AIP Applied Physics Letters

Clustering of N impurities in ZnO

J. Furthmüller, F. Hachenberg, A. Schleife, D. Rogers, F. Hosseini Teherani et al.

Citation: Appl. Phys. Lett. **100**, 022107 (2012); doi: 10.1063/1.3675867

View online: http://dx.doi.org/10.1063/1.3675867

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v100/i2

Published by the American Institute of Physics.

APPLIED PHYSICS LETTERS **100**, 022107 (2012)

Clustering of N impurities in ZnO

J. Furthmüller,[1,a)] F. Hachenberg,[1] A. Schleife,[1] D. Rogers,[2] F. Hosseini Teherani,[2] and F. Bechstedt[1]
[1]*Institut für Festkörpertheorie und -Optik, Friedrich-Schiller-Universität and European Theoretical Spectroscopy Facility (ETSF), Max-Wien-Platz 1, 07743 Jena, Germany*
[2]*Nanovation SARL, 103b Rue de Versailles, 91400 Orsay, France*

(Received 27 October 2011; accepted 18 December 2011; published online 10 January 2012)

Ab initio density functional theory and quasiparticle calculations for the incorporation of nitrogen atoms on oxygen sites in ZnO are presented. It is demonstrated that clustering of N atoms is energetically favored over the isolated N_0 substitutional impurity. Tetrahedrons of N_0 give rise to promising quasiparticle band structures with impurity states slightly above the valence band maximum (VBM), which, however, shift to higher energies with increasing negative ionization. The lowest recharging level $\varepsilon(0/-)$ tends to a value 0.4 eV above the VBM, which is too deep for anything other than a weak *p*-doping. © *2012 American Institute of Physics*. [doi:10.1063/1.3675867]

Zinc oxide (ZnO) has been widely investigated for use in efficient short wavelength light-emitting diodes and diode lasers based on $p-n$ homojunctions.[1] In spite of these expectations, this topic remains a source of conjecture, with the possibility of reliably achieving the required levels of shallow *p*-doping still under debate.[2,3] Substitutional doping with nitrogen (N) has been the predominant experimental approach[4] because of obvious features including its trivalence and similar ionic radius to the oxygen ion O^{2-}.

Some early first-principles computational studies into the possibility of *p*-doping ZnO were focused on the concept of N incorporation in the form of N-oxygen (O) molecules.[5] However, more advanced modeling (confirmed by experiment) found that substitutional N doping on an O site (N_O) gives rise to a deep acceptor with an ionization energy, E_i, of 1.3 eV and, hence, cannot lead to a substantial hole-based conductivity[6] because the corresponding high carrier activation energy E_A prevents significant levels of thermal activation. Alternative acceptor candidates, which could have lower E_A, including Zn-P clusters, have been suggested.[7] The high E_A for N_O can be understood from the effective-mass approximation combined with a hydrogen based model. This leads to a hole binding energy of $E_A = (13.6\,\mathrm{eV}) \cdot m_h^*/(m\varepsilon^2)$, where the Rydberg constant for hydrogen is reduced by the hole mass m_h^* and the static dielectric constant ε of the ZnO host. A rough estimate with a hole mass $m_h^* \approx 0.6\,\mathrm{m}$ and an electronic $\varepsilon \approx 3.7$ (see collection in Ref. 8) gives an E_A of 0.6 eV and a hole orbit radius of 3.3 Å. This estimate indicates just how difficult it is to generate shallow, effective-mass-like, acceptors in ZnO. In order to have a substantial proportion of acceptors ionized at room temperature, therefore, alternative defect-complex acceptors are being investigated. A promising idea is co-doping or cluster-doping with more than one N and gallium (Ga) or even aluminium (Al) which was already investigated in detail in a theoretical study of Wang and Zunger.[9] Formation of clusters with a larger number of N atoms, e.g., GaN_4 or GaN_3O, turns out to be most favorable. A yet unanswered question is whether already the formation of Zn-N clusters alone, e.g., ZnN_4 might not be more favorable than single N impurities and could lower the acceptor binding energy as well.

