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The role of the V_{Zn}-N_O-H complex in the p-type conductivity in ZnO

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Past research efforts aiming at obtaining stable p-type ZnO have been based on complexes involving nitrogen doping. A recent experiment (J. G. Reynolds *et al.*, Appl. Phys. Lett. 102, 152114, 2013), demonstrated a significant ($\sim 10^{18} cm^{-3}$) p-type behavior in N-doped ZnO films after appropriate annealing. The p-type conductivity was attributed to a V_{Zn}-N_O-H shallow acceptor complex, formed by a Zn vacancy (V_{Zn}), N substituting O (N_O), and H interstitial (H_i). We present here a first-principles hybrid functional study of this complex compared to the one without hydrogen. Our results confirm that the V_{Zn}-N_O-H complex acts as an acceptor in ZnO. We find that H plays an important role, because it lowers the formation energy of the complex with respect to V_{Zn}-N_O, a complex known to exhibit (unstable) p-type behavior. However, this additional H atom also occupies the hole level at the origin of the shallow behavior of V_{Zn}-N_O, leaving only two states empty higher in the band gap and making the V_{Zn}-N_O-H complex a deep acceptor. Therefore, we conclude that the cause of the observed p-type conductivity in experiment is not the presence of the V_{Zn}-N_O-H complex, but probably the formation of the V_{Zn}-N_O complex during the annealing process.

1 Introduction

There are many well known n-type transparent conducting oxides (TCOs), but the lack of good p-type TCOs limits the manufacturing of active devices based on transparent conducting elements. Finding appropriate acceptor dopants for semiconductors that are transparent in the optical frequency range is therefore a very active field of research. Both single atoms and complexes of atoms have been considered as potential candidates in the past. Complexes of dopants are particularly promising, since the interaction between donor and acceptor dopants might limit compensation and lower the acceptor level formation energy, providing a more stable system compared to the corresponding isolated dopants.

N-doping has been used to make p-type ZnO by many groups[1–4], and hole concentrations of $\sim 10^{16} cm^{-3}$ have been achieved in ZnO films. It was shown theoretically that the p-type conductivity of N-doped ZnO can originate from the shallow acceptor complex V_{Zn}-N_O, which actually evolves from the double-donor state of V_O-N_{Zn}[5]. Recently, it has also been shown experimentally that a much higher hole concentration ($\sim 10^{18} cm^{-3}$) can be reached in N-doped ZnO under appropriate annealing[6]. Several characterization techniques indicate that a V_{Zn}-N_O-H defect complex is the cause of this behavior and that it acts as a shallow acceptor with an ionization energy of 130 meV. The doping process in this experiment is not straightforward. Different techniques are used and the doping process is mainly divided into three steps. First, N-doped ZnO films are annealed at low Zn partial pressure to induce the formation of V_{Zn}. Incorporation of N atoms (originating from N_2 gas, nitric oxide (NO) and nitrous oxide (N_2O)) causes the creation of a substitutional N on the Zn sublattice (N_{Zn}). In a second step, a high Zn partial pressure is used for the formation of oxygen vacancies (V_O). Finally, by further annealing the obtained complex, a V_O-N_{Zn} double donor, is converted into V_{Zn}-N_O-H, which is claimed to be the origin of the heavy p-type behavior at room temperature.

In order to shed more light on the role of the V_{Zn}-N_O-H complex on the p-type conductivity observed in ZnO, we investigate in the present paper the formation of the (charged) complex and its acceptor behavior by means of first principles calculations.

2 Computational details

We perform spin polarized density functional theory (DFT) calculations, as implemented in the Vienna ab initio simulation package[7,8]. Since the introduction of (charged) defects can involve the occupation of levels in the band gap, a correct value of the formation energy depends sensitively on the correct position of the defect levels and thus on the value of the band gap. This poses a major hurdle to standard DFT defect calculations using the LDA or GGA functionals[9]. On the other hand, the hybrid HSE06 functional[10] does not suffer from the band gap problem and has proven to be reliable to obtain realistic defect formation energies[9,11,12]. Therefore, the formation energy calculations are performed with the HSE06 functional. We use an optimized 37.5% Hartree-Fock exchange mixing in the HSE06 functional. This mixing correctly reproduces the experimental value of the band gap in ZnO[13]. Electron-ion interactions are treated using projector augmented wave potentials[14–16]. A large supercell consisting of 108 atoms is used ($3 \times 3 \times 3$ unit cells). Therefore, the concentration is equivalent to the dilute limit and defects act basically as isolated entities. The Zn

