

Electron-beam-induced migration of hydrogen in Mg-doped GaN using Eu as a probe

B. Mitchell,¹ D. Lee,² D. Lee,³ A. Koizumi,³ J. Poplawsky,^{4,5} Y. Fujiwara,³ and V. Dierolf¹

¹*Lehigh University, 16 Memorial Drive East, Bethlehem, Pennsylvania 18015, USA*

²*Lawrence Livermore National Laboratory, 7000 East Avenue L-413, Livermore, California 94550, USA*

³*Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

⁴*Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee 37831, USA*

⁵*University of Tennessee, 1508 Middle Drive, Knoxville, Tennessee 37996, USA*

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We demonstrate the use of hydrogen-induced changes in the emission of isoelectric Eu ions, in Mg-doped *p*-type GaN, as a powerful probe to study the dynamics of hydrogen movement under electron-beam irradiation. We identify, experimentally, a two-step process in the dissociation of Mg-H complexes and propose, based on density functional theory, that the presence of minority carriers and the resulting charge states of hydrogen drive this process.

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The realization of an efficient nitride-based light-emitting diode (LED) relies on the optimization of *p*-type conductivity. Magnesium is commonly used as an acceptor dopant to obtain *p*-type conductivity in GaN, however, the presence of hydrogen has been known to electrically passivate these acceptors.¹ This passivation has been attributed to the formations of neutral Mg-H complexes where the hydrogen is bonded interstitially to a neighboring nitrogen atom.²⁻⁴ It is known that *p*-type conductivity can be achieved after thermal annealing at temperatures above 700 °C or low energy electron-beam irradiation (LEEBI), both of which break up these complexes.⁵⁻⁷ Previous luminescence and dissociation kinetics studies, which were performed on Mg-doped GaN (GaN:Mg), have been somewhat contradictory and difficult to interpret.⁷⁻¹⁴

The reported discrepancies arise due to differences in both growth methods and conditions, as well as the precise thermal history of the sample at the time it was studied being either as-grown or thermally activated *p*-type GaN:Mg. However, we also point out that photoluminescence (PL) studies involving transitions from donors, acceptors, and band levels tend to be difficult to interpret. Changes in the luminescence can have a variety of reasons, including the modifications of donors and acceptors and the opening of new excitation channels, which can compete with channels existing in the as-grown state. Circumventing this difficulty, we have investigated modifications of the Eu emission spectra in GaN:Mg codoped with Eu, since changes in the emission spectra directly reflect alterations in the environment of the Eu ion.¹⁵ To this end, in this Rapid Communication we exploit Eu as a probe to track modifications induced by electron-beam irradiation.

Mg- and Eu-codoped GaN (GaN:Eu,Mg) layers (400 nm thick) were grown by organometallic vapor phase epitaxy (OMVPE) on a sapphire substrate with an initial GaN buffer layer and capped by a 10 nm GaN capping layer. No activation other than a cooldown in NH₃ ambient was performed on the samples. The Eu and Mg concentrations were determined to be 3.0×10^{19} and 2.4×10^{19} cm⁻³, respectively, by secondary ion-mass spectroscopy. For comparison, additional samples without Mg and with lower Mg concentrations were studied as well.

The cathodoluminescence (CL) measurements were performed in a JEOL6400 scanning electron microscope (SEM). The samples were mounted onto two different stages, the first of which is a standard copper cold finger capable of reaching temperatures of 30 K. The second is a newly developed confocal microscope stage capable of simultaneous CL and site-selective PL studies.¹⁶ A single mode fiber with a 3.5 μm core was used to collect the emission from the sample. A spot size of 35 μm or a raster area of roughly 80 μm × 80 μm was used to ensure that any modifications were evenly distributed over the collection area when using this stage. The mount for the sample is attached to a copper braid which allows for the sample to be cooled to roughly 105 K. For all measurements the accelerating voltage was held at 10 keV to ensure optimal penetration into the doped layer and minimal penetration into the undoped buffer layer.