Therefore, in this letter, the energetic and electronic properties of tetrahedral ZnN_4^{n-} complexes in different ionization states $n = 0,1,\ldots,4$ embedded in wurtzite ZnO are investigated. The study considers a cluster in which all four nearest neighbor host O atoms of a central Zn atom are substituted by N atoms (rather than a single substitution with an isolated impurity N_O). These defect complexes are modeled using supercell geometries containing 192 atoms (electronic properties) or 300 atoms (energetic and structural properties). Test calculations using different supercell sizes (72, 128, 192, 300 atoms) indicate that these supercell sizes provide a reasonable accuracy, even for ionized defects (errors of 0.1 eV or less for total-energies or eigenvalues). First-principles calculations are made based on spin-polarized density functional theory (DFT) as implemented in the Vienna *ab-initio* Simulation Package (VASP) code[10,11] using a semi-local approach of exchange and correlation (XC) within the generalized-gradient approximation (GGA) following Perdew, Burke, and Ernzerhof (PBE).[12] Wave functions and pseudopotentials are generated using the projector-augmented wave (PAW) method.[11] The plane-wave cut-off is 300 eV. Convergence tests for smaller supercells and bulk ZnO indicated that this cut-off provides sufficient accuracy (10 meV or better). Brillouin zone (BZ) integrations are replaced by summations over $3 \times 3 \times 2$ (smaller supercell) or $2 \times 2 \times 2$ (larger supercell) **k**-point meshes. The shape of the supercell and the atomic positions are relaxed until Hellmann-Feynman forces are smaller than 1 meV/Å. The volume was fixed at the (theoretical) value for ideal bulk ZnO.

Since electronic-structure calculations in DFT ignore excitation considerations, this leads to a significant underestimation of the energy gap between occupied and empty bands, i.e., to a fundamental band gap, E_g, of 0.73 eV for ZnO,[13] compared with an experimental value of 3.44 eV.[4,14] Unfortunately, converged quasiparticle (QP) calculations[15,16] are not possible for supercells with several hundreds of atoms. Such calculations are performed in an approximate manner based on Slater's transition state. This is the

---

[a)] Author to whom correspondence should be addressed. Electronic mail: juergen.furthmueller@uni-jena.de.

0003-6951/2012/100(2)/022107/3/$30.00

GGA $-\frac{1}{2}$ method.[17] GGA $-\frac{1}{2}$ yields an E_g of 3.3 eV, which is very close to the experimental one.

The formation energies $E_f(N\mathrm{N}_\mathrm{O}^q)$ of the cluster ($N = 4$) or the isolated impurity ($N = 1$) in the charge state q are obtained from

$$E_f(N\mathrm{N}_\mathrm{O}^q) = E_\mathrm{tot}(N\mathrm{N}_\mathrm{O}^q) - E_\mathrm{tot}(\mathrm{ZnO}) + N(\mu_\mathrm{O} - \mu_\mathrm{N}) + qE_\mathrm{F}, \tag{1}$$

where $E_\mathrm{tot}(N\mathrm{N}_\mathrm{O}^q)[E_\mathrm{tot}\,(\mathrm{ZnO})]$ is the total energy of the supercell containing $N\mathrm{N}_\mathrm{O}^q$ in charge state q [defect-free ZnO]. μ_O and μ_N are the chemical potentials of the O and N reservoirs, respectively. μ_O is varied between -5.93 eV (corresponding to Zn-rich growth conditions) and -3.03 eV (corresponding to an O-rich growth environment). The latter value is half of the binding energy of an O_2 molecule, $\frac{1}{2}E(O_2)$, the lower bound of μ_O is determined by $\frac{1}{2}E(O_2)$ minus the formation enthalpy ΔH_f of ZnO from the reaction of Zn metal with O_2 gas. All chemical potentials are derived from calculated values for the binding energies of Zn bulk, ZnO bulk, and O_2 molecules using DFT and the PBE GGA. μ_N is fixed at -5.28 eV (assuming N_2 dimers and, hence, a gas of N_2 molecules). This gives a variation within $-0.65\,\mathrm{eV} \leq \mu_\mathrm{O} - \mu_\mathrm{N} \leq 2.25\,\mathrm{eV}$. A value of $\mu_\mathrm{O} - \mu_\mathrm{N} = -0.65$ eV was adopted for Zn-rich conditions. The position of the Fermi level of the electrons is replaced by $E_\mathrm{F} = \varepsilon_\mathrm{VBM} + \varepsilon_\mathrm{F}$ with the valence band maximum (VBM) value $\varepsilon_\mathrm{VBM} = 1.045$ eV in conventional GGA-PBE calculations for bulk ZnO and an increase of ε_F from 0 (VBM) to E_g (conduction band minimum).