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$(4s^2 3d^{10})$, H $(1s^1)$, N $(2s^2 2p^3)$, and O $(2s^2 2p^6)$ electrons are treated as valence electrons. Wave functions are expanded with plane wave basis sets up to a cutoff energy of 400 eV, and the Brillouin zone is sampled with a k-point grid of $2 \times 2 \times 2$. Convergence of the self-consistent iterations is assumed when the total energy difference between cycles is less than 10^{-4} eV, and the atomic positions are relaxed until the magnitude of residual forces on the atoms are less than 0.05 eV/Å*. A single N atom is chosen to substitute an O atom and one of its Zn nearest neighbors is removed to have a Zn vacancy. For the H atom, an extensive number of positions around the substituted N element are considered. The formation energy is calculated for the most stable configuration of each charge state.

3 Results and discussion

3.1 Structural properties

The doped ZnO structure is shown schematically in Fig. 1. For the interstitial hydrogen H_i defect, for all charge states, the lowest formation energy is obtained when the H atom is located in between the N and the Zn vacancy atom. The formation energy for the H atom between the O and the Zn vacancy is higher by at least 0.39 eV. With the H at other interstitial positions the difference between the formation energies is larger than 2 eV. The N-H distance in the three charge states (0, +1, -1) is about 1.03 Å, which is consistent with the N-H bond length observed in experiment[6]. This indicates the formation of a bond between N and H atoms.

3.2 Formation energies calculations

The formation energy of a point defect or impurity is a key quantity, playing a central role in the determination of its thermodynamic stability and its equilibrium concentration. The formation energy of a defect or impurity D in charge state q is defined as[17,18]

$$E_f[D^q] = E_{tot}[D^q] - E_{tot}[bulk] + \sum_i n_i \mu_i + q[E_F + E_V + \Delta V].$$
(1)

$E_{tot}[D^q]$ is the total energy from a supercell calculation with one impurity D in the cell, and $E_{tot}[bulk]$ is the total energy for the equivalent perfect supercell. n_i indicates the number of atoms of type i that have been added ($n_i < 0$) or removed ($n_i > 0$) from the supercell, and μ_i are the chemical potentials of corresponding species. E_F is the Fermi level with respect to the top of the valence band, E_V. ΔV aligns the potentials in the

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* We have verified that this is sufficient for the purposes of the present work by performing the relaxation in a few cases with 0.01 eV/Å as a force criterion. We found that the changes in total energy were at most of the order of a few meV.
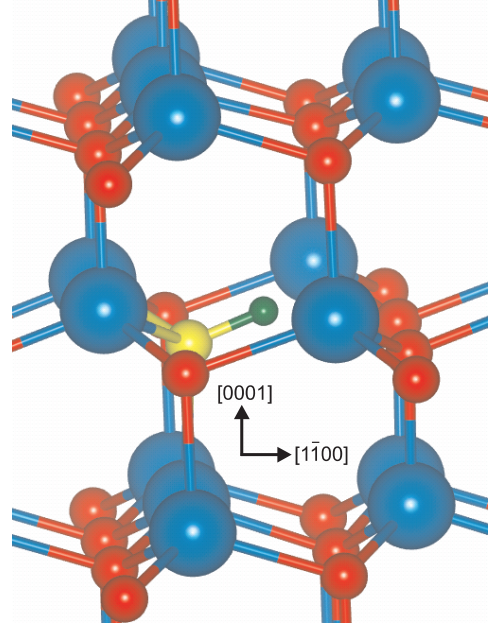

Fig. 1 The N-H neutral complex. Blue atom is Zn, red atom is O, yellow atom is N, and green atom is H.

perfect and doped supercells in a region far from the defect[19,20]. We calculate ΔV following the procedure introduced in Ref.[20].

Equation (1) indicates that the defect formation energy depends sensitively on the chemical potential of both atomic species and electrons (often referred to as the Fermi energy - E_F). This is because in forming the defect, atoms are exchanged between the host material and the chemical reservoirs. These chemical potentials depend on the experimental growth conditions, which can be either Zn-rich, O-rich, or anything in between. As mentioned in the introduction, different techniques are used in the formation process of the V_{Zn}-N_O-H complex[6]. These techniques are meant to optimize the formation of the final complex in the material. Therefore, we consider thermodynamically most favorable conditions (which lower the formation energy of the V_{Zn}-N_O-H complex in ZnO) in our calculations. The enthalpy of formation of bulk ZnO is given by

$$\Delta H_f[ZnO] = E[ZnO] - \mu_{Zn}^{Zn\,bulk} - \mu_O^{O_2\,mol}$$
(2)

