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 >400ºC is modeled by using energies and vibration 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 greatly affects electrical properties, notably in p-type GaN doped with Mg where it can reduce the carrier concentration by orders of magnitude [2]. Application of density-functional theory to the zincblende[3] and wurtzite [4] forms of GaN has indicated that dissociated H in interstitial solution can assume positive, neutral, and negative charge states, with the neutral species being 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. Objectives are to facilitate comparison of theory with experiment and, ultimately, to describe quantitatively H behavior pertinent to device processing. Herein we summarize work relating to p-type GaN(Mg), with details to follow in a more comprehensive article.

THEORETICAL FORMALISM AND PARAMETER EVALUATION

The diffusion flux of H in GaN along the c-axis direction is given by

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

where brackets denote concentration, the quantities D are diffusion coefficients, E_f is the Fermi energy, and E_v is the energy of the valence-band edge. The final term on the right 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 >400ºC of concern herein. One then has [6]

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$$\frac{\left[H^{+}\right]}{\left[H^{0}\right]} = \exp\left(\frac{G_{H}^{+\backslash 0} - E_{f}}{kT}\right) \tag{2}$$

$$\frac{\left[H^{0}\right]}{\left[H^{-}\right]} = \exp\left(\frac{G_{H}^{0\backslash -} - E_{f}}{kT}\right) \tag{3}$$

where the quantities G_H are bandgap levels associated with the electronic transitions and are defined to include degeneracy. Populations relating to the Mg acceptor are given by

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

$$\frac{\left[Mg^{0}\right]}{\left[Mg^{-}\right]} = \exp\left(\frac{G_{Mg}^{0\backslash -} - E_{f}}{kT}\right) \tag{5}$$

where N_{GaN} is the formula-unit density of GaN, MgH is the neutral complex, and G_{MgH} is the nonconfigurational part of the change in Gibbs free energy arising from dissociation of the MgH complex. The hole concentration is

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

where N_{val} is the density of states in the valence band and F_h is the Fermi distribution function for holes. The electron concentration is given by an analogous integral of the conduction band. The description is completed by imposing charge neutrality. Equilibrium with external H_2 gas is described by the solubility equation

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

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 using zero-temperature results from density functional theory for wurtzite GaN. The theoretical procedure and some results have been reported previously [4]. Using the H atom in vacuum 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 ionization level for the Mg acceptor is taken from experimental studies to be E_v+0.16 eV [7]. The diffusion activation energies from density functional theory are 0.5 eV for H^0, 0.7 eV for H^+, and 1.6 eV for H^-; the

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diffusion prefactors are set equal to 0.001 cm^2/s, which is representative for interstitials. The densities of states for the valence and conduction bands are evaluated from density functional theory.

The quantities G in Eqs. (1)-(7) differ between 0 K, where the results of density functional theory apply directly, and the elevated temperatures of interest. Causes include the temperature-dependent thermodynamics of H_2 gas and the enthalpy and entropy arising from H vibrations in the semiconductor. We treat these effects for deuterium (D), the isotope used in our experiments. The Gibbs free energy of D_2 gas is taken from the literature [8]. Vibrational effects are included for the dominant D states in p-type GaN(Mg), D^+ and the Mg-D complex. Density functional theory reveals two nearly degenerate energy minima of D^+, one at the N antibonding site oriented transverse to the c-axis, and the other at the c-axis bond-center position. Computed vibrational rates for D at the antibonding site are 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-D complex has a single stable configuration with the D at a N antibonding site diagonally opposite from a Mg neighbor along a bond direction transverse to the c-axis. The vibrations of this D are taken to be the same as for the N antibonding site without Mg. The vibrational enthalpy and entropy are computed from these results in the harmonic approximation [9].