In order to compare our observations with previously published findings, LEEBI experiments were performed at room temperature and 30 K, and the changes in the luminescence close to the band edge were analyzed. Starting with an as-grown sample and using a beam current of 10 nA, we tracked the changes in the CL spectra every second for 20 s, after which there are no more significant variations [Fig. 1 (left)]. The peak at 3.38 eV has been assigned to the near-band emission (NBE) and is not attributed to Mg due to its presence in undoped samples.^{7,9,17} As a result of the LEEBI treatment, broad bands around 3.20 and 3.26 eV were seen to increase in intensity. No shift in energy was seen as the bands increased in intensity, which is in agreement with the theory that these bands can be attributed to a free electron to acceptor transition.^{7,10,18}

At 30 K, spectra were recorded every 0.5 s and yielded much more detailed results [Fig. 1 (right)]. The as-grown spectra consisted of resolved peaks at 3.38, 3.29, and 3.20 eV as well as a broad peak at 3.12 eV. The 3.29 eV peak has been attributed to a zero phonon donor-acceptor-pair (DAP) transition with the 3.20 and 3.12 eV peaks being its phonon replicas. This increase was observed after LEEBI (Ref. 7) and also after thermal annealing around 500 °C.¹⁹ After 5 s, the NBE peak at 3.38 eV almost vanished and the other peaks nearly tripled in intensity. Simultaneously, the 3.20 eV band shifted to 3.21 eV.

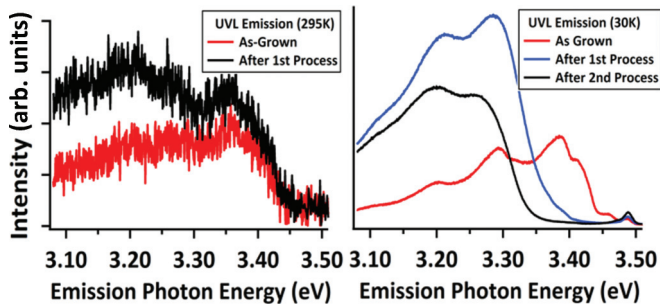


FIG. 1. (Color online) Left: UV light (UVL) CL spectra taken at room temperature before irradiation (red) and after (black). An increase in a band centered 3.20 eV is observed. Right: UVL CL spectra taken at 30 K. Two steps are observed, one occurring after 5 s (blue) and the other after 55 s (black).

After continuing the irradiation for another 30 s, the peaks at 3.29 and 3.21 eV decreased, switched in relative intensities, and shifted to 3.27 and 3.20 eV, respectively.

These observations clearly point to a two-step process in the modification of the Mg-related centers at low temperatures: a first step, during which the 3.29 eV peak and its replicas appear, and a second step, which decreases them and introduces new bands. The second step and the associated peaks have also been observed by Gelhausen *et al.*⁹ as well and attributed to a DAP with a deeper donor, perhaps a nitrogen vacancy (V_N).²⁰ Coleman *et al.*⁷ observed that the modification processes take much longer and require a higher power density at room temperature compared to low. Most importantly, for the context of this Rapid Communication, since our NBE observations in GaN:Eu,Mg demonstrate the same type of dissociation processes that take place in GaN:Mg and are absent in GaN:Eu, they can be used as solid points of reference as we move to our studies to the Eu-related red emission, which we use as a probe.

Figure 2 shows the CL spectra in the Eu emission range, which contains distinct features that are only found in Mg-codoped samples, and which increase with increasing Mg concentration. This indicates that the addition of Mg introduces new Eu centers which are perturbed by the presence of Mg. In the as-grown state, one of these centers, labeled Mg/Eu1, dominates the CL emission due to its apparent superior excitation efficiency. The LEEBI procedures described above were duplicated in this region for three different temperatures and

the CL response of the Eu ions was detected (Fig. 2). We find a conversion among Mg perturbed Eu centers, which indicates, as long as we assume that neither Eu nor Mg is mobile on its own, that we are dealing with Mg-H complexes, which change their configuration under electron-beam irradiation. As above, we find a two-step conversion that can be probed by the Eu emission.

