

9

LDA + U and Hybrid Functional Calculations for Defects in ZnO, SnO₂, and TiO₂

Anderson Janotti and Chris G. Van de Walle

9.1

Introduction

Defects and impurities greatly influence the optical and electrical properties of semiconductors. Control of their concentration and their effects is essential for enabling the utilization of a semiconductor material for electronic and optoelectronic device applications [1–3]. As examples, ZnO, SnO₂, and TiO₂ are promising materials for light emitters, transparent contacts, and photocatalysis; nevertheless, their use in devices has been hindered by the inability to control their electrical and optical properties, which are strongly affected by the presence of native defects and background impurities [4–8]. ZnO has a direct band gap of 3.4 eV and shows excellent luminescence and carrier-transport properties, but the lack of p-type conductivity prevents the use of ZnO in LEDs and lasers. Better control over the n-type conductivity would also improve its prospects as a transparent electrical contact [4–6]. SnO₂ has a band gap of 3.6 eV and has been considered as an alternative to the transparent conducting oxide Sn-doped In₂O₃ (ITO) [7]. Similar to ZnO, SnO₂ would greatly benefit from an improved control over doping and defect concentrations. TiO₂ has a band gap of 3.0 eV and its expanded use in photocatalysis and photoelectrolysis depends on engineering its band gap for extending its activity to the visible spectrum, as well as on controlling carrier transport and unwanted carrier recombination [8]. These properties are again strongly influenced by impurities and native point defects.

Calculations based on the density functional theory (DFT) within the local density approximation (LDA) or its semilocal extensions, such as the generalized gradient approximation (GGA), form the standard approach for studying defects in semiconductors and insulators [10]. The problem with the DFT-LDA or GGA is the severe underestimation of band gaps [9], which impart typically large errors in the calculated formation energies and the position of transition levels [10, 11]. Empirical corrections, such as applying a scissors operator, have been proposed over the years, with conclusions varying qualitatively from one research group to another [10, 12]. Recently, the use of LDA + U [13] and the development of screened hybrid functionals [14] have led to significant progress toward a quantitative description of

defects in semiconductors. In particular, a systematic approach based on LDA + U has been proposed and applied for defects in ZnO [11]. The extra Coulomb potential U has been added to improve the description of the Zn semi-core d states in a justified physical manner. As a consequence, the interaction between the Zn d states and O p states that compose the upper valence band states, and the position of the Zn 4s states are also affected, leading to a partial correction of the band gap in ZnO [15, 16]. An extrapolation based on LDA and LDA + U results was then performed and corrected transition levels and formation energies for all native point defects have been obtained [11, 17, 18]. As a main result, it has been predicted that oxygen vacancies are not responsible for the unintentional n-type conductivity in ZnO since it is a deep donor. These results have been favorably compared to recent experimental measurements on high quality ZnO single crystals [19, 20].

The use of LDA + U for studying defects is limited to materials with semicore d states such as the d-bands in ZnO, SnO₂, or InN [11, 21, 22]. In our opinion, the use of LDA + U for states that are more appropriately described as delocalized or itinerant bands is unwarranted and may lead to spurious results. For instance, applying LDA + U to the Ti d states of TiO₂ and related materials, or to the O p states in any of these oxides is not physically justified, since these states clearly lead to extended states in the band structure. The advent of screened hybrid functionals [14] and its implementation with periodic boundary conditions has allowed overcoming this limitation [23]. Mixing a fraction of non-local Hartree–Fock exchange with the GGA exchange potential [24] and imposing a screening length leads to an improved description of the electronic properties of a wide range of materials. By adjusting the mixing parameter it is possible to accurately describe band gaps. The imposition of a screening length is essential for describing semiconductors and metals on the same footing [25], which is necessary for determining formation energies in which metallic phases enter as references for reservoir energies. Based on Heyd, Scuseria, and Ernzerhof (HSE) it has been possible to describe the different charge states of the oxygen vacancy in TiO₂ [26].

