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## Stability of nitrogen in ZnSe and its role in the degradation of ZnSe lasers

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We use density functional theory to examine the stability of defects in *p*-ZnSe that are formed by a transition of the nitrogen acceptor to the interstitial site. We find that the threefold positive complex of the interstitial nitrogen with the remaining vacancy is considerably more stable than the nitrogen acceptor. The formation of the complex is, however, limited by a kinetic barrier of 1.8 eV for the site transition, and the fact that the charge of the defect must change. The energetic position of the defect in the energy gap is about 2 eV above the valence band edge. This is in agreement with optical degradation experiments which show the formation of a deep defect in the *p*-doped waveguide with a transition energy of about 2.1 eV and the diffusion of a positively charged species. [S0163-1829(99)52548-4]

In data storage as well as display technology there is an urgent need for reliable and cheap light emitters in the blue and green spectral range. Since the first successful demonstration of a ZnSe based blue laser diode in 1991,<sup>1</sup> ZnSe has been a promising candidate for such devices. It was soon recognized, however, that ZnSe based devices tend to degrade rapidly. Stacking faults play an important role in this degradation process, and it was demonstrated that the device lifetime is directly correlated to the stacking fault density,<sup>2</sup> and there was hope that stacking fault free devices would not degrade. In the meantime, improvements in the epitaxy of ZnSe allowed the production of such devices. Nevertheless, their lifetime is not as high as expected, and the highest reported lifetimes for cw operation at room temperature are several hundred, hours<sup>3</sup> which is not enough for commercial applications. While the degradation mechanism in samples with stacking faults has been studied extensively,<sup>4</sup> the nature of the degradation mechanism in stacking fault free samples is rather unclear.We have shown earlier that this mechanism is also present in samples with stacking faults, where it leads to a slow homogeneous darkening of the regions between dark line defects.<sup>5</sup>

It is obvious that point defects play an important role in such a process. There have been a number of attempts to clarify the formation of point defects in ZnSe theoretically, especially by calculating the total energy and the resulting equilibrium defect concentrations with density functional theory.<sup>6-8</sup> Pöykkö et al.<sup>9</sup> showed recently that a complex formed from substitutional nitrogen and a Zn interstitial is more stable than the substitutional nitrogen acceptor and suggest that such complexes form during degradation. For two reasons this defect is, however, not likely to play a dominant role in the degradation process of a real device: On the one hand, growth of a ZnSe laser is always carried out under Se rich conditions, so that the formation of a high concentration of Zn interstitials is unlikely. On the other hand, recent degradation studies in our group showed that in the case of optical degradation by means of a focused Ar ion laser, the degradation rate is nearly identical for samples with an extremely different degree of compensation.<sup>10</sup> This fact suggests that the degradation rate is determined by a destruction of the nitrogen acceptor, and not simply by an agglomeration of pre-existing defects. This motivated us to investigate the the total energy of defect complexes that are derived from a removal of the nitrogen from the substitutional to an interstitial position. The result is a complex ( $N_i + V_{Se}$ ) involving a nitrogen interstitial together with the remaining Se vacancy. Since it is known that in GaAs the energy of native defects depends strongly on their charge,<sup>11</sup> this defect is investigated in three charge states from +1 to +3.

Our simulations employ density functional theory in the local density approximation,<sup>12</sup> first-principle pseudopotentials,<sup>13</sup> and a plane wave basis set. The Zn 3*d* states were included in the frozen core and the nonlinear core correction<sup>14</sup> was employed for this species. The plane wave cutoff energy was set to 30 Rydberg in all simulations. By simulating the elastic constants  $C_{11}$  and  $C_{12}$  for ZnSe bulk and the vibration frequency of a  $N_2$  dimer, we asserted the quality of our pseudopotentials. We used the simulation package *fhi96md* Ref. (15) for our calculations.

A cubic supercell containing 64 atoms was used to simulate one defect in the center of the cube. The positions of all atoms except those at the faces of the cube were allowed to relax until the self-consistently calculated forces amounted to less than 0.002 eV/nm. Different charge states were simulated by adjusting the number of valence electrons in the supercell but eliminating Coulomb repulsion by setting the total charge of the supercell to zero. We omitted most of the charge states featuring an odd number of electrons since we assume that configurations with partially filled orbitals play only a minor role in a real crystal due to Jahn-Teller instabilities.

