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Ion-implanted hydrogen in gallium nitride

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Hydrogen was ion-implanted into GaN at concentrations ranging over two orders of magnitude, and its states and microstructural effects during annealing up to 1000°C were characterized by nuclear-reaction profiling, ion-channeling analysis, transmission electron microscopy, and infrared spectroscopy of H vibrational modes.

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I. Introduction

We investigated the behavior and microstructural effects of ion-implanted H in GaN. Wurtzite-phase films $\sim 2 \mu\text{m}$ thick were grown epitaxially on sapphire by metal-organic chemical vapor deposition (MOCVD) with the c-axis normal to the film. Implantation of H to concentrations from hundredths to several at.% was followed by vacuum annealing at temperatures up to 1000°C . Characterization was by nuclear-reaction profiling of the H, ion-channeling analysis, transmission electron microscopy (TEM), and infrared (IR) spectroscopy of H vibrational modes. Results illuminated the transport of the H and its strongly-bound immobile states. Faceted bubbles at higher concentrations revealed the low-energy surfaces of GaN in the presence of passivating H, and the N-H centers on these surfaces were observed by IR spectroscopy. Our findings contribute to understanding of the interrelated behaviors of H and defects in GaN, an emerging photonic material where H effects have exceptional importance [1]. The results specifically characterize the response of GaN to H implantation, of potential interest for electrical isolation, defect passivation, controlled layer separation, and gettering.

II. Retention of implanted hydrogen to elevated temperatures

The retention of ion-implanted H was measured as a function of anneal temperature by using the deuterium isotope ^2H and counting protons from the ^3He -induced reaction $^2\text{H}(^3\text{He},p)^4\text{He}$ [2]. Implantations of 10^{15} , 10^{16} , and $10^{17} \text{ } ^2\text{H}/\text{cm}^2$ at 50 keV and room temperature produced the calculated [3] concentration profiles in Fig. 1. Specimens then received a series of 1-hour, high-vacuum anneals at intervals of $\sim 100^\circ\text{C}$, and the retained areal density was monitored using 850 keV ^3He , for which the depth-dependent cross section is shown in the figure. Results are presented in Fig. 2. At the lowest implantation dose, retention was greater for locations on the sample analyzed before annealing, and so each analysis was performed at a fresh spot. After the anneal at 886°C , the ^2H was depth-profiled by measuring nuclear-reaction yield as a function of analysis-beam energy and performing a deconvolution [2]. For all of the implanted doses, the retained ^2H remained localized near its implantation depth rather than undergoing diffusion broadening. Vacuum annealing at 980°C caused GaN loss as

observed by ion-backscattering analysis, so that the plotted datum at this temperature does not characterize ^2H loss by diffusion.

Figure 2 shows that implanted H is retained to exceptionally high temperatures in GaN; in comparable experiments performed by us on Si, Ge, and GaAs, the midpoint of the release stage occurred at $\sim 500^\circ\text{C}$ or less, a difference of $\sim 400^\circ\text{C}$. The aforementioned absence of profile broadening indicates that, at elevated temperatures, the retained H resides in bound states within the implanted layer rather than in interstitial solution sites. The release temperature is nearly invariant for implanted concentrations extending over two orders of magnitude.

III. Formation of bubbles and stacking faults at high concentrations

The microstructure of H-implanted GaN was examined by TEM after annealing for 1 hour at 886°C , in the temperature range of H release. For doses of 2×10^{16} and 10^{17} H/cm², where the injected concentration extended above 1 at.%, bubbles formed with a typical size of 10 nm. These were pyramidal in shape, having a hexagonal base in the (0001) plane and six $\{10\bar{1}1\}$ faces, as seen from the plan-view and cross-section images in Fig. 3. The bubbles also exhibited a unique orientation with respect to the c-axis: the (0001) basal facet was always toward the upper surface with the apex of the pyramid toward the substrate.

The bubble shape indicates that the (0001) and $\{10\bar{1}1\}$ surfaces have relatively low energy. Moreover, the directionality along $\langle 0001 \rangle$ illuminates to the polarity of the preferred surfaces, that is, whether the close-packed Ga-N bilayers have Ga or N atoms uppermost. It has been found that MOCVD GaN on sapphire is oriented with Ga uppermost on the (0001) external surface [4]; this implies that the downward-facing base of the pyramidal bubbles, and also the upward-tilted side walls, have N uppermost. This leaves the strongly reactive N atom incompletely coordinated in the absence of substantial reconstruction, suggesting H passivation.

Infrared spectroscopy evidenced N-H bonding on the walls of the bubbles. These experiments were performed on specimens containing either 2 or 5 implanted layers for greater absorption. At the implanted concentrations of bubble formation, but not at lower concentrations, prominent local vibrational modes occurred at 3183 and 3219 cm⁻¹ for the ^1H

isotope, as illustrated in Fig. 4, and at 2364 and 2386 cm^{-1} for ^2H . These reflect stretch modes of N-H centers based on comparisons with N-H frequencies in other materials such as amorphous SiN(H) and also on the isotope-shift ratio of 1.35, which departs from $\sqrt{2}$ by an amount appropriate to the mass of N. The integrated strength of the absorptions indicates that $\sim 4\%$ of the implanted H existed as N-H rather than IR-inactive H_2 ; as discussed in Section IV, this is consistent with monolayer coverage of the bubble walls.

Bubble layers also contained numerous (0001) planar defects with a typical lateral dimension of 50 nm. High resolution cross-section images, such as that in Fig. 5, revealed these to be extrinsic stacking faults; the images are consistent with an extra Ga-N bilayer having zinc-blende stacking immediately above and below, giving rise to a lattice offset in the basal plane [5]. We hypothesize that, in GaN, the added volume from bubbles drives the formation of this particular fault rather than the interstitial dislocation loops observed in many systems.