PREDICTIONS AND COMPARISON WITH EXPERIMENT

Figure 1 shows the solubility of D in GaN(Mg) at 700ºC 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 900ºC and then heated in D_2 gas at 700ºC. The D concentration was measured using the nuclear reaction $^2D(^3He,p)^4He$ [10]. That the introduced D behaved as expected was evidenced by infrared spectroscopy, which exhibited the absorption near 2320 cm^{-1} ascribed to the Mg-D complex [5], and also by electrical measurements, which showed an increase in

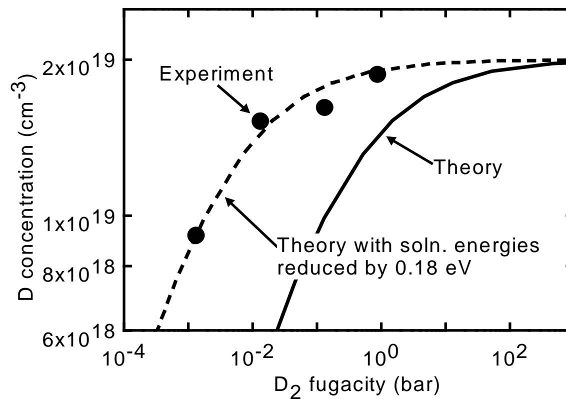

Figure 1. *Solubility of D in GaN(Mg) at 700ºC as a function of D_2 fugacity.*

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room-temperature resistivity from 3 to 14,000 Ω-cm upon D charging. In the model calculation, the concentration of electrically active Mg acceptors is 2.4×10^{19} cm^{-3}, somewhat below the total Mg concentration of ~5×10^{19} cm^{-3}, and compensating shallow donors are included at a concentration of 0.4×10^{19} cm^{-3}. These plausible choices produce agreement with the observed saturation of D uptake at ~2×10^{19} cm^{-3} and with the room-temperature hole concentration of ~4×10^{17} cm^{-3} measured before D introduction. Other parameters are evaluated as discussed in the preceding section.

The horizontal displacement between theory and experiment in Fig. 1 provides a 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.

We also used the theoretical model to treat thermal release of D from GaN(Mg), initially assuming no surface barrier. This yielded a much greater release rate than observed in our experiments; during vacuum annealing at 700ºC, the measured release rate exceeded predictions by 6 orders of magnitude. Similarly large disparities were found for uptake from D_2 gas. This leads us to propose a surface permeation barrier. The barrier is provisionally modeled in the conventional manner by assuming equilibrium between solution and surface states so that the rate-determining step is desorption with H_2 formation for release and dissociative adsorption for uptake [11]. The D atomic flux through the surface is then given by

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

$$\frac{\theta_{sur}}{1-\theta_{sur}} = \frac{\left[H^0\right]_{x\to 0}}{N_{GaN}} \exp\left(-\frac{E_{sur}^0}{kT}\right) \tag{9}$$

where Φ_0^{in} and Φ_0^{out} are constant prefactors, θ_{sur} is the fractional occupation of surface sites, and $\left[H^0\right]_{x\to 0}$ is the solution concentration near the surface. The first, uptake term on the right is parameterized using two measured uptake D fluxes, ~3×10^{11} cm^{-2}s^{-1} for 700ºC and a D_2 pressure of 0.013 bar, and ~3×10^{11} cm^{-2}s^{-1} for 500ºC and 0.88 bar. This yields E_{ads} = 1.36 eV and $\Phi_0^{in} = 2.3\times10^{20}$ cm^{-2}s^{-1}. In the second, release term, the barrier E_{des} is estimated to be 1.8 eV from surface desorption studies [12]; E_{sur}^0 and Φ_0^{out} are then evaluated by requiring that Eq. (7) hold when $\Phi_{sur} = 0$ 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 800ºC. The second-order release kinetics of Eq. (8) 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 nearly linearly with time. The experimental data are seen in

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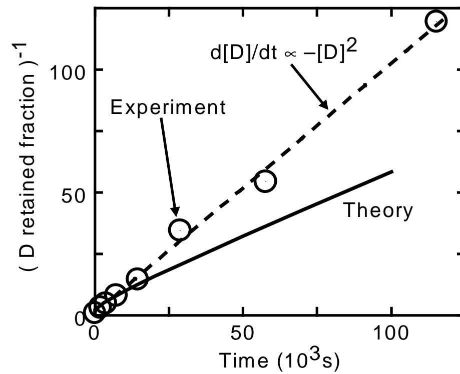