In the present work, we discuss the results for native defects in ZnO and SnO₂ using the LDA/LDA + U extrapolation and the HSE hybrid functional. We address the advantages and limitations of these two methods, and draw comparisons with experimental data where available. We also present results for oxygen vacancies in TiO₂ based on HSE, shedding light on the differences among the wide range of results and conclusions reported in the literature.

9.2

Methods

Formal definitions of formation energies and transition levels are given in the paper by Janotti and Van de Walle in this volume [27] and will not be repeated here. Instead, we focus on the uncertainties introduced by the use of DFT. The standard approach based on DFT-LDA or GGA for calculating defects in semiconductors fails to provide quantitative predictions of transition levels and formation energies. This failure can

be largely attributed to the band-gap error in semiconductors and insulators. LDA and GGA underestimate band gaps by more than 50%, and the errors are usually in the position of both valence and conduction bands. As a consequence, calculated transition levels that describe transitions between charge states of the defect carry uncertainties that can be as large as the band-gap error [10, 11]. Transition levels are defined as total energy differences between adding an electron and/or removing an electron from defect-induced gap states. This is analogous to the definition of the band gap as an energy difference between adding an electron to the conduction band and removing an electron from the valence band. Thus, transition levels suffer from the same error as band gaps in the LDA or GGA [9].

An often-overlooked problem is the error in formation energies due to the band-gap underestimation in the LDA/GGA [11]. It is often assumed that the formation energy of a neutral defect is a ground-state property that is well described within DFT-LDA or GGA. However, if the defect induces single-particle states in the band gap that are occupied with electrons, the error in the energetic position of these levels will also affect the formation energy. As the band gap is corrected by going beyond the LDA/GGA approximations, the defect-induced states shift with respect to the valence-band maximum, resulting in changes in the defect formation energy. As an extreme example, in the case of shallow acceptors, the defect-induced states are expected to shift with the valence band and the correction in the formation energy of the acceptor when the Fermi level is at the valence-band maximum is directly related to the correction in the position of the valence-band maximum on an absolute energy scale [12]. In the case of deep acceptors (or donors), the correction to the formation energies results from both the shift in the occupied single-particle states in the gap and the correction in the valence-band maximum (or conduction-band minimum) [11].

Various approaches to correct defect formation energies have recently been developed, including the LDA + U , hybrid functionals, and GW [11, 26, 28, 29]. In this paper we discuss the first two. The LDA + U has been applied to defects in materials with semicore d states such as ZnO, SnO₂, and InN [11, 21, 22]. An external Coulomb potential is added to the semicore d electrons of the metal atom, leading to a downshift of the d bands, which become more localized and narrower, and indirectly affects both the valence-band and conduction-band edges. It affects the states at the top of the valence band through the coupling with the O p states. As the ionic cores are more screened by the localization of the d states, it shifts the s states of the metal atoms, which compose the conduction-band minimum in these materials, upward in energy. These two effects lead to an opening of the band gap [15, 16]. Note that LDA + U provides only a partial correction to the band gap, through the correction of the semicore d states, since the LDA/GGA problem associated with the discontinuity of the exchange-correlation potential as a function of the number of electrons still persists [9]. Since the LDA + U improvements affect the position of the band edges, defect states which are derived from valence- and conduction-band states are also affected. Hence, one can perform calculations based on LDA and LDA + U , and inspect how defect transition levels change in response to a partial band-gap correction. Based on this information, one can extrapolate transition levels and correct formation energies, as described in Refs. [11, 18]. The extrapolation scheme

has a physics basis, since the states of the host crystal form a complete basis set for expressing the defect-related states. Therefore, by going from LDA to LDA + *U*, the defect-related single-particle states in the gap change according to their conduction-versus valence-band character.