IV. Hydrogen transport and immobile states at high concentrations

Isothermal release was measured by using the reaction $^2\text{H}(^3\text{He},p)^4\text{He}$ to monitor the retained areal density of ^2H . A representative isotherm, obtained at 900°C from GaN implanted with $10^{17} \text{ } ^2\text{H}/\text{cm}^2$ at 50 keV, is shown in Fig. 6. Most of the release occurred at times < 10 hours and is ascribed to removal of H_2 gas from the bubbles by dissociation and atomic diffusion from the sample. A small residual is released much more slowly, reflecting some more stably bound state of the H. The latter was approximated as an exponential decay and subtracted, leaving the gas-related part, which is plotted in Fig. 7 as the square root of retained quantity.

The release from the gas phase is expected to be given by

$$(d/dt)\Lambda = -D n_0 (P^*/P_0)^{1/2} / x \quad (1)$$

with Λ the retained areal density of H, D the diffusion coefficient, n_0 the solubility of H in equilibrium with H_2 gas at standard pressure P_0 , P^* the fugacity of the gas, and x the diffusion distance. The fugacity is

$$\ln(P^*/P_0) = (kT)^{-1} \int_{P_0}^P v(P') dP' \quad (2)$$

where $v(P)$ is the molecular volume and is related to pressure P by the known equation of state;

at lower pressures where the equation of state is ideal, $P^* \rightarrow P$. The formulation is completed by

$$v(P) = 2V_a/\Lambda \quad (3)$$

where V_a is the cavity volume per unit sample area. When $P^* \rightarrow P$, $\Lambda^{1/2}$ decreases linearly with time; however, when the starting pressure is large, a rapid initial transient is predicted. Such behavior is seen in Fig. 7. We fitted the solution of Eqs. (1)-(3) to the data by adjusting the initial bubble pressure P_1 and the diffusivity-solubility product Dn_0 , giving the curve in Fig. 7. This gave $P_1 = 10$ GPa and $Dn_0 = 1.50 \times 10^6$ atoms/cm/s for $P_0 = 1$ bar. A similar experiment at 800°C yielded $Dn_0 = 3.4 \times 10^5$ atoms/cm/s, corresponding to an activation energy of ≈ 1.6 eV.

As noted in Section III, IR spectroscopy evidenced that $\sim 4\%$ of the implanted H was chemisorbed as N-H on the walls of the bubbles. During isochronal annealing sequences similar to those of Fig. 2, the spectroscopic yield from this state decreased to undetectability in the approximate range 700 - 900°C ; this suggests that the chemisorbed state is less stable than the gas.

The above considerations leave unidentified the strongly bound state of the H responsible for the extended tail in Fig. 7 and a similar residual at 800°C . We did not detect IR absorptions due to N-H or Ga-H bonding in this annealing regime. A speculative possibility is that the loss of H removes the passivation of electrically active defects and so shifts the Fermi level, altering the charge state of the H and thereby modifying its transport as predicted [6]. The persistent, IR-inactive H might then simply be residual H_2 in the bubbles.

V. Hydrogen states at low implanted concentrations

Implantation of H into GaN at the lower dose of 10^{15} cm^{-2} led to atomic bonding of the H within the host lattice. This was indicated by IR absorption peaks in the range 2983 to 3150 cm^{-1} ; these were previously reported by other workers [7] for similar implantation conditions and ascribed to N-H bonding within the Ga vacancy based on theoretical results [8]. Moreover, $\langle 0001 \rangle$ ion-channeling analysis of the implanted ^2H showed structure indicative of a well defined lattice site, as seen by the results in Fig. 8 obtained after room-temperature implantation. These bound states are not the ones from which the release shown in Fig. 2 occurred, however, since the IR absorptions and ^2H channeling both disappear at about 700°C ,

while the release stage is centered near 900°C. We performed cross-section TEM after annealing to 900°C and did not discern bubbles or other extended defects. Hence, one is again left with a relatively strongly bound state of H in GaN whose character remains to be established.

VI. Summary

Our results indicate that ion-implanted H is bound within GaN to exceptionally elevated temperatures and that it exists in several distinct states including H₂ gas within bubbles, chemisorption on the N-terminated walls of such bubbles, N-H centers perhaps associated with vacancy defects, and one or possibly two strongly bound states whose characters remain to be established. The diffusivity-solubility product of H in GaN was determined. Analysis of bubble microstructures indicated that, in the presence of passivating H, (0001) and $\{10\bar{1}1\}$ -type N-terminated surfaces are energetically preferred.

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Figure captions

1. Calculated profiles of implanted ^2H and the cross section of the $^2\text{H}(^3\text{He},\text{p})^4\text{He}$ reaction.
2. Retention of implanted ^2H during isochronal annealing.
3. High-resolution plan-view (a) and cross-section (b) images of representative bubbles.
4. IR absorption after implanting $2 \times 10^{16} \text{ } ^1\text{H}/\text{cm}^2$ in each of 5 layers and annealing at 600°C .
5. High-resolution cross-section image showing portion of stacking fault in bubble layer.
6. Isothermal release of ^2H at 900°C .
7. Isothermal decrease of ^2H in gas bubbles at 900°C .
8. $\langle 0001 \rangle$ channeling analysis of implanted ^2H and the GaN host lattice, obtained with 850-keV ^3He and 2-MeV ^4He .

^2H CONCENTRATION (at.%)

3a

31-