PHYSICAL REVIEW B **72**, 073205 (2005)

Electronic behavior of rare-earth dopants in AlN: A density-functional study

S. Petit* and R. Jones
School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom

M. J. Shaw and P. R. Briddon
School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, United Kingdom

B. Hourahine and T. Frauenheim
Theoretische Physik, Universität Paderborn, Warburger Strasse 100, 33098 Paderborn, Germany

(Received 20 January 2005; revised manuscript received 15 April 2005; published 11 August 2005)

Local density functional calculations are carried out on Er, Eu, and Tm rare-earth (RE) dopants in hexagonal AlN. We find that the isolated impurities prefer to substitute for Al and, in contrast with isolated RE dopants in GaAs and GaN, $\mathrm{RE_{Al}}$ defects are electrically active and introduce deep donor levels around $E_v+0.5$ eV. RE complexes with oxygen and vacancies are discussed; some of these have deep levels in the upper third of the gap and could account for a threshold excitation energy around 4 eV observed for intra-*f* transitions at 465 and 478 nm in AlN:Tm.

DOI: 10.1103/PhysRevB.72.073205 PACS number(s): 71.55.Eq, 68.55.Ln, 61.72.Ji, 71.15.Mb

I. INTRODUCTION

Rare-earth (RE) doped semiconductors exhibit sharp intra-*f* optical transitions which have long been of interest for displays. Recently, it has become apparent that in wide-band materials such as GaN and SiC, and in contrast with Si and GaAs, the luminescence is not quenched at room temperature.

As far as we are aware, all confirmed optical transitions in doped semiconductors are due to the RE defect in a trivalent oxidation state $\mathrm{RE^{3+}}$. Thus, irrespective of doping and material, the *f* shell of Er, for example, contains a fixed number of 11 electrons. The localized nature of the *f* shell ensures that the influence of the crystal field of the host on the RE is slight and confined to splitting the degenerate multiplet states of the RE and relaxing the selection rules for dipole-allowed transitions. However, it is by no means obvious that the RE defect does not seriously perturb the electronic structure of the host. The size of the RE ion, the number of valence electrons, and its electronegativity may differ from the host; thus, it may be expected that the RE could induce one or more gap levels occupied by valence electrons and not those of the *f* shell. This is particularly true for group IV semiconductors, where the RE has a different valence from the host.[1] However, we have previously shown that RE impurities, substituting Ga in two III–V semiconductors GaAs and GaN, do not introduce any gap levels.[2,3] Consequently, the RE defect is unable to bind photogenerated electrons or holes, and excitation of the *f* shell is inefficient. This suggests that complexes with other defects are required to act as exciton or carrier traps which survive room temperature and which recombine through an excitation of the *f* shell. This immediately explains why large doping concentrations of the RE ($\sim 1\%$) are required,[4] and that high-resolution photoluminescence (PL) and photoluminescent excitation spectroscopy (PLE) reveal[5] the presence of many RE optical defects with low symmetry. In GaAs, it appears that RE oxygen defects are the most important,[2] while in GaN the RE-$\mathrm{V_N}$ defect has been suggested to be a dominant trap.[3] Nevertheless, it is no means obvious *a priori* that substitutional RE defects do not bind carriers in all III–V materials, and this is less likely in wider band gap materials. Indeed, we show here that Er, Tm, and Eu dopants in hexagonal AlN, having a gap of 6.12 eV, introduce a deep donor level around 0.5 eV above the valence band. This result points to a unique property of RE dopants in AlN.