The advent of hybrid functionals, in particular the screened form proposed by HSE represents a significant improvement in the predictive power of defect calculations in semiconductors and insulators [14]. By adding a fraction of Hartree-Fock exchange to the GGA exchange only within a fixed radius (screening length), the HSE has been successful in describing the structure and electronic properties of many materials [14, 23, 25]. However, there are now two adjustable parameters, namely the fraction of Hartree-Fock exchange and the screening length. No rigorous *ab initio* procedures exist to determine the choice of these parameters, although a screening length of 10 Å and a mixing parameter of 0.25 are frequently assumed. It is to be expected that the screening length and the amount of Hartree-Fock exchange may vary from material to material. A common approach has been to fix the screening length at 10 Å and to vary the fraction of Hartree-Fock exchange in order to reproduce the band gap of a given material. This is acceptable in the absence of rigorous prescriptions, but prudence dictates that the sensitivity of the results to the value of the mixing parameter be examined. In our own work, we always ensure that the qualitative conclusions of our studies are independent of the precise value of the mixing parameter.

In the following we will discuss the results of LDA + *U* and HSE applied to the study of selected defects in ZnO, SnO₂, TiO₂. Formation energies as a function of chemical potentials and Fermi level position are calculated as described in Refs. [10, 11].

9.2.1

ZnO

With a direct band gap of 3.4 eV, an exciton binding energy of 60 meV, and being available as large single crystals, ZnO is a promising material for light emitting diodes, laser diodes, and high-power transistors. Since optical transitions from the lowest conduction band to the next available conduction-band states involve photons with energies in the UV range, ZnO has also been considered as transparent electrode. However, the development of ZnO for these applications has been hindered by a lack of understanding and difficulties in controlling the electrical conductivity [4–6]. ZnO in bulk and thin-film forms is almost always n-type, the cause of which has been highly debated. p-Type ZnO has been reported by many authors, but reliability and reproducibility are questionable [4–6].

The unintentional n-type conductivity in ZnO has long been attributed to the presence of native point defects such as oxygen vacancies or zinc interstitials [4]. However, the identification of such defects in as-grown (as opposed to irradiated) material has been elusive, and the evidence of their relation to the observed conductivity has always been indirect, *e.g.*, based on the variation of conductivity with O₂ partial pressure in the annealing environment. In the absence of reliable

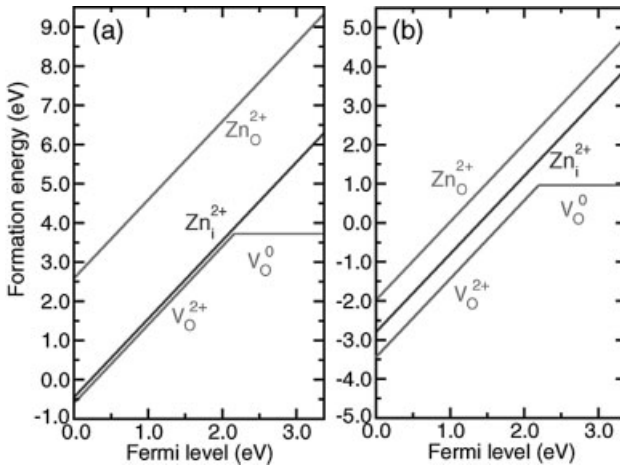


Figure 9.1 (online colour at: www.pss-b.com) Formation energy as a function of Fermi level for donor-type native point defects in ZnO: oxygen vacancies (V_O), zinc interstitials (Zn_i), and zinc antisites (Zn_O). (a) Energies according to the

LDA/LDA + U method [11]. (b) Energies according to the HSE approach, after Oba *et al.* [28]. Both plots represent Zn-rich conditions. The Fermi level is referenced to the valence-band maximum.

experiments, first-principles calculations can provide direct insight in the role played by native point defects. The conclusion is that neither O vacancies nor Zn interstitials can explain the observed n-type conductivity in ZnO [11]. Recent experiments on high-quality bulk single crystals indeed agree with the conclusions based on first-principles calculations [19, 20].