The formation energies of the defects were evaluated using the standard expression

$$\Omega_D = E_D + q_D \mu_e - n_{\mathrm{Se}} \mu_{\mathrm{ZnSe}}^{\mathrm{bulk}} - (n_{\mathrm{Zn}} - n_{\mathrm{Se}}) \mu_{\mathrm{Zn}} - n_{\mathrm{N}} \mu_{\mathrm{N}},$$
(1)

where  $E_D$  and  $q_D$  are the total energy and charge of a supercell, respectively, and  $\mu_e$  is the chemical potential of the electrons relative to the valence band edge. The energies  $E_D$ were corrected for band alignment and differences in the effective potential. Since the stoichiometry is the same for all configurations under consideration, all formation energies

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FIG. 1. Formation energies of the nitrogen related defects from density functional simulations. The energies are plotted relative to that of one neutral nitrogen atom in the substitutional site. The small vertical arrows point to the energy levels of the  $(N_i + V_{Se})$  defect complex.

are plotted relative to that of the neutral substitutional nitrogen site as functions of the electron chemical potential  $\mu_e$  in Fig. 1. The most remarkable result is that in a range of about 0.4 eV above the conduction band edge (corresponding to a free hole concentration of about  $10^{14} \text{ cm}^{-3}$ ) the threefold positive complex  $(N_i + V_{Se})^{3+}$  is considerably more stable than the negatively charged acceptor  $(N_{Se})^{-}$ . As a consequence, in thermal equilibrium this defect should be formed instead of the acceptor state. The fact that hole concentrations as high as  $10^{18} \text{ cm}^{-3}$  are observed experimentally<sup>16</sup> indicates that the formation of this defect is kinetically limited.

In order to quantify the kinetic barrier for the transition of a nitrogen atom from the substitutional to the interstitial site, we performed total energy calculations where the nitrogen atom was fixed at different positions along the [111] direction between the substitutional and the interstitial sites while the neighboring Zn and Se atoms were allowed to relax. The resulting total energy as a function of the nitrogen position is shown in Fig. 2 for the singly and threefold positively charged states. The energies in this plot are computed by assuming the electronic chemical potential  $\mu_{e}$  to be located at the valence band edge. While for the singly positive state the transition towards the interstitial site is energetically unfavorable, the threefold positive state exhibits a global minimum of the formation energy there, but the formation of the  $(N_i + V_{Se})^{3+}$  defect is inhibited by an energy barrier of about 1.8 eV. This value is considerably lower than the energy of photons emitted by a ZnSe laser, so that the barrier could be easily overcome in an operating laser diode. However, in addition to the change in position, the defect has to change its charge to become stable. At least the first ionization step must involve the removal of an electron from the nitrogen acceptor into an empty state. The nearest empty state in an ideal sample without donor states is the conduction band, i.e., an energy of  $E_g$ - $E_a$  must be supplied, where  $E_g$  denotes



FIG. 2. Energy profiles for the transition of one nitrogen atom from the substitutional to the interstitial site for the singly and threefold positive charge states.

the energy gap in the doped region and  $E_a$  the acceptor binding energy. Since the doping is located in the waveguide or the cladding of the laser, this energy can be considerably *higher* than the energy of the photons produced in an operating diode, so that in a real diode the destruction of the acceptor can be a slow process.

An estimate for the energetic position of the  $(N_i + V_{Se})^{3+}$  defect in the band gap can be deduced from Fig. 1: Typically the crossing between two lines in such a plot that denote two different charge states of the same defect is supposed to correspond to the energy of the defect level.<sup>7</sup> In Fig. 1 the crossings between the threefold, twofold, and singly positive charge states of the  $(N_i + V_{Se})$  defect occur in the range between 1.65 and 1.95 eV above the conduction band edge. The accuracy that may be expected from such an evaluation can be concluded from the observation that the crossing between the neutral and the negatively ionized nitrogen acceptor is located approximately 0.2 eV below the experimental acceptor level, so that the real energy may be estimated to be of the order of 2 eV.

In the following, we compare the theoretical results to optical degradation experiments on a typical laser sample consisting of *p*- and *n*-doped ZnMgSSe cladding layers, a  $ZnS_{0.07}Se$  waveguide which is only partially doped, and a  $Cd_xZn_{1-x}Se$  quantum well.

