Simulation of H Behavior in p-GaN(Mg) at Elevated Temperatures

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ABSTRACT

The behavior of H in p-GaN(Mg) at temperatures $>400^{\circ}\text{C}$ is modeled by using energies and vibrational frequencies from density-functional theory to parameterize transport and reaction equations. Predictions agree semiquantitatively with experiment for the solubility, uptake, and release of the H when account is taken of a surface barrier.

INTRODUCTION

Hydrogen is introduced into GaN during growth by metal-organic chemical vapor deposition (MOCVD) and subsequent device processing [1]. This impurity affects electrical properties substantially, notably in p-type GaN doped with Mg where it reduces the effective acceptor concentration [2]. Application of density-functional theory to the zincblende[3] and wurtzite [4] forms of GaN has indicated that dissociated H in interstitial solution assumes positive, neutral, and negative charge states. The neutral species is found to be less stable than one or the other of the charged states for all Fermi energies. Hydrogen is predicted to form a bound neutral complex with Mg, and a local vibrational mode ascribed to this complex has been observed [5].

We are developing a unified mathematical description of the diffusion, reactions, uptake, and release of H in GaN at the elevated temperatures of growth and processing. Our treatment is based on zero-temperature energies from density functional theory. One objective is to assess the consistency of theory with experiment at a more quantitative level than previously. A further goal is prediction of H behavior pertinent to device processing. Herein we discuss aspects relating to p-type GaN(Mg).

THEORETICAL FORMALISM AND PARAMETER EVALUATION

The diffusion flux of H in GaN is given by

$$\begin{aligned} \Phi_{\text{dif}} = & -D^0 \frac{\partial}{\partial x} [H^0] - D^+ \frac{\partial}{\partial x} [H^+] - D^- \frac{\partial}{\partial x} [H^-] \\ & - \left(D^+ [H^+] - D^- [H^-] \right) \left(\frac{1}{kT} \right) \frac{\partial}{\partial x} (E_f - E_v) \end{aligned} \quad (1)$$

where brackets denote concentration, E_f is the Fermi energy, and E_v is the energy of the valence-band edge. Equation (1) takes account of differing diffusion rates for the three charge states, and the final term describes driven migration due to spatial variation of the Fermi level. We assume rapid local equilibration among the H states, which is believed appropriate for the temperatures $>400^{\circ}\text{C}$ of concern herein. On then has

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$$\frac{[H^+]}{[H^0]} = \exp\left(\frac{G_H^{+0} - E_f}{kT}\right) \quad (2)$$

$$\frac{[H^0]}{[H^-]} = \exp\left(\frac{G_H^{0-} - E_f}{kT}\right) \quad (3)$$

where the quantities G_H are bandgap levels associated with the electronic transitions.

State populations relating to the Mg acceptor are given by

$$\frac{N_h [MgH]}{[Mg^-] [H^+]} = \exp\left(\frac{G_{MgH}^{+}}{kT}\right) \quad (4)$$

$$\frac{[Mg^0]}{[Mg^-]} = \exp\left(\frac{G_{Mg}^{0-} - E_f}{kT}\right) \quad (5)$$

where N_h is the atomic density of GaN, MgH is the neutral complex, and the quantities G are changes in the nonconfigurational part of the Gibbs free energy arising from the reactions. The hole concentration is

$$[h^+] = \int_{-\infty}^{E_v} N_{val}(E) F_h(E) dE \quad (6)$$

where N_{val} is the density of states in the valence band and F_h is the Fermi distribution function for holes. An analogous equation gives the electron concentration. The description is completed by imposing charge neutrality. Finally, equilibrium with external H_2 gas is included through the solubility equation

$$[H^0]^{eq} = N_h (P_{gas}^*)^{1/2} \exp\left(-\frac{G_{sol}^0}{kT}\right) \quad (7)$$

where P_{gas}^* is the fugacity of the gas. This relationship is expressed in terms of H^0 to avoid a dependence on Fermi level. The system of equations is solved numerically.