The resulting formation energies are depicted in Fig. 1 based on total energies for the 300-atom cell. For simpler comparison, the energies for a single $4\mathrm{N}_\mathrm{O}$ cluster are plotted versus those for four isolated N_O impurities. A reduced ε_F range is shown (between 0 and 1.5 eV) since this is where most crossings (ionization levels) occur. The isolated N_O defect as well as the $4\mathrm{N}_\mathrm{O}$ complex can be stable in either the neutral or single negative charge states. Higher charge states may occur for the $4\,\mathrm{N}_\mathrm{O}$ cluster. The clustering of the N impurities on O sites is energetically more favorable except in the case of the $4\mathrm{N}_\mathrm{O}^{4-}$ defect which is less stable than four isolated N_O^-. This is an important result since it indicates that N impurities should exhibit a tendency for clustering. Moreover, the possibility of the formation of even larger cluster complexes or even small zinc nitride crystallites cannot be excluded for very high N doping concentrations.

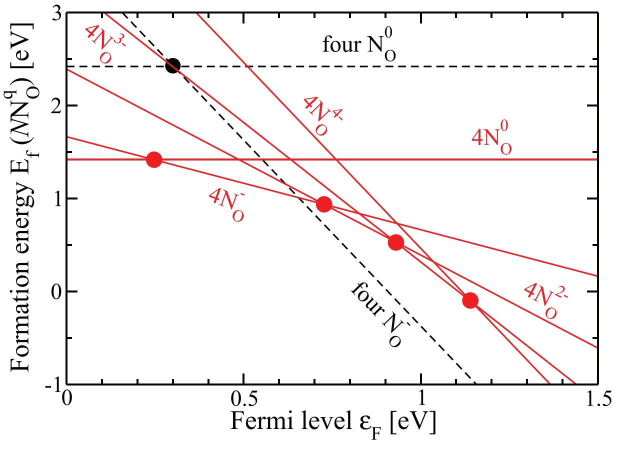

FIG. 1. (Color online) Formation energy as a function of ε_F for one $4\mathrm{N}_\mathrm{O}$ cluster (solid red lines) and four isolated N_O (dashed black lines) in ZnO under Zn-rich conditions. The reference for ε_F is the VBM described in PBE-GGA approach. The ionization levels (0/-) are indicated.

The ionization energies (thermodynamic transition levels or charge transition levels) $\varepsilon(q/q-1)$ are equal to the Fermi-level position at which the formation energies $E_f(N\mathrm{N}_\mathrm{O}^q)$ and $E_f(N\mathrm{N}_\mathrm{O}^{q-1})$ of the two charge states are the same, i.e.,

$$\varepsilon(q/q-1) = E_\mathrm{tot}(N\mathrm{N}_\mathrm{O}^{q-1}) - E_\mathrm{tot}(N\mathrm{N}_\mathrm{O}^q) - \varepsilon_\mathrm{VBM}. \tag{2}$$

Relatively low acceptor levels are found with $\varepsilon(0/-) = 0.30$ eV ($\mathrm{N}_\mathrm{O)}$ or $\varepsilon(0/-) = 0.25$ eV ($4\mathrm{N}_\mathrm{O}$) which is not too far from the value estimated using the hydrogen-based model. The higher $4\mathrm{N}_\mathrm{O}$ ionization levels amount to $\varepsilon(-,2-) = 0.73$ eV, $\varepsilon(2-,3-) = 0.93$ eV, and $\varepsilon(3-,4-) = 1.15$ eV.