In Figure 9.1(a) we show the formation energy *versus* Fermi-level position for donor-type native point defects in ZnO, in the Zn-rich limit. These results were based on an extrapolation of LDA and LDA + U calculations as described in Refs. [11, 18]. As a main result, it has been found that the oxygen vacancy is a deep donor with a transition level ($2+/0$) at about 1 eV below the conduction band. Therefore, V_O cannot explain the observed n-type conductivity in ZnO. The zinc interstitial is a shallow donor, but it is unstable. With a migration barrier of only 0.6 eV [11], Zn interstitials are mobile even below room temperature. Zinc antisites (Zn_O) are also shallow donors, stable in the $2+$ charge state for Fermi-level positions near the conduction band. The large off-site displacement of the Zn atom indicates that Zn_O^{2+} is actually a complex of V_O^0 and Zn_i^{2+} . The high formation energy in n-type ZnO indicates that Zn_O^{2+} is unlikely to play a role in the observed unintentional conductivity in as-grown or annealed materials, unless Zn_O^{2+} is created by non-equilibrium processes such as irradiation. The transition levels related to higher charge states, Zn_O^{3+} and Zn_O^{4+} , are not shown in Figure 9.1.

Note that LDA + U applied to the Zn d states only results in a partial correction to the band gap (1.5 eV for $U = 4.7$ eV vs. 0.8 eV from LDA). Further opening of the band gap in order to recover the experimental value of 3.4 eV can in principle be obtained by applying very large values of U ($U_s = 43.5$ eV) to the Zn s states [30]. Such large values

of U lead to unphysical effects, *e.g.*, an artificially increased electron effective mass. It also explains the observed downward shift in defect transition levels of the oxygen vacancy [30]. The vacancy-related states in the gap are composed of Zn dangling bonds, which have s and p character. Contrary to the case in which U is only applied to the Zn d states, U_s therefore acts directly on the defect states themselves. If these defect states are occupied (such as in the case of the neutral charge state of an oxygen vacancy), the state will shift downwards, resulting in a lowering of the $(2 + /0)$ transition level. In our opinion it is unclear whether this effect of applying U_s reflects the correct physics.

In Figure 9.1(b) we show the results of HSE hybrid functional calculations for donor defects in ZnO [28]. These HSE calculations were performed with an adjusted mixing parameter of 37.5% in order to reproduce the experimental value of the band gap of ZnO. We note that the positions of the transition levels with respect to the band edges are in remarkable agreement with the results obtained with extrapolation of LDA and LDA + U results [Figure 9.1(a)]. However, the formation energies themselves for these donor defects are lower in the HSE approach, although the main conclusions regarding their relation to the unintentional n-type conductivity in ZnO are unchanged. That is, the oxygen vacancy is a deep donor, and zinc interstitials and zinc antisites are shallow donors but have very high formation energies under n-type conditions and are hence unlikely to be responsible for the observed n-type conductivity.

It is interesting to note that for V_O^{2+} and Zn_i^{2+} the difference in formation energies in Figures. 9.1(a) and (b) is roughly equal to twice the valence-band offset of 1.4 eV between LDA + U and HSE estimated from Ref. [15, 31]. That is, we can attribute the formation-energy difference largely to a downward shift of the valence-band maximum on an absolute energy scale. In the LDA/LDA + U approach, no further correction was assumed for the valence-band-maximum beyond the effects of U on the Zn d states. It has now become clear that, in fact, further corrections to the valence-band positions are necessary. Such corrections are included in the HSE [31].

It is important to note that the results for V_O using LDA or GGA are qualitatively different from those using the LDA/LDA + U approach and the HSE. In the LDA/GGA the $(2 + /0)$ transition level is within 0.2 eV from the conduction-band minimum [11], implying that V_O could be a source of conductivity in ZnO. In contrast, according to the LDA/LDA + U or HSE results the $(2 + /0)$ level is ~ 1 eV below the conduction-band minimum, ruling out the possibility of V_O contributing electrons to the conduction band by thermal ionization.

9.2.2

SnO₂

Tin dioxide is a wide-band-gap semiconductor of high interest for transparent electrodes [7]. It crystallizes in the rutile structure and has a band gap of 3.6 eV [32]. The ease of making it n-type, its highly dispersive conduction band (small effective mass), and the large energy difference between the conduction-band minimum and the next-higher conduction band at Γ contribute to SnO₂ supporting high carrier concentrations while still maintaining a high degree of optical transparency [7].