Parameters in Eqs. (1)-(7) are evaluated mostly using zero-temperature results from density functional theory for wurtzite GaN. The theoretical procedure and some results have been reported previously [4]. With a H atom in vacuum taken as the reference state, we find an energy of +0.34 eV for interstitial H^0 , -2.67 eV + $(E_f - E_v)$ for H^+ , and +1.52 eV - $(E_f - E_v)$ for H^- . The formation of the neutral Mg-H complex from Mg^- and H^+ has a binding energy of 0.70 eV. The zero-temperature dissociation energy of the H_2 molecule in vacuum is equated to 2.28 eV, the value for the deuterium (D) isotope. The ionization level for the Mg acceptor is taken from experimental studies to be $E_v + 0.16$ eV [6]. The diffusion activation energies from density functional theory are

0.5 eV for H^0 , 0.7 eV for H^+ , and 1.7 eV for H^- ; the corresponding prefactors are set equal to $0.001 \text{ cm}^2/\text{s}$, a representative value for interstitial solutes. The densities of states for the valence and conduction bands are also evaluated using density functional theory.

The free energies of reaction G appearing in Eqs. (1)-(7) vary with temperature, so that values for the temperatures of interest here differ from those for 0 K obtained using density functional theory. Causes of this variation include thermal expansion, the temperature dependence of the Gibbs free energy of H_2 gas, and the enthalpy and entropy arising from H vibrations. The first of these effects is neglected here. Full account is taken of the second by using published thermodynamics for D_2 gas [7]. Vibrational effects are included for the dominant H states in p-type GaN(Mg), H^+ and the Mg-H complex, but not for H^0 because there is no significant consequence for measured properties. Density functional theory reveals two nearly degenerate energy minima of H^+ , one at the N antibonding site oriented away from the c-axis, and the other at the c-axis bond-center position. Vibrational rates for D at the antibonding site are computed to be 2100 cm^{-1} (stretch) and 599 cm^{-1} (wag), while for the bond-center site we find 2418 cm^{-1} (stretch) and 355 cm^{-1} (wag). The Mg-H complex has a single stable configuration with the H at a N antibonding site diagonally opposite from a Mg neighbor along a bond direction transverse to the c-axis. The vibrational rates of this H are taken to be the same as for the N antibonding site without Mg. The vibrational enthalpy and entropy are evaluated from these results using the harmonic approximation [8].

PREDICTIONS AND COMPARISON WITH EXPERIMENT

Figure 1 shows the solubility of D in GaN(Mg) at 700°C as predicted by the theoretical model. Also given are experimental results for MOCVD GaN(Mg) on sapphire that was first activated by vacuum annealing for 1 hour at 900°C and then heated in D_2 gas at 700°C . The D concentration was measured using the nuclear reaction $^2D(^3\text{He,p})^4\text{He}$ [9]. That the introduced D behaved as expected was evidenced by infrared spectroscopy, which exhibited the absorption near 2320 cm^{-1} ascribed to the Mg-H center [5], and also by electrical measurements, which showed an increase in room-temperature resistivity from 3 to $14,000 \Omega\text{-cm}$ upon D charging. In the model calculation, the concentration of electrically active Mg acceptors was $2.4 \times 10^{19} \text{ cm}^{-3}$, somewhat below the total Mg concentration of $\sim 5 \times 10^{19} \text{ cm}^{-3}$, and compensating shallow donors were included at a concentration of $0.4 \times 10^{19} \text{ cm}^{-3}$. These plausible choices produced agreement with the observed saturation of D uptake at $\sim 2 \times 10^{19} \text{ cm}^{-3}$ and with the room-temperature hole concentration of $\sim 4 \times 10^{17} \text{ cm}^{-3}$ measured before D introduction. Other parameters were evaluated as discussed in the preceding section.

The horizontal displacement between theory and experiment in Fig. 1 provides a stringent test of the mechanistic assumptions and computed H energies of the theoretical model. Interpretation is facilitated by applying a single offset to all of the D energies in the solid relative to D in vacuum so as to produce agreement with experiment. The result, given by the dashed line in Fig. 1, is achieved by reducing the energies in the solid by 0.18 eV. This shift is believed to be less than the combined theoretical

uncertainties. Moreover, thermal expansion is expected to reduce the energies of interstitial D at 700°C, so that inclusion of this effect would reduce the disparity.