One important problem for all electronic structure calculations of defects by means of Eq. (2) is the determination of the valence-band maximum ε_VBM with respect to an internal reference level, e.g., the average effective potential as in VASP code. Since the charge transition levels (Eq. (2)) basically represent excitation energies, the excitation aspect and, hence, the formation of quasiparticles in defect states have to be taken into account.[18] In a QP calculation for defect-free ZnO, starting from a Heyd, Scuseria, and Ernzerhof (HSE) hybrid functional[19] and the GW approximation for the exchange-correlation self-energy,[15] a QP correction to the VBM of about $\Delta_\mathrm{VBM} = -1.2$ eV is computed.

The main contribution to the transition levels $\varepsilon(q/q-1)$, however, arises from ground-state total-energy differences (cf. Eq. (2)). Due to the fact that the defect states are rather localized they can be interpreted as real QP values as in the Δ self-consistent field method. The reaction of the electronic system to the increase/decrease of the ionization energy is taken into account in the total-energy difference in (Eq. (2)). It may be argued that a proper QP eigenvalue should be inserted for ε_VBM instead of a DFT-GGA eigenvalue. Incorporating, for instance, a QP shift of -1.2 eV gives $\varepsilon(0/-) = 1.5$ eV for an isolated substitutional nitrogen impurity N_O which is very close to a value of 1.3 eV recently computed using a spatially non-local hybrid functional to describe XC.[6] However, GGA $-\frac{1}{2}$ band structure calculations like the ones used in this work do not support this argument since the difference of the GGA $-\frac{1}{2}$ eigenvalues, which directly provides the single-particle excitation energy $\varepsilon(0/-)$, gives a value of about 0.4 eV which is rather close to the value 0.3 eV derived from ground-state total-energy-differences (cf. Eq. (2)) inserting the DFT-GGA value for ε_VBM.

In contrast, the results derived from the total energy calculations and the use of the DFT value of ε_VBM are supported by the approximate QP band structures depicted in Fig. 2, which, for the $4\mathrm{N}_\mathrm{O}$ cluster, indicate the presence of many defect states in the gap near the VBM. In the neutral case, these levels are concentrated in an energy interval of less than 0.5 eV. With increasing negative ionization of the defect complex, however, this interval increases and the uppermost defect-complex states in the fundamental gap are shifted towards higher energies 0.9 eV (for $q = -1$), 1.45 eV (for $q = -2$), 2.25 eV (for $q = -3$), and 3.05 eV (for $q = -4$).

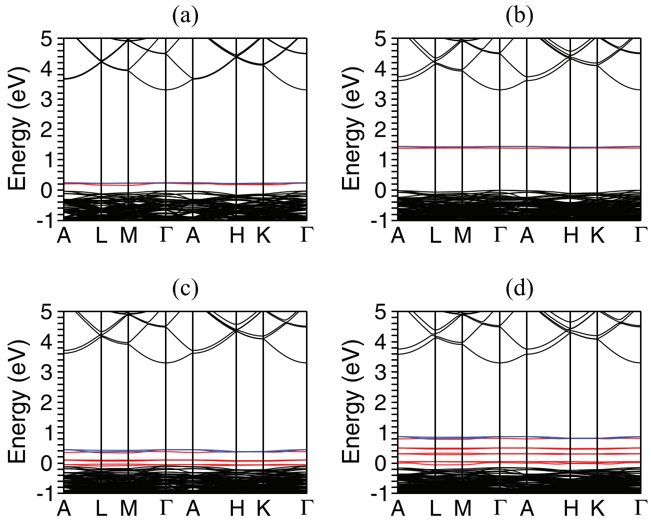

FIG. 2. (Color online) Approximate QP band structures of neutral N_O^0 (a), charged N_O^- (b), neutral $4N_O^0$ (c), and charged $4N_O^-$ (d) complexes in ZnO. The electronic bands due to the defect states appear in the lower part of the gap as isolated lines (above the dense black area). In the color online version they are indicated by red (fully occupied) and blue (topmost defect state, partially occupied or empty in the neutral case and hence indicating the position of the Fermi level) lines, whereas ZnO band states are described by black solid lines (dense black region in the black-and-white print version). The energy zero is set to the VBM for undoped ZnO.