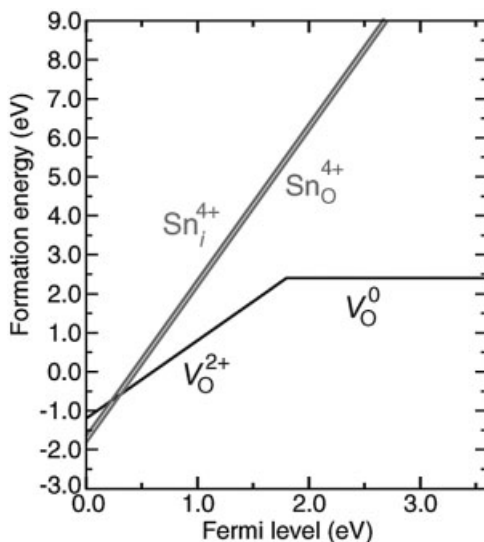


Figure 9.2 (online colour at: www.pss-b.com) Formation energy as a function of Fermi level for donor-type native defects in SnO_2 obtained by the LDA/LDA + U approach [21]. For Fermi-

level positions near the conduction band V_O is stable in the neutral charge state whereas Sn_i and Sn_O are stable in the 4 + charge state.

SnO_2 can be made n-type by adding impurities such as Sb or F, which incorporate on Sn and O sites, respectively. In addition, it has been widely believed that oxygen vacancies are also a source on n-type conductivity. In analogy to ZnO, the evidence for oxygen vacancies has been based on the correlation between electron concentrations and oxygen partial pressure in annealing experiments: increasing the oxygen partial pressure leads to lower conductivities [7]. However, the attribution of conductivity to oxygen vacancies is not supported by recent first-principles calculations [21].

In Figure 9.2 we show the calculated formation energies of donor native point defects in SnO_2 . These results were obtained from a combination of LDA and LDA + U calculations as described in Ref. [21]. Similarly to ZnO, the oxygen vacancy is a deep donor, and the Sn interstitial is unstable with very high formation energy if the Fermi level is positioned near the conduction-band minimum. The Sn antisite has even higher formation energy and is also an unlikely source of conductivity in SnO_2 . Therefore, the unintentional n-type conductivity is probably caused by the presence of impurities. For example, hydrogen in either the interstitial form or substituting for oxygen has been predicted to act as a shallow donor in SnO_2 [21, 33].

9.2.3

TiO_2

Titania is most stable in the rutile crystal structure, with a band gap of 3.1 eV [32]. The upper part of the valence band is composed of O 2p states, and the lower part of the

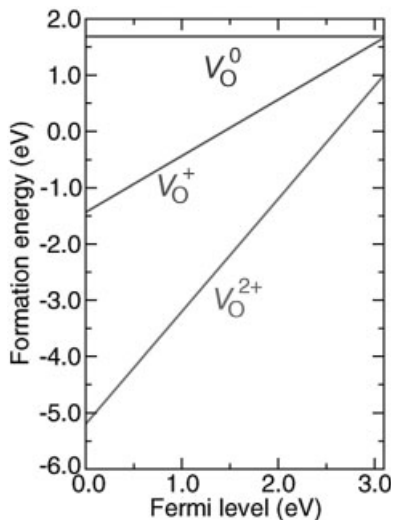


Figure 9.3 (online colour at: www.pss-b.com) Formation energy as a function of Fermi level for the oxygen vacancy (V_O) in TiO₂ in the Ti-rich limit using the HSE hybrid functional. V_O^{2+} is lower in energy than V_O^+ and V_O^0 even for the Fermi level positioned at the conduction-band minimum.

conduction band of Ti 3d states [26]. TiO₂ can be made n-type by incorporation of shallow donor impurities (e.g., Nb, F, and H), and by annealing in reducing environments [8]. Because its conductivity varies with O₂ partial pressure, it is often argued that oxygen vacancies and/or titanium interstitials are sources of conductivity in TiO₂ [8].