In order to take full advantage of this, we performed site-selective combined excitation-emission spectroscopy (CEES) before and after electron-beam exposure, using a beam current of 6 nA at 105 K [Figures 3(a) and 3(b)]. In this technique, the different Eu centers are resonantly excited, by tuning the excitation wavelength, and their respective emission spectra are recorded. Comparing the results to earlier studies performed on GaN:Eu (Ref. 21) allows the identification of Mg-H-related centers in terms of their unique excitation and emission energies, and the determination of their relative numbers to be about 10% of the unperturbed Eu centers.

After irradiation for 1 min, Mg/Eu1 is destroyed and another new site, labeled Mg/Eu2, is formed. Additionally, after irradiation, a significant increase in the center labeled Mg/Eu3 occurs. This site has the same emission profile as the majority center (Eu1) found in GaN:Eu, but has a much higher excitation efficiency than the very inefficient Eu1 center²¹ under indirect excitation, as can be seen by taking the intensity ratios of the CL and resonant PL spectra. More specifically, we find that both Mg/Eu3 and Mg/Eu2 have comparable excitation efficiencies to Mg/Eu1, suggesting that the three centers share a common excitation pathway that involves the Mg-H complex.

To study the thermal stability of the modification, we initially irradiated the sample at 105 K, subsequently heated it to room temperature, and finally cooled it back down to 105 K. An interesting center modification was observed in which the initially created Mg/Eu3 centers were significantly reduced, the Mg/Eu2 increased, and the initially depleted Mg/Eu1 partially recovered. This was observed in both CL and CEES measurements shown in Figs. 3(c) and 4(a). No such modification was detected when the sample was irradiated at room temperature and cycled to lower temperatures [Fig. 4(b)].

The sample was also annealed in NH_3 at 800 °C, which was the only process in which the sample reverted to its as-grown state with all of the original relative intensities restored [Fig. 4(c)]. We believe that at these temperatures, in a hydrogen rich environment, the hydrogen are recaptured into the most energetically favorable (as-grown) configurations. It should

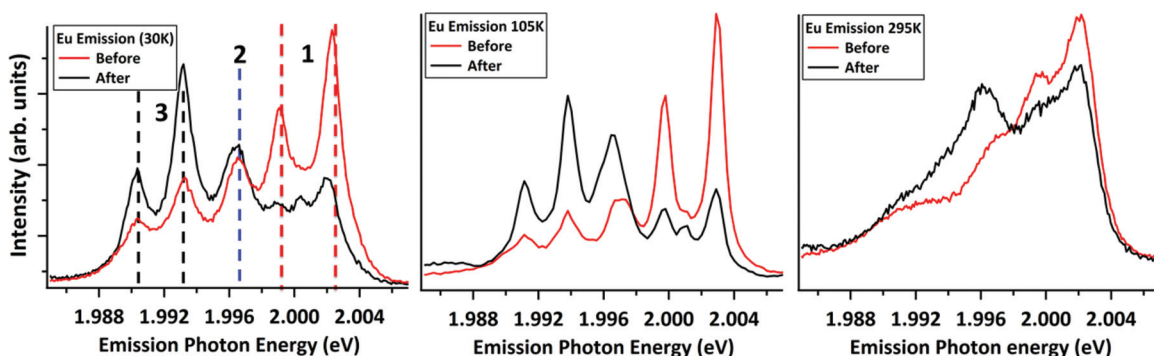


FIG. 2. (Color online) Eu emission spectra taken before and after electron-beam irradiation at three different temperatures.

