepitaxial GaN in order to assess the role of the extended defects present in the currently available heteroepitaxial material.

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