In Figure 9.3 we show the calculated formation energies for oxygen vacancies in TiO₂ according to the HSE hybrid functional [26]. These results were corrected for the effects of using a finite-size supercell by performing GGA calculations for V_O^{2+} and V_O^+ using supercells of 72, 216, and 576 atoms and extrapolating to the dilute limit. We conclude that oxygen vacancies are shallow donors, with V_O^+ and V_O^0 higher in energy than V_O^{2+} for any value of the Fermi level within the band gap [26].

The formation energy of V_O^{2+} in the extreme Ti-rich limit is relatively low even when the Fermi level is positioned near the conduction-band-minimum. This might lead us to conclude that oxygen vacancies are the cause of conductivity in vacuum-annealed TiO₂. However, care should be taken, since the extreme Ti-rich limit is probably not experimentally accessible since it corresponds to very low oxygen partial pressures. We also need to keep in mind that impurities that act as shallow donors, such as hydrogen, also likely contribute to the observed conductivity [34].

The use of the HSE hybrid functional is essential for describing the neutral and positive charge states of V_O in TiO₂. In the LDA and GGA the single-particle state induced by V_O^0 and V_O^+ is above the conduction-band minimum, so that these charge states cannot be stabilized [26, 35, 36], prohibiting drawing reliable conclusions about the relative energetic stability of the various charge states. In HSE, the neutral and

positive charge states can be explicitly calculated and their energy compared with that of the $2+$ charge state [26].

9.3

Summary

We have discussed the results of calculations that go beyond the LDA and GGA approximations to describe defects in oxide semiconductors. The LDA/GGA deficiency in describing band gaps leads to large errors in transition levels and formation energies, and corrections or methods that overcome the band gap problems are necessary for quantitative predictions. We argue that an extrapolation of LDA and LDA + U calculations for systems with semicore d states (such as ZnO and SnO₂) is a reliable method for predicting transition levels, while formation energies depend on how well LDA + U describes the absolute position of the valence-band maximum. The HSE hybrid functional approach is more general but also much more computationally demanding. It has been shown to be promising for describing the structural and electronic properties of defects in semiconductors and insulators. HSE can describe all possible charge states of the oxygen vacancy in TiO₂, resulting in a physical picture that is much closer to what is expected experimentally than that provided by the LDA and GGA.

Acknowledgements

We acknowledge fruitful collaborations and discussions with J. Lyons, J. Varley, A. K. Singh, P. Rinke, N. Umezawa, and G. Kresse. This work was supported by the NSF MRSEC Program under Award No. DMR05-20415, by the UCSB Solid State Lighting and Energy Center, and by the MURI program of the Army Research Office under Grant No. W911-NF-09-1-0398. It made use of the CNSI Computing Facility under NSF grant No. CHE-0321368 and Teragrid.

References

- 1 Lannoo, M. and Bourgoin, J. (1981) *Point Defects in Semiconductors I: Theoretical Aspects* (Springer-Verlag, Berlin 1983); *Point Defects in Semiconductors II: Experimental Aspects* (Springer-Verlag, Berlin 1983).
- 2 Pandelides, S.T. (ed.) (1992) *Deep Centers in Semiconductors: A State-of-the-Art Approach*, second ed. (Gordon and Breach Science, Yverdon).
- 3 Stavola, M. (ed.) (1999) *Identification of Defects in Semiconductors, Semiconductors and Semimetals*, vol. 51A, 51B (Academic, San Diego).
- 4 Look, D.C. (2001) *Mater. Sci. Eng. B*, **80**, 383.
- 5 Janotti, A. and C.G. Van de Walle (2009) *Rep. Prog. Phys.*, **72**, 126501.
- 6 McCluskey, M.D. and Jokela, S.J. (2009) *J. Appl. Phys.*, **106**, 071101.
- 7 Dawar, A.L., Jain, A.K., Jagadish, C., and Hartnagel, H.L. (1995) *Semiconducting Transparent Thin Films* (Institute of Physics, London).