We also used the theoretical model to treat thermal release of D from GaN(Mg), initially under the assumption of no surface barrier. This yielded a much greater release rate than observed in our experiments. In the case of isothermal vacuum annealing at 700°C, for example, the measured release rate exceeded predictions by more than 6 orders of magnitude. Similarly large disparities were found for uptake from D₂ gas. This leads us to propose a surface permeation barrier. The barrier is modeled in the conventional manner by assuming that there is rapid equilibration between solution and surface sites and that the rate-determining step is recombinative desorption for release and dissociative adsorption for uptake. The flux at the surface is then given by

$$\Phi_{\text{sur}} = \Phi_0^{\text{in}} P_{\text{gas}}^* (1 - \theta_{\text{sur}})^2 \exp\left(-\frac{E_{\text{ads}}}{kT}\right) - \Phi_0^{\text{out}} (\theta_{\text{sur}})^2 \exp\left(-\frac{E_{\text{des}}}{kT}\right) \quad (8)$$

$$\frac{\theta_{\text{sur}}}{1 - \theta_{\text{sur}}} = \frac{[H^0]}{N_h} \exp\left(\frac{E_{\text{sur}}^0}{kT}\right) \quad (9)$$

where θ_{sur} is the fractional occupation of surface sites. The uptake term is parameterized using two measured uptake atomic fluxes, $\sim 3 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$ for 700°C and a D₂ pressure of 0.013 bar, and $\sim 3 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$ for 500°C and a pressure of 0.88 bar. This yields $E_{\text{ads}} = 1.36 \text{ eV}$ and $\Phi_0^{\text{in}} = 2.3 \times 10^{20} \text{ cm}^{-2}\text{s}^{-1}$. In the release term, the desorption activation barrier E_{des} is estimated to be 1.8 eV from surface desorption studies in ultrahigh-vacuum [10]. The remaining parameters E_{sur}^0 and Φ_0^{out} are then evaluated by requiring that Eq. (7) be satisfied when $\Phi_{\text{sur}} = 0$ in Eq. (8).

In Fig. 2, the predictions of the model with surface barrier included are compared with measurements of isothermal release into vacuum at 800°C. Two aspects of the comparison are noteworthy. First, the second-order release kinetics of Eq. (2) imply that, after the residual concentration of D has become small enough to have little influence on the Fermi level, the reciprocal of retained D concentration should vary linearly with time. The experimental data conform accurately to this prediction as seen in the figure. The second test is simply the degree to which the magnitudes of the predicted and measured release rates agree. The difference is seen to be less than a factor of 2.

Figure 3 shows predictions of the theoretical model for D release from initially saturated GaN(Mg) during isothermal annealing along with the resultant increase of hole concentration at 300 K. Release data for 700 and 800°C are included for comparison and are semiquantitatively consistent with the model. Comparison can also be made with published data for electrical activation of MOCVD GaN(Mg) during 20-minute isochronal anneals at 100°C intervals [11]. Our model simulation yields 36% recovery of the hole concentration at 300 K after the anneal at 700°C, whereas the measured room-temperature conductivity reached $\sim 1/2$ of its ultimate value at this temperature.

CONCLUSIONS AND IMPLICATIONS

The semiquantitative agreement found in this study between the predicted and

measured solubilities of D in GaN(Mg) supports the H configurational energies obtained from density functional theory. Our combined theoretical and experimental results for uptake and release are indicative of a surface permeation barrier characterized by second-order release kinetics.

The modeling with surface barrier included reproduces a feature of the thermal activation of GaN(Mg) that has been considered anomalous, namely, increases in hole concentration at temperatures as low as 500°C despite retention of H to >800°C. The key new insight is that, in the presence of the surface barrier, the H release rate varies relatively modestly with temperature while decreasing rapidly as a function of remaining H concentration, as seen in Fig. 3. As a consequence, H release and the associated electrical activation can extend over several hundred °C in an isochronal anneal sequence.

In our view, the modeling approach presented here has the potential for quantitative prediction of H behavior at temperatures above about 400°C where local equilibrium among H states can be assumed, although such accuracy is still to be demonstrated. A remaining area of uncertainty is the surface barrier, whose properties may, for example, depend on temperature and ambient. At lower temperatures where the activated transitions between H states are not all rapid, the simplifying assumption of local equilibration must give way to an explicit treatment of the reaction rates.

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Figure 1. Solubility of D in GaN(Mg) at 700°C as a function of D_2 fugacity

Figure 2. Isothermal release of D from GaN(Mg) at 800°C from theory and experiment.

Figure 3. Predicted isothermal release of D from GaN(Mg) and associated increase of hole concentration at 300 K.