Several RE optical transitions have been reported in AlN. The 1.54 μm transition due to $\mathrm{Er^{3+}}$ has been closely studied.[6,7] PLE studies show a broad band with excitation energies above about 2 eV; superimposed on this band are sharp spikes. This indicates at least two classes of $\mathrm{Er^{3+}}$ centers. The broad band is attributed to optically excited Er-related defects possessing gap levels and the spikes to direct intra-*f* excitation.[6] PL studies of AlN:Tm reveal intense 465 and 478 nm blue lines when excited above 4.3 and 4 eV, respectively, possibly relating to two different defects.[8] RE doping of AlN and AlGaN alloys seems to result in more efficient and temperature-stable luminescence than GaN.[7,6] Moreover, the PL intensity of $\mathrm{Al_xGa_{1-x}N}$:Tb (Ref. 9) and the CL intensity of $\mathrm{Al_xGa_{1-x}N}$:Eu (Ref. 10) increase dramatically with x up to 15%. Lattice location studies demonstrate that implanted Er,[11] Yb, and Tm (Ref. 12) primarily lie at substitutional Al sites, although more recent RBS data[13] suggest some displacement away from the Al site.

We investigate here the structure and electrical properties of RE dopants in AlN. In Sec. II we describe the theoretical method that is used. In Sec. III, we apply the method to study non-RE defects, namely the $\mathrm{Si_{Al}}$, $\mathrm{O_{Al}}$, and the nitrogen vacancy $\mathrm{V_N}$ to assess the errors likely to be encountered. In Sec. IV we analyze the structure and electronic behavior of Er, Eu, and Tm defects in AlN, and conclude in Sec. V.

II. METHOD

We use a spin-polarized local density functional code, AIMPRO, with localized basis sets of Gaussian *s*, *p*, *d*, and *f* orbitals. Hartwigsen-Goedecker-Hutter[14] pseudopotentials are also used to eliminate core electrons. These pseudopotentials were developed for Gaussian basis sets. Following earlier studies,[3] the *f* shell for the RE defects is frozen and treated as part of the core. All atoms were relaxed in 72 atom supercells formed with lattice vectors 3**a**, 3**b**, and 2**c**, where **a**, **b**, and **c** are the unit vectors of bulk AlN. A Monkhorst-Pack 3^3 sampling scheme[15] was used for these supercells. We found lattice parameters of bulk AlN to be $a=3.076$ Å and $c=4.930$ Å, which are within 1% of experiment,[16] and a bulk modulus B equal to 201 GPa and consistent with experimental values of 185–212 GPa.[16] The calculated heat of formation of AlN, 3.38 eV, is found from the energies of bulk AlN, Al, and N_2 gas,[17] and close to the experimental value of 3.30 eV.[16] The band structure is similar to that found in a previous study.[18]

Let $E^q[R]$ denote the energy of a defective supercell in charge state q with structure defined by R and made up of n_i atoms of species i with chemical potential μ_i. If $R(q)$ denotes the most stable structure for the charge state q, then the defect formation energy is given by $E_f=E^q[R(q)]-\Sigma_i n_i\mu_i-q(E_F-E_v)$, where q is the excess electron charge, E_F and E_v the Fermi energy and valence band maximum, respectively. The chemical potentials for Al and N are assumed to be for stoichiometric growth conditions. The chemical potential for O is derived from the O_2 molecule, while that of the RE is found from hexagonal RE-nitride.[3] The formation energy E_f is related to the equilibrium concentration of impurities and of intrinsic defects. These concentrations are given by $gN\exp(-E_f/kT)$, where N is the density of lattice locations for the defect and g is the orientational degeneracy. Experience with other defects indicates less than perfect quantitative agreement with solubility data, but they give a guide to the expected equilibrium defect concentration.

The electrical levels of the defect are related to the electron affinities and ionization energies or differences in formation energies between charged defects. However, the theoretical band gap evaluated from $E^-[R(-)]+E^+[R(+)]-2E^0[R(0)]$ is 5.27 and 0.8 eV below the experimental gap. The Kohn-Sham energy gap derived from the band structure is even smaller at $\sim$4.2 eV. These well-known underestimates are a consequence of local density functional theory, and cause difficulties in relating the levels to the band edges. As an alternative, the levels can be found by *comparing* the defect ionization energy with that of the host or preferably another defect with similar levels.[2] In this last method, we first evaluate $E^-[R(-)]-E^0[R(0)]$ and $E^0[R(0)]-E^+[R(+)]$. The relaxation resulting in differences in the structures $R(0)$ and $R(-)$ is taken into account in these expressions. To extract the electrical levels, these energies are compared with similar ones for a marker defect with known levels; hence, the relative levels can be found. Such a method eliminates systematic errors in the calculation of the energies. In particular, Makov-Payne correction terms would largely vanish if the two defects had similar charge distributions. The method works best when the defect levels are close to those of the standard. Here, we choose Si_{Al} to be the standard defect which has donor and acceptor levels[19] found experimentally at $E_v+6.06$ eV and $E_c-0.32$ eV. This donor level is close to a PL line attributed to a Si bound exciton at 6.024 eV.[20]

