Nitrogen Vacancy Diffusion and Trapping in Mg-doped Wurtzite GaN

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Motivation—The development of group-III nitride light-emitting diodes and laser diodes was enabled by the discovery that Mg acceptors in wurtzite GaN grown via metalorganic chemical vapor deposition (MOCVD) can be activated using a thermal anneal treatment. Following this discovery, it was established that the anneal removes H, which incorporates during growth and passivates the Mg acceptors. Although the dominance of H passivation in MOCVD Mg-doped GaN is not disputed, recent experimental results indicate that the N vacancy (V_N) may play a similar, albeit secondary role in passivating Mg acceptors. Motivated by these results, we have examined aspects of V_N behavior in Mg-doped GaN using density-functional theory (DFT). The goal of these examinations was to gain a deeper understanding of this defect and thereby aid in the development of more efficient group-III nitride light-emitting devices.

Accomplishments—We have used DFT to investigate V_N diffusion in wurtzite GaN and complexes of V_N with an Mg acceptor. The DFT calculations made use of recent enhancements in DFT techniques, which have been demonstrated to improve the accuracy of DFT results. These enhancements include the generalized-gradient approximation for exchange and correlation, the treatment of the Mg 2*p* and Ga 3*d* as valence electrons, thereby allowing them to participate in the formation of bonds, and the nudged-elastic-band and dimer methods which are used to identify V_N diffusion paths and the associated transition states.

Two V_N diffusion paths were identified: a *perpendicular* path producing V_N movement strictly perpendicular to the wurtzite *c* axis and a *diagonal* path producing V_N movement both perpendicular and parallel to the *c* axis. The V_N charge state was found to strongly influence the diffusion activation energies, which range from 2.49 eV for the +3 charge state to 3.55 eV for the +1 charge state along the perpendicular path, and from 2.65 eV in the +3 charge state to 3.96 eV in the +1 charge state along the diagonal path. The sequence of atomic configurations involved in V_N diffusion along the diagonal path is shown in Fig. 1 for the case of the +3 charge state. The transition state is shown in Fig. 1b and is characterized by an N atom bonded to two Ga atoms instead of four as in bulk GaN.

Two types of MgV_N complexes were identified: a *parallel* configuration with V_N located next to Mg and along the *c* axis from it, and a *perpendicular* configuration with V_N located next to Mg and perpendicular to the *c* axis from it. The dissociation energies of these complexes were found to range from 0.29 to 0.58 eV, depending on the configuration and charge state. The local-energy-minimum configurations of MgV_N in the +2 charge state are shown in Fig. 2. The dissociation energy of the perpendicular configuration, 0.58 eV, is comparable to the dissociation energy of the MgH complex in GaN.

Significance—The DFT results suggest that V_N should be present in Mg-doped MOCVD GaN and difficult to remove with thermal anneal treatments. Furthermore, the charge states of V_N and MgV_N are predicted to change during thermal anneal treatments due to the ensuing shift in the Fermi level as H is removed from the material. The consequences of these DFT results are being explored at Sandia via experimental and diffusion-reaction modeling studies.

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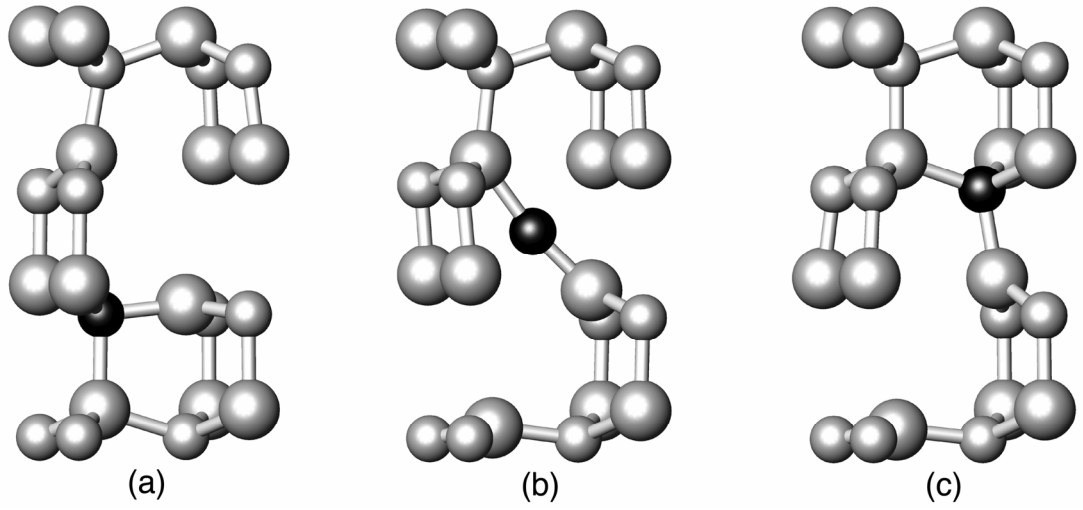

Figure 1. Diagonal diffusion path for V in the +3 charge state. (a) and (c) are local-energy-minimum configurations and (b) is the energy saddle-point configuration. Large, light colored spheres denote Ga atoms, small, light colored spheres denote N atoms, and the small, dark colored sphere denotes the N atom that changes place with V along the diffusion path. The views are orthographic with the view direction rotated ≈10° from [1, -1, 0, 0].

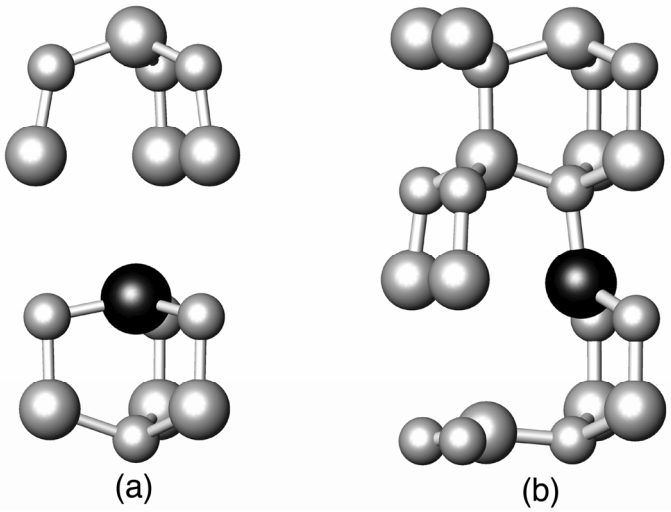

Figure 2. Local-energy-minimum configurations for MgV in the +2 charge state. (a) shows the parallel configuration and (b) shows the perpendicular configuration. Large, light colored spheres denote Ga atoms, small, light colored spheres denote N atoms, and large, dark colored spheres denote Mg atoms. The views are orthographic with the view direction rotated ≈ 10° from [1,-1,0,0].