First we look at low temperature photoluminescence. Since optical degradation is carried out at room temperature, care has to be taken to find the degraded region in the low temperature experiment. Thus  $25 \times 25 \,\mu$ m mesas were etched out of the laser layer. The area of the mesa was then optically degraded with a photon energy of 2.71 eV (about the energy gap of the waveguide layer) at a power density of 5kW/cm<sup>2</sup>. After 100 s the quantum well luminescence intensity decreased by two orders of magnitude. Cathodoluminescence images taken after degradation showed a homogeneous darkening of the entire mesa, confirming that the mesa was in fact free of stacking faults. Figure 3 shows 10 K photoluminescence spectra of an undegraded and a degraded mesa in comparison. It is evident that the intensity of a broad deep luminescence signal around 2.1 eV increases with degradation. This increase is still more pronounced under strong



FIG. 3. Low temperature photoluminescence spectra from an undegraded and a degraded mesa in comparison.

excitiation at room temperature.<sup>10</sup> Since the excitation energy is below the gap of the ZnMgSSe cladding layers, and the signal does not appear in electroluminescence (which occurs in the quantum well) this signal can be assigned to an increase of the concentration of deep centers in the *p*-doped part of the waveguide, exactly in the region where an eventual photolysis of the acceptor would occur under the given experimental conditions. The luminescence energy is in reasonable agreement with the 2 eV expected for a transition from the (N<sub>i</sub>+V<sub>Se</sub>) complex to the valence band.

This increase is accompanied by a strong decrease of the signal originating from the exciton bound to the nitrogen acceptor in the waveguide at 2.83 eV. Normalized to the waveguide emission the deep luminescence at 2.1 eV increases by the same factor as the excitonic luminescence decreases. Since the overall radiative recombination in the waveguide decreases also, this reduction can be assigned to the redistribution of the photoluminescence into a nonradiative channel and a radiative deep channel. This is a strong indication that the concentration of nitrogen acceptors decreased in exchange for the formation of deep centers.

If the  $(N_i + V_{Se})$  complex is generated in the waveguide, it must diffuse to the quantum well to produce the observed degradation of the quantum well luminescence. Since the complex is charged, an electric field should influence the diffusion. To test this assumption, we performed degradation experiments under external bias where the irradiation with a microfocused laser beam was done through a 10 nm thick semitransparent gold contact on top of the sample. The electric field was applied in reverse direction in order to avoid electroluminescence. During the degradation a reverse bias of -4 V was alternately switched on and off. Under the assumption that the entire voltage drops in the 100 nm thick intrinsic region of the device this corresponds to an external field of  $4 \times 10^7$  V/m in the quantum well region. Together with the built-in field of the diode, which can be calculated from the doping profile, the total field F in the intrinsic zone



FIG. 4. Integrated quantum well intensity as a function of the time during the application of an electric field.

is about  $6 \times 10^7$  V/m. The integrated quantum well intensity as a function of time is shown in Fig. 4. During the application of the field, the photoluminescence intensity decreases strongly, a fact that can be understood as a leaking of the carriers out of the quantum well which is strongly tilted in the electric field. It can be seen that the degradation rate during the application of the field (dashed line) is three times lower than the rate without field (solid line).

The observed reduction is a sign that the degradation is influenced by the diffusion of a positively charged particle that diffuses against the field. Such a diffusion should change its rate by  $\exp(-\Delta E/kT)$ , where  $\Delta E$  is the change in the diffusion barrier, which is determined by the electric field as  $\Delta E = q \times F \times x$ .<sup>17</sup> For a distance *x* of 0.42 nm between the minimum and the maximum in the diffusion potential, which is of the order of a bond length, exp  $(-\Delta E/kT)$  at room temperature is 0.36, a value close to the observed reduction.

As an alternative to this interpretation one could suggest that the degradation is due to a recombination enhanced reaction in the quantum well, as has been proposed for degrading diodes containing stacking faults.<sup>18</sup> In this case, the effect of the electric field would be indirect: The generation rate of nonradiative defects in the quantum well would then be proportional to the product  $n \times p$  of the electron and hole concentrations in the quantum well.<sup>18</sup> In our experiment, the photoluminescence, which is a direct measure of  $n \times p$ , drops by a factor of 30, while the degradation rate is thus clearly not proportional to  $n \times p$ , so that a recombination enhanced defect reaction can be excluded in our experiment.

In conclusion, we have shown that a threefold positive complex of a nitrogen interstitial and a Se vacancy in ZnSe is energetically favorable to the nitrogen acceptor and should result in a defect energy level about 2 eV above the valence band. The formation of such a defect is kinetically limited by a reaction barrier of 1.8 eV and the fact that the acceptor state must change its charge. Optical degradation experiments show, in fact, the generation of a deep level at 2.1 eV in the photoluminescence signal of the *p*-doped part of the waveguide, which is accompanied by a strong decrease of the luminescence from the nitrogen bound exciton in the waveguide. The degradation rate decreases under reverse

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bias, showing that degradation involves in fact the diffusion of a positively charged particle.

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