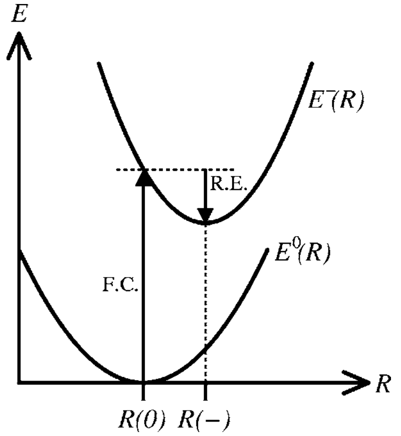

FIG. 1. Schematics of the energy configurations describing the capture of an electron by a neutral defect resulting in a vertical optical transition. The Franck-Condon absorption energy (FC) is $E^-[R(0)]-E^0[R(0)]-E_v$. This energy is numerically the sum of the acceptor level of the defect referenced to the valence band, $E^-[R(-)]-E^0[R(0)]-E_v$, together with the relaxation energy (R.E.), which is $E^-[R(0)]-E^-[R(-)]$.

If there are large lattice relaxations in one or more charge states of the defect, then optical transitions may not be directly related to the donor or acceptor levels. For example, the energy for a vertical Franck-Condon transition, taking an electron from the top of the valence band and adding it to the neutral defect, is the acceptor level referenced to the valence band, together with the relaxation energy $E^-[R(0)]-E^-[R(-)]$ (see Fig. 1). The relaxation energy may be considerable and leads to a broad PL spectrum typically seen in large band gap semiconductors. RE defects are an exception, as the internal excitation will the 4*f* shell will not lead to any appreciable structural change.

We examined the convergence in the structure and energies of some defects using a larger cell of 192 atoms. For example, in the defect Er_{Al}-$(O_N)_2$, the Er—O bond lengths along the *c* axis and in the basal plane are 2.36 and 2.10 Å, respectively, in the 72 atom cell, and 2.36 and 2.09 Å in the larger cell. Clearly, the structure of the defects is well converged. Energy differences are more sensitive to cell size. However, $E^-[R(-)]-E^0[R(0)]$ and $E^0[R(0)]-E^+[R(+)]$ are −10.397 and 9.282 eV in the 72 atom cells, and −10.288 and 9.467 eV in the 192 atom cell, respectively. Thus, these energy differences are converged to about 0.2 eV.

III. SILICON, OXYGEN, AND VACANCY-NITROGEN DEFECTS

We find both the neutral and the positively charged Si_{Al} defect to lie on-site but, in the negative charge state, the Si—N bond along **c** (Ref. 21) breaks, rather than one of the Si—N bonds lying near the basal plane.[22,23] Using the bulk ionization energy and electron affinity as a marker, the calculated Si donor and acceptor levels are $E_v+5.22$ eV and $E_c-0.53$ eV, respectively. These values are deeper than the experimental values of E_v+6.06 eV and E_c−0.32 eV mentioned above. The underestimate of the donor level is almost the same as the underestimate of the gap. The theoretical levels indicate a positive-U behavior, as the donor level at $E_v+5.22=E_c-0.9$ eV lies below the E_c−0.53 eV acceptor level. This is in conflict with the experimental donor and acceptor levels at E_c−0.06 and E_c−0.32 eV. However, the difference is relatively small. The optical (Franck-Condon) ionization energy of the negative defect, resulting in the formation of a neutral defect and an electron in the conduction band, is $E_c+E^0[R(-)]-E^-[R(-)]$. This can be written as $E_c-(E^-[R(-)]-E^0[R(-)])$ or the depth of the acceptor level, $E_c-(E^-[R(-)]-E^0[R(0)])$, together with the relaxation energy $E^0[R(-)]-E^0[R(0)]$, and is found to be 2.09 eV. Experimentally, a broad photoconductivity spectrum with a peak around 2.0 eV and a threshold around 1.5 eV is found.[19]