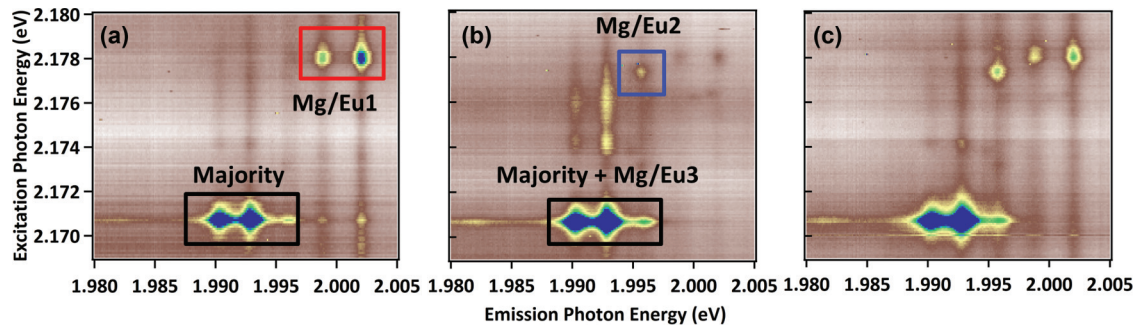


FIG. 3. (Color online) CEES taken (a) before and (b) after irradiation with a beam current of 6 nA. At this current the increase in Mg/Eu3 is accompanied by the appearance of a new site Mg/Eu2. (c) A partial recovery of Mg/Eu1 and 2 is observed after heating the sample to room temperature and returning to 105 K.

be noted that when GaN:Eu samples are annealed in an NH_3 ambient, no new centers are created nor are changes in the luminescence properties observed [Fig. 4(d)].

In interpreting the structure of the Mg-related Eu centers, we need to keep in mind that the observed transitions within the $4f$ shell of the Eu electronic configuration are sensitive mainly to the nearby environment and the displacement of the ion in regards to the lattice position of the Ga ion that it replaces. In this regard, the Mg/Eu3 center is of particular interest because no spectral shift is observed, the excitation efficiency compared to the majority center Eu1. We propose that the Eu1 center consists of a Eu ion which is perturbed by a V_N . This configuration is quite possible, since electron paramagnetic resonance (EPR) studies revealed that the majority Er center is perturbed by a nearby V_N in GaN.²² In addition, we suggest that the Mg in the Mg/Eu3 center is sufficiently distant from

the Eu ion to prevent any direct perturbation, yet close enough to positively influence the excitation efficiency.

To gain further insight on the configurations of different Mg/Eu centers and their kinetics, we performed density functional theory (DFT) calculations.²³ In these calculations, the bulk GaN system is constructed by a 128 atom supercell ($4 \times 2 \times 2$ unit cell) and Eu and Mg dopants are assumed to replace Ga site forming Eu_{Ga}^x and Mg'_{Ga} , while the hydrogen atom goes into an interstitial site (H_i^\bullet). In order to compensate for the effect of charged defects in the system, the neutralizing background charge of the opposite sign is implicitly introduced in our calculations.

We performed rigorous searches on diverse arrangements of four different defects (Eu_{Ga}^x , Mg'_{Ga} , $V_N^{\bullet\bullet\bullet}$, and H_i^\bullet) and the possible potential permutations for defect complexes. In a first step, we were able to confirm that the $\text{Eu}_{\text{Ga}}^x - V_N$ center (Eu1 center) is an energetically favorable configuration