Figure 2. *Isothermal D release from GaN(Mg) at 800ºC.*

the figure to exhibit this property. Since few alternative rate-determining processes would show such kinetics, the finding evidences the presence of the barrier. Moreover, the predicted and measured release rates differ by 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 and the resultant increase in hole concentration at 300 K. Release data for 700 and 800ºC are included and agree semiquantitatively with the model. Comparison can also be made with published data for electrical activation of MOCVD GaN(Mg) during 20-minute isochronal anneals at 100ºC intervals [13]. Our model simulation yields 36% recovery of the hole concentration at 300 K after the anneal at 700ºC, whereas the measured room-temperature conductivity rose to ~1/2 of its ultimate value at this temperature.

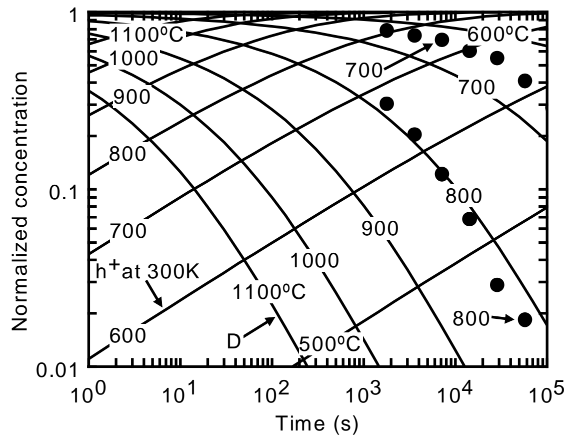

Figure 3. *Predicted isothermal release of D from GaN(Mg) and associated increase of hole concentration at 300 K.*

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CONCLUSIONS AND IMPLICATIONS

The semiquantitative agreement found in this study between predicted and measured solubilities of D in GaN(Mg) supports the H energies obtained from density functional theory. Our combined theoretical and experimental results for uptake and release indicate a surface barrier with second-order release kinetics.

In our view, the modeling approach presented here has the potential ultimately for quantitative prediction of H behavior at temperatures >400ºC where local equilibrium among H states is expected. Remaining areas for refinement include the surface barrier, whose properties are incompletely known. At lower temperatures where the activated transitions between H states are not rapid, the assumption of local equilibration should give way to an explicit treatment of the reaction rates.

ACKNOWLEDGMENT

This work was supported by the U. S. Dept. of Energy under Contract DE-AC04-94AL85000, primarily under the auspices of the Office of Basic Energy Sciences.

REFERENCES

1. S. J. Pearton, J. C. Zolper, R. J. Shul, and F. Ren, *J. Appl. Phys.*, **86**, 1 (1999).
2. S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, *Jpn. J. Appl. Phys.*, **31**, 1258 (1992).
3. J. Neugebauer and C. G. Van de Walle, *Phys. Rev. Lett.*, **75**, 4452 (1995).
4. A. F. Wright, *Phys. Rev. B*, **60**, R5101 (1999).
5. W. Götz, N. M. Johnson, D. P. Bour, M. D. McCluskey, and E. E. Haller, *Appl. Phys. Lett.*, **69**, 3725 (1996).
6. C. Herring and N. M. Johnson, in *Hydrogen in Semiconductors,* edited by J. I. Pankove and N. M. Johnson (Academic, New York, 1991) pp. 234-235.
7. W. Götz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, *Appl. Phys. Lett.*, **68**, 667 (1996), and citations therein.
8. *J. Phys. Chem. Ref. Data*, Vol. 14, Suppl. 1, p. 1002 (1985).
9. T. L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986) pp. 86-93.
10. S. M. Myers, G. R. Caskey, Jr., D. E. Rawl, Jr., and R. D. Sisson, Jr., *Metall. Trans. A,* **14**, 2261 (1983).
11. F. C. Tompkins, *Chemisorption of Gases on Metals* (Academic, New York, 1978).
12. R. Shekhar and K. F. Jensen, *Surf. Sci.*, **381**, L581 (1997).
13. S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, *Jpn. J. Appl. Phys.*, **31**, L139 (1992).

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