The formation energy of the substitutional oxygen defect, O_N, is −1.1 eV. This is 2.3 eV lower than that of interstitial oxygen, demonstrating that the interstitial species would be a minority one. The negative value of the formation energy of O_N indicates that AlN would be readily oxidized, and material with a large concentration of oxygen would be anticipated. In the neutral and positive charge states, the oxygen atom stays on-site but, in the negative charge state, one of the three Al—O_N lying in the basal plane breaks[22] rather than the bond Al—O_N along **c**.[23] O_N has a donor level at 0.21 eV deeper than Si and, using Si as the marker, is placed at E_v+5.85 eV or E_c−0.27 eV. An acceptor level is also evaluated 0.75 eV below that of Si and is then placed at E_c −1.06 eV. Like Si_{Al}, O_N is a DX center, in agreement with previous work.[22,23] The optical (Franck-Condon) ionization energy for O_N^- is found to be 2.25 eV, and close to a 2.8–2.9 eV optical absorption peak reported in AlN:O.[24] The low formation energy for O_{Al} in AlN suggests that high concentrations can be expected and larger oxygen aggregates are readily formed. A close-by pair of O_N defects is the most stable among defects with two oxygen atoms, and this possesses a donor level at E_v+4.54 eV. The depth of this level from E_c shows a possible link with an oxygen-related PL band at 2.05 eV.[25] As the acceptor level is close to that of Si, at E_c−0.53 eV, the O_N—O_N complex is not a DX center in contrast with O_N.

Other defects investigated also have deep levels. V_N^+ has C_{3v} symmetry, but a small distortion of the four Al atoms around the vacant site lowers the symmetry of the neutral and negative charge states from C_{3v} to C_{1h}. The donor and acceptor levels lie around E_v+4.64 and E_c−1.36 eV, respectively, showing that V_N is a positive-U defect[26] in contrast with an earlier report.[27] The high formation energy of 4.98 eV of the neutral defect indicates a low equilibrium concentration, although the defect could be readily formed during growth or implantation.

IV. RARE-EARTH DEFECTS

We now turn to the properties of RE defects in AlN. Different sites for the RE atom have been investigated: the RE_{Al} and RE_N substitutional sites, as well as the corresponding interstitial sites. We find RE_{Al} is the most stable in agreement with site-location studies.[11,12] With respect to solid RE nitride, the formation energies of the substitutional Er, Eu, and Tm defects lie between 1.6 and 2.2 eV. These positive energies reveal that the isolated defects are less stable than a corresponding RE-nitride precipitate. RE_{Al} defects have C_{3v} symmetry with three equal RE–N bonds of lengths 2.10, 2.08, and 2.15 Å for, respectively, Er, Tm, and Eu. The fourth RE–N bond along **c** is ~0.05 Å longer.

In contrast with GaN (Ref. 3) and GaAs (Ref. 2), we find that substitutional Er, Eu, and Tm defects in AlN are deep donors. Comparing the ionization energy of the defect with bulk AlN reveals that donor levels lie around E_v+0.5 eV. Thus, photoionization of an isolated RE center, with radiation with an energy greater than about 5.6 eV, should lead to RE-related CL, EL, and PL spectra.