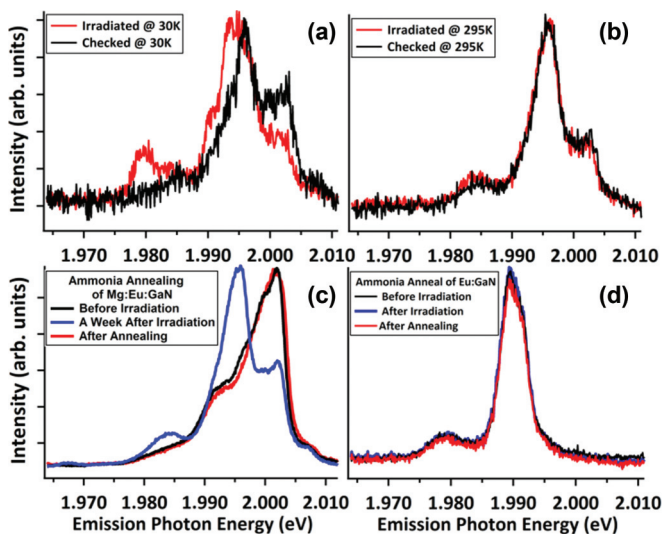


FIG. 4. (Color online) (a) The partial recovery of Mg/Eu1 and 2 is observed after irradiation is performed at 30 K and the sample is heated to room temperature and brought back down to 30 K. (b) No recovery is seen when the sample is irradiated at 295 K and cycled to 30 K. (c) The original spectra only returned after annealing in NH_3 , which gives support to the H nature of the complex. (d) No change is observed for either electron-beam irradiation or annealing for undoped Eu:GaN.

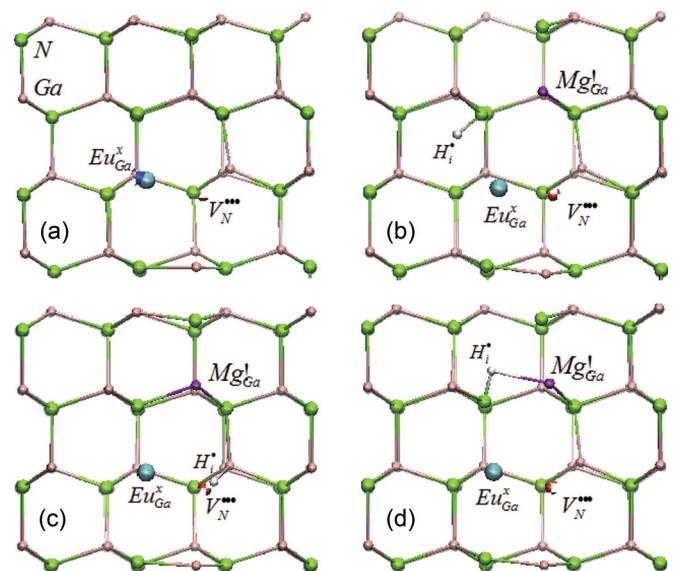


FIG. 5. (Color online) DFT models for four different configurations of the defect complex in Eu/Mg-codoped GaN: (a) A $\text{Eu} - V_N$ center which does not contain Mg or H (Eu1 center). (b) The as-grown configuration (Mg/Eu1). (c) The configuration in which the hydrogen is captured by the nearest neighbor V_N after LEEBI (Mg/Eu2). (d) Metastable configuration of the hydrogen which induces a minimal perturbation on the Eu ion (Mg/Eu3).

[see Fig. 5(a)]. Further investigations on other defects show that V_N attracts other defects and ultimately forms a cluster configuration as shown in Fig. 5(b). This Eu-H-N-Mg- V_N configuration resembles the H-N-Mg arrangement, in which the hydrogen can capture electrons during electron-beam irradiation, proposed by Meyer *et al.*⁴ Since the interstitial hydrogen atom strongly interacts with Eu_{Ga}^x , this configuration leads to a significant modification of the Eu_{Ga}^x position compared to the Eu- V_N center. This leads us to the conclusion that this initial cluster configuration corresponds to the observed Mg/Eu1 center.