Figure 2 and the calculated ionization levels indicate that clustering of N impurities does not significantly (charged case) or not at all (neutral case) reduce the distance of defect states from the VBM and (even for very high N concentrations) cannot, therefore, contribute to a significant increase in the proportion of *p*-type charge carriers in the valence band. Nevertheless, the clear tendency to N impurity clustering in ZnO may also explain why complexes containing more than one N impurity may form easily upon co-doping or cluster-doping with other impurities, e.g., Ga or even Al.[9,20] Our results support the viewpoint of Wang and Zunger that N doping alone cannot lead to a sufficiently shallow acceptor level due to the weaker Zn-N bonds which are energetically too far away from the strong Zn-O bonds. According to their findings, only replacement of the central Zn atom neighboring the N atoms of a local cluster with more than one N by atoms which can form much stronger bonds with N than Zn (they suggested Ga or even Al) may lead to some success. Along this line, it becomes even questionable whether not even replacement of more than one Zn atom (also outside the N cluster) by Ga or Al might even improve the situation, e.g., formation of Ga_2N_4 clusters. However, this is beyond the scope of this letter and should be a matter of future studies.

In conclusion, the incorporation of N clusters on O sites in ZnO has been studied using DFT computations within a semi-local XC description and approximate QP band structure calculations based on the $\text{GGA} - \frac{1}{2}$ method. It was found that clustering of N atoms is energetically more favorable than the formation of isolated N_O impurities. The calculated ionization levels indicate that even for the case of clustering, N incorporation promotes the formation of relatively deep acceptor states. The accompanying QP electronic structure calculations confirm this hypothesis. Indeed, although many defect states are generated close to the VBM, they are progressively shifted further into the gap with increasing negative ionization of the complex. This infers that doping with alternative N atom complexes, e.g., structurally different Zn_3N_2 clusters, would not induce defect states closer to the VBM either. Rather, we believe that the idea of co-doping or cluster-doping with Ga or even Al may be the only promising path towards successful *p*-doping of ZnO. It is hoped that these findings will stimulate further theoretical and experimental studies into possible shallow N-related acceptors in ZnO.

We are indebted to B. Meyer for several helpful discussions and the suggestion to study nitrogen clusters. The research presented here has received funding from the European Community in the Seventh Framework Programme (FP7/2007-2013) within e-i3 ETSF under Grant Agreement No. 211956.

[1] Y.-S. Choi, J.-W. Kang, D.-K. Hwang, and S.-Y. Park, IEEE Trans. Electron Devices **57**, 26 (2010).
[2] D. C. Look and B. Claflin, Phys. Status. Solidi B **241**, 624 (2004).
[3] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa *et al.*, Nature Mater. **4**, 42 (2005).
[4] U. Özgür, Y. I. Alivov, C. Liu, A. Tek, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).
[5] Y. Yan, S. B. Zhang, and S. T. Pantelides, Phys. Rev. Lett. **86**, 5723 (2001).
[6] J. L. Lyons, A. Janotti, and C. G. V. de Walle, Appl. Phys. Lett. **95**, 252105 (2009).
[7] S. Limpijumnong, L. Gordon, M. Miao, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. **97**, 072112 (2010).
[8] W. R. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall, and B. K. Meyer, Phys. Rev. B **65**, 075207 (2002).
[9] L. G. Wang and A. Zunger, Phys. Rev. Lett. **90**, 256401 (2003).
[10] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[11] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[12] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[13] A. Schleife, F. Fuchs, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **73**, 245212 (2006).
[14] C. Klingshirn, Phys. Status Solidi B **244**, 3027 (2007).
[15] F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, and G. Kresse, Phys. Rev. B **76**, 115109 (2007).
[16] B.-C. Shih, Y. Xue, P. Zhang, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **105**, 146401 (2010).
[17] L. G. Ferreira, M. Marques, and L. K. Teles, Phys. Rev. B **78**, 125116 (2008).
[18] P. Rinke, A. Janotti, M. Scheffler, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 026402 (2009).
[19] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
[20] Y. Yan, J. Li, S.-H. Wei, and M. M. Al-Jassim, Phys. Rev. Lett. **98**, 135506 (2007).