We next studied RE-defect complexes starting with RE_{Al} -V_N. There are two inequivalent types of Al atoms bordering a nitrogen vacancy. Their replacement by RE leads to either a C_{3v} or C_{1h} defect. The latter is more stable by about 0.36 eV. Despite a binding energy between the isolated vacancy and the RE impurity of more than 1.3 eV, the formation energy of RE_{Al}-V_N complexes is very large (>5.2 eV) and the equilibrium concentration of this defect negligible. This is a consequence of the high formation energy of the vacancy. However, it might be introduced during growth or ion implantation. Deep single donor and acceptor levels lie around E_v+4.4 eV and E_c−1.5 eV, respectively. Second levels might also exist but have not been considered here. Capture of an electron excited from the valence band by the neutral RE_{Al}-V_N defect requires about 5.0 eV. This threshold would be reduced for the excitation of a RE_{Al}-V_N–RE_{Al} pair separated by, say, 5 Å. The reduction is 0.5 eV due to the donor level of the RE_{Al} and ~1 eV due to the electrostatic energy of the charged defects. The resulting threshold is comparable with the reported one for efficient excitation of the 478 nm blue line of Tm (4 eV).[8]

As oxygen impurities seem to be unavoidable in AlN, we have investigated the RE_{Al}-complex with one oxygen atom. In the stable C_{1h} configuration, RE_{Al} is bound to O_N lying in the basal plane with an energy of 0.9 eV and similar to the binding energy of Er_{Al} with O_{As} in GaAs (Ref. 2) but greater than found in GaN.[3] The formation energies of these RE_{Al} -O_N complexes are around −0.1 eV. In the negative charge state, the oxygen atom is displaced from its site. As the defects possess a donor level around E_v+5.7 eV and an acceptor level about E_c−0.8 eV, they are negative-U centers. Electron capture by the neutral defect requires around 6 eV but optical ionization of the DX-negative charge state requires 2.0 eV. In GaAs, complexes of Er with two oxygen atoms are found in EXAFS studies[28] and may play a part in RE luminescence.[2] Similarly in AlN, RE_{Al}-$(O_N)_2$ defects have very low formation energies around −3 eV and would impede precipitation of the RE. These defects have a deep donor level around E_v+4.3 eV and an acceptor level around E_c−0.5 eV. Electron capture by the neutral defect then requires around 5.9 eV. Such thresholds could be reduced by the involvement of close-by RE_{Al} defects as discussed above, and these defects could then be involved in the enhancement of the 465 nm blue line of Tm for excitation above 4.2 eV.[8] Several RE_{Al}-O_N—O_i defects, which possess very similar formation energies around −2 eV, exhibit acceptor levels between $E_v+1.8$ eV and $E_v+2.8$ eV. These levels are much lower than other defects. Such complexes might be involved in a broad PLE band with an onset around 2 eV detected in AlN:Er.[6]

V. CONCLUSION

In summary, we have performed density-functional calculations to investigate Er, Eu, and Tm dopants in hexagonal AlN. We find that these impurities substitute for Al atoms and, in contrast with isolated rare-earth (RE) dopants in GaAs and GaN, introduce deep donor levels ($E_v+0.5$ eV) which may be involved in the luminescence mechanism, especially during electro- and cathdoluminescence. They could, for example, account for the enhanced CL intensity observed in $Al_xGa_{1-x}N$:Eu for $x>0.15$.[10] However, substitutional RE defects are less stable than RE-N precipitates. On the contrary, complexes with two substitutional oxygen atoms are more stable than RE-N precipitate, and act to prevent precipitation. The RE_{Al}-O_N, RE_{Al}-$(O_N)_2$ and RE_{Al}-V_N defects possess acceptor and donor levels in the upper third of the gap. Excitations of these defects, especially when paired with deep donors like RE_{Al}, could account for the threshold excitation energy around 4 eV observed[8] for prominent intra-*f* transitions for AlN:Tm.

ACKNOWLEDGMENTS

This work was funded by the European Commission through the RENiBEl (Rare Earths Doped Nitrides for High Brightness Electroluminescence Emitters) Network (Contract No. HPRN-CT-2001-00297).

---

*Present address: SIFCOM (Ex LERMAT) CNRS UMR 6176, 6 Bd Maréchal Juin, 14050 Caen Cedex, France.

[1] D. Prezzi, T. A. G. Eberlein, J. S. Filhol, R. Jones, M. J. Shaw, P. R. Briddon, and S. Öberg, Phys. Rev. B **69**, 193202 (2004).