Under electron-beam irradiation, and a potential change of charge of the hydrogen from H^+ to H^0 , however, DFT predicts that the Mg/Eu1 is no longer the most energetically favorable configuration. With an excess electron in the system, the Mg/Eu1 become energetically less favorable, and the configuration in which hydrogen sits on the $V_N^{\bullet\bullet}$ site is 0.17 eV lower in energy [see Fig. 5(c)]. We correlate this arrangement to the Eu/Mg2 center since this configuration leads to an intermediate perturbation ($\Delta = 0.065 \text{ \AA}$) of the Eu_{Ga}^x center. In addition, a configuration in which the hydrogen moves away from Eu_{Ga}^x toward the Mg'_{Ga} is equally preferable to the Mg/Eu1 [see Fig. 5(d)]. We correlate this structure, in which the modification of Eu_{Ga}^x position compared to the Eu- V_N center is negligible ($\Delta = 0.003 \text{ \AA}$), to the observed Mg/Eu3. The energetic preference of the Mg/Eu3 increases as the number of excess electrons increases, and is 0.22 eV lower in energy than Mg/Eu1 when two excess electrons are present in the system.

Furthermore, our DFT calculations on the defect clusters without Eu_{Ga}^x show that the Eu dopant is, in fact, a quite benign probe in GaN:Mg and that the energetics of the system is dictated by the interactions among the other three complex constituents. In essence, from the DFT calculations we find three stable center configurations which exist under different charge conditions, suggesting that the addition of charge is driving the modification.

To understand the observed temperature dependence and recovery during temperature cycling, we have further performed nudged elastic band (NEB) calculations.²⁴ Our calculations predict that the energy barrier associated with hydrogen movement from an interstitial site to a V_N site is significantly higher than the movement between two interstitial sites. The energy barrier for the transition of Mg/Eu1 to Mg/Eu2 is 1.91 eV, while that to Mg/Eu3 is only 0.74 eV, with one electron added to the system. As a result, although the Mg/Eu2 is the most energetically favorable configuration under irradiation, the movement to the metastable Mg/Eu3 is more likely at lower temperatures and power densities.

Therefore, it appears that the temperature and power dependences of our system are governed by the combination of the overcoming of energy barriers and the ability of the system to hold charge. The temperature dependence of the

conductivity in GaN has been studied, and it was observed that the dark current increases drastically at temperatures above 100 K.²⁵ We suggest that the system is able to hold charge more easily, at lower temperatures, and this drives the hydrogen from Mg/Eu1 to Mg/Eu3. The metastable Eu/Mg3 will have a motivation to go back to the Eu/Mg1 by losing excess electrons, or to move into the V_N site by overcoming the energy barrier at the elevated temperature, and thus Mg/Eu3 is not observed after thermal cycles beginning at low temperature. At higher temperatures, the movement of the hydrogen is less efficient and so we must increase the power density to drive the modification. The combination of higher power densities and increased thermal energy gives the hydrogen the 1.91 eV it requires to move to Mg/Eu2, where it is more favorable and stable. As a result, above 100 K, we see a more equivalent preference for the hydrogen to move to either Mg/Eu2 or Mg/Eu3, and by room temperature the movement is predominantly into Mg/Eu2. Mg/Eu2 is a quite stable configuration and no movement to Mg/Eu1 is observed when the sample is cycled to lower temperatures or when left at room temperature.

In summary, we have shown that there is a strong correlation between the changes seen in the emission from both the Eu ions and the normal emission in GaN:Mg. This correlation shows that the isoelectric nature of Eu appears to make it a good probe, and, as evidenced by the results discussed herein, capably demonstrating that under LEEBI the hydrogen migrates locally within the vicinity of its as grown complex. We have verified the two distinct steps in the activation of the Mg acceptors that have been previously observed. The first involves the dissociation and charging of the Mg-H complex. The neutral hydrogen defects are then trapped locally, forming V_N -H complexes. The second step involves the further charging and migration of the hydrogen out of the complex, yet remaining close enough to be recaptured upon heating. A pronounced temperature dependence was observed and was attributed to the reduction of activation barriers and hydrogen mobility, as well as increased conductivity at higher temperatures. Our calculations indicate that a V_N is necessary for these observations to occur. The possible change in favorable Mg-H configurations and stabilities as a function of the Fermi level needs to be studied.

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¹S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, *Jpn. J. Appl. Phys.* **31**, 1258 (1992).