- 8 Linsebigler, A.L., Lu, G., and Yates, J.T., Jr. (1995) *Chem. Rev.*, **95**, 735.
- 9 Perdew, J.P. and Levy, M. (1983) *Phys. Rev. Lett.*, **51**, 1884.
- 10 C.G. Van de Walle and Neugebauer, J. (2004) *J. Appl. Phys.*, **95**, 3851.
- 11 Janotti, A. and C.G. Van de Walle (2007) *Phys. Rev. B*, **76**, 165202.
- 12 Zhang, S.B., Wei, S.H., and Zunger, A. (2001) *Phys. Rev. B*, **63**, 075205.
- 13 Anisimov, V.I., Aryasetiawan, F., and Liechtenstein, A.I. (1997) *J. Phys.: Condens. Matter*, **9**, 767.
- 14 Heyd, J., Scuseria, G.E., and Ernzerhof, M. (2003) *J. Chem. Phys.*, **118**, 8207; *J. Chem. Phys.*, **124**, 219906 (2006).
- 15 Janotti, A., Segev, D., and Van de Walle, C.G. (2006) *Phys. Rev. B*, **74**, 045202.
- 16 Janotti, A. and Van de Walle, C.G. (2007) *Phys. Rev. B*, **75**, 121201.
- 17 Janotti, A. and Van de Walle, C.G. (2005) *Appl. Phys. Lett.*, **87**, 122102.
- 18 Janotti, A. and Van de Walle, C.G. (2006) *J. Cryst. Growth*, **287**, 58.
- 19 Vlasenko, L.S. and Watkins, G.D. (2005) *Phys. Rev. B*, **71**, 125210.
- 20 Wang, X.J., Vlasenko, L.S., Pearton, S.J., Chen, W.M., and Buyanova, I.A. (2009) *J. Phys. D, Appl. Phys.*, **42**, 175411.
- 21 Singh, A.K., Janotti, A., Scheffler, M., and Van de Walle, C.G. (2008) *Phys. Rev. Lett.*, **101**, 055502.
- 22 Janotti, A. and Van de Walle, C.G. (2008) *Appl. Phys. Lett.*, **92**, 032104.
- 23 Paier, J., Marsman, M., Hummer, K., Kresse, G., Gerber, I.C., and Ángyán, J.G., (2006) *J. Chem. Phys.*, **124**, 154709.
- 24 Perdew, J.P., Burke, K., and Ernzerhof, M. (1996) *Phys. Rev. Lett.*, **77**, 3865.
- 25 Marsman, M., Paier, J., Stroppa, A., and Kresse, G. (2008) *J. Phys.: Condens. Matter*, **20**, 064201.
- 26 Janotti, A., Varley, J.B., Rinke, P., Umezawa, N., Kresse, G., and Van de Walle, C.G. (2010) *Phys. Rev. B*, **81**, 085212.
- 27 Van de Walle C.G. , and Janotti, A. (2010) *Phys. Status Solidi B*, published online, doi: 10.1002/pssb.201046290
- 28 Oba, F., Togo, A., Tanaka, I., Paier, J., and Kresse, G. (2008) *Phys. Rev. B*, **77**, 245202.
- 29 Rinke, P., Janotti, A., Scheffler, M., and Van de Walle C.G. (2009) *Phys. Rev. Lett.*, **102**, 026402.
- 30 Paudel, T.R., and W.R.L. Lambrecht (2008) *Phys. Rev. B*, **77**, 205202.
- 31 Lyons, J.L., Janotti, A., and Van de Walle, C.G. (2009) *Phys. Rev. B*, **80**, 205113.
- 32 Dean, J.A. (ed.) 1992) *Lange's Handbook of Chemistry*, fourteenth ed. (McGraw-Hill, Inc. New York.
- 33 Varley, J.B., Janotti, A., Singh, A.K., and Van de Walle, C.G. (2009) *Phys. Rev. B*, **79**, 245206.
- 34 DeFord, J.W. and Johnson, O.W. (1983) *J. Appl. Phys.*, **54**, 889.
- 35 Sullivan, J.M. and Erwin, E.C. (2003) *Phys. Rev. B*, **67**, 144415.
- 36 S. Na-Phattalung, Smith, M.F., Kim, K., Du, M.H., Wei, S.H., Zhang, S.B., and Limpijumngong, S. (2006) *Phys. Rev. B*, **73**, 125205.