[2] J. Coutinho, R. Jones, M. J. Shaw, P. R. Briddon, and S. Öberg, Appl. Phys. Lett. **84**, 1683 (2004).

[3] J. S. Filhol, R. Jones, M. J. Shaw, and P. R. Briddon, Appl. Phys. Lett. **84**, 2841 (2004).

[4] D. S. Lee, J. Heikenfeld, A. J. Steckl, U. Hömmerich, J. T. Seo, A. Braud, and J. Zavada, Appl. Phys. Lett. **79**, 719 (2001).

[5] S. Kim, S. J. Rhee, X. Li, J. J. Coleman, and S. G. Bishop, Appl. Phys. Lett. **76**, 2403 (2000).

[6] X. Wu, U. Hömmerich, J. D. MacKenzie, C. R. Abernathy, S. J. Pearton, R. G. Wilson, R. N. Schwartz, and J. M. Zavada, J. Lumin. **72–74**, 284 (1997).

[7] F. Lu, R. Carius, A. Alam, M. Heuken, A. Rizzi, and C. Buchal, Thin Solid Films **425**, 171 (2003).

[8] U. Hömmerich, E. E. Nyein, D. S. Lee, A. J. Steckl, and J. M. Zavada, Appl. Phys. Lett. **83**, 4556 (2003).

[9] Y. Nakanishi, A. Wakahara, H. Okada, A. Yoshida, T. Ohshima, and H. Itoh, Phys. Status Solidi B **240**, 372 (2003).

[10] Y. Nakanishi, A. Wakahara, H. Okada, A. Yoshida, T. Ohshima, H. Itoh, T. Shibata, and M. Tanaka, Phys. Status Solidi C **0**, 2623 (2003).

[11] F. Lu, A. Rizzi, and R. Carius, Chin. Phys. Lett. **19**, 1844 (2002).

[12] U. Vetter, J. Zenneck, and H. Hofsäss, Appl. Phys. Lett. **83**, 2145 (2003).

[13] K. Lorenz, E. Alves, T. Monteiro, M. J. Soares, M. Peres, and P. J. M. Smulders, Nucl. Instrum. Methods Phys. Res. B (to be published).

[14] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).

[15] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[16] C. Stampfl and C. G. Van de Walle, Phys. Rev. B **59**, 5521 (1999).

[17] C. D. Latham, R. M. Nieminen, C. J. Fall, R. Jones, S. Öberg, and P. R. Briddon, Phys. Rev. B **67**, 205206 (2003).

[18] F. Litimein, B. Bouhafs, Z. Dridi, and P. Ruterana, New J. Phys. **4**, 64 (2002).

[19] R. Zeisel, M. W. Bayerl, S. T. B. Goennenwein, R. Dimitrov, O. Ambacher, M. S. Brandt, and M. Stutzmann, Phys. Rev. B **61**, R16283 (2000).

[20] K. B. Nam, M. L. Nakarmi, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **83**, 2787 (2003).

[21] P. Boguslawski and J. Bernholc, Phys. Rev. B **56**, 9496 (1997).

[22] C. H. Park and D. J. Chadi, Phys. Rev. B **55**, 12995 (1997).

[23] C. G. Van de Walle, Phys. Rev. B **57**, R2033 (1998).

[24] G. A. Slack, L. J. Schowalter, D. Morelli, and J. A. Freitas, Jr., J. Cryst. Growth **246**, 287 (2002).

[25] B. Berzina, L. Trinkler, J. Sils, and K. Atobe, Radiat. Eff. Defects Solids **157**, 1089 (2002).

[26] A. Fara, F. Bernardini, and V. Fiorentini, J. Appl. Phys. **85**, 2001 (1999).

[27] B. Szûcs, A. Gali, Z. Hajnal, P. Deák, and C. G. Van de Walle, Phys. Rev. B **68**, 085202 (2003).

[28] H. Ofuchi, T. Kubo, M. Tabuchi, K. Takahei, and Y. Takeda, Microelectron. Eng. **51**, 715 (2000).