²J. Neugebauer and C. G. Van De Walle, *Phys. Rev. Lett.* **75**, 4452 (1995).

³B. Clerjaud, D. Côte, A. Lebkiri, C. Naud, J. M. Baranowski, K. Pakula, D. Wasik, and T. Suski, *Phys. Rev. B* **61**, 8238 (2000).

⁴S. M. Myers, C. H. Seager, A. F. Wright, B. L. Vaandrager, and J. S. Nelson, *J. Appl. Phys.* **92**, 6630 (2002).

- ⁵H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, *Jpn. J. Appl. Phys.* **28**, L2112 (1989).
- ⁶S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, *Jpn. J. Appl. Phys.* **31**, L139 (1992).
- ⁷X. Li and J. J. Coleman, *Appl. Phys. Lett.* **69**, 1605 (1996).
- ⁸Y. Koide, D. E. Walker, B. D. White, L. J. Brillson, M. Murakami, S. Kamiyama, H. Amano, and I. Akasaki, *J. Appl. Phys.* **92**, 3657 (2002).
- ⁹O. Gelhausen, H. N. Klein, M. R. Phillips, and E. M. Goldys, *Appl. Phys. Lett.* **81**, 3747 (2002).
- ¹⁰O. Gelhausen, H. N. Klein, M. R. Phillips, and E. M. Goldys, *Appl. Phys. Lett.* **83**, 3293 (2003).
- ¹¹O. Gelhausen, M. R. Phillips, and E. M. Goldys, *J. Phys. D* **36**, 2976 (2003).
- ¹²O. Gelhausen, M. R. Phillips, E. M. Goldys, T. Paskova, B. Monemar, M. Strassburg, and A. Hoffmann, *Phys. Rev. B* **69**, 125210 (2004).
- ¹³A. M. Fischer, S. Srinivasan, F. A. Ponce, B. Monemar, F. Bertram, and J. Christen, *Appl. Phys. Lett.* **93**, 151901 (2008).
- ¹⁴W. Götz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, *Appl. Phys. Lett.* **68**, 667 (1996).
- ¹⁵D. Lee, A. Nishikawa, Y. Terai, and Y. Fujiwara, *Appl. Phys. Lett.* **100**, 171904 (2012).
- ¹⁶J. Poplawsky and V. Dierolf, *Microsc. Microanal.* **18**, 1263 (2012).
- ¹⁷G. M. Criado, A. Cros, A. Cantarero, R. Dimitrov, O. Ambacher, and M. Stutzmann, *J. Appl. Phys.* **88**, 3470 (2000).
- ¹⁸M. A. Reshchikov, G.-C. Yi, and B. W. Wessels, *Phys. Rev. B* **59**, 13176 (1999).
- ¹⁹A. K. Viswanath, E. Shin, J. I. Lee, S. Yu, D. Kim, B. Kim, Y. Choi, and C. Hong, *J. Appl. Phys.* **83**, 2272 (1998).
- ²⁰C. G. Van de Walle, *Phys. Rev. B* **56**, R10020 (1997).
- ²¹N. Woodward, J. Poplawsky, B. Mitchell, A. Nishikawa, Y. Fujiwara, and V. Dierolf, *Appl. Phys. Lett.* **98**, 011102 (2011).
- ²²A. Uedono, C. Shaoqiang, S. Jongwon, K. Ito, H. Nakamori, N. Honda, S. Tomita, K. Akimoto, H. Kudo, and S. Ishibashi, *J. Appl. Phys.* **103**, 104505 (2008).
- ²³W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ²⁴H. Jónsson, G. Mills, and K. W. Jacobsen, *Nudged Elastic Band Method for Finding Minimum Energy Paths of Transitions* (World Scientific, Singapore, 1998).
- ²⁵S. J. Chung, B. Karunakaran, M. Senthilkumar, and E.-K. Suh, *J. Korean Phys. Soc.* **49**, 177 (2006).