where $E[ZnO]$ is the total energy of bulk ZnO, $\mu_{Zn}^{Zn\,bulk}$ is the Zn chemical from Zn bulk, and $\mu_O^{O_2\,mol}$ is the O chemical from the O$_2$ molecule. Through the thermodynamic stability condition, $E[ZnO]$ is related to the chemical potentials by $E[ZnO] = \mu_{Zn} + \mu_O$. Calculations show that the lowest formation energies for the different charge states of the complex require extreme Zn-rich conditions. These conditions correspond to the upper limit of the Zn chemical potential, given by $\mu_{Zn}^{max} = \mu_{Zn}^{Zn\,bulk}$. This upper limit for Zn leads to the lower

limit for the O chemical potential through the above stability condition for ZnO, resulting in

$$\mu_O^{\min} = \mu_O^{O_2\,\mathrm{mol}} + \Delta H_f[ZnO]. \tag{3}$$

The chemical potentials of N and H are also coupled with the O chemical potential. Indeed, the limits of the chemical potentials of N and H are determined by the enthalpies of formation of H_2O, N_2O, and NO, which can be written as

$$\Delta H_f(H_2O) + \mu_H^{H_2\,\mathrm{mol}} + \mu_O^{O_2\,\mathrm{mol}} = 2\mu_H + \mu_O$$
$$\Delta H_f(N_2O) + \mu_N^{N_2\,\mathrm{mol}} + \mu_O^{O_2\,\mathrm{mol}} = 2\mu_N + \mu_O$$
$$\Delta H_f(NO) + \mu_N^{N_2\,\mathrm{mol}} + \mu_O^{O_2\,\mathrm{mol}} = \mu_N + \mu_O. \tag{4}$$

Table 1 shows the calculated enthalpy of formations for different considered compounds, with the corresponding experimental values. In Ref. [6] annealing is done in N_2O. However, since we are interested in the possibility of forming a V_{Zn}-N_O-H complex, for N we also consider the chemical potential determined by NO. As seen in Table 1, the latter has a higher enthalpy of formation compared to N_2O and can therefore shift down the formation energy of the complex.

Table 1 The calculated and experimental enthalpy of formations for different considered structures.

Oxide	Experimental (eV)[21]	HSE06 (eV)
ΔH (ZnO)	-3.60	-3.12
ΔH (H_2O)	-2.96	-2.72
ΔH (N_2O)	0.85	0.62
ΔH (NO)	0.94	0.93

Figure 2 shows the formation energy of the complex V_{Zn}-N_O-H as a function of Fermi level E_F for the most stable charge states, 0, -1 and -2, for two different N chemical potentials and under Zn-rich (O-poor) conditions. (Under O-rich conditions the formation energies increase because of the O higher chemical potential, making the formation of the complex less likely.) The transition point, indicated with a dot in Fig. 2, between the neutral and negative charge state is about 0.77 eV above the valence band maximum (VBM). Therefore, the complex does not have the potential to act as a shallow acceptor in ZnO. To understand the reason for the deep acceptor behavior of the V_{Zn}-N_O-H complex, it is useful to compare it with the V_{Zn}-N_O complex. As mentioned in the Introduction, it was shown before that the V_{Zn}-N_O complex acts itself as a shallow acceptor in ZnO, and can be the cause of p-type conductivity of N-doped ZnO.[5] As shown in Fig. 2, we find indeed that the transition level $(0,-)$ for this complex is 0.28 eV above the VBM. A similar value is found in Ref. [22]. We further find that the $(-1,-2)$ and $(-2,-3)$ transitions occur at 1.2 eV and 3.3 eV, respectively. The origin of these transition levels can be

be understood by analyzing the electronic structure of the complex. An inspection of the occupancy of bands for spin up and down in the V_{Zn}-N_O complex, shows that there are 3 electrons more with spin up than with spin down at the Γ point. The missing electrons stem from the V_{Zn} (2) and N_O (1) defects. To characterize the three empty spin-down states we consider the projected density of states at the Γ point. Fig. 3(a) presents the density of states of pure ZnO, for reference, with the peak around 3.4 eV corresponding to the conduction band minimum. Fig. 3(b) clearly shows three empty localized spin-down states, of mainly Op and Np character (indicated by arrows in the figure)[23]. These empty states give rise to optical transition levels, but at the same time are at the origin of the (thermodynamic) transition levels in Fig. 2 (the latter are shifted with respect to the former because of relaxation of atomic positions). Turning to V_{Zn}-N_O-H, we plot its projected density of states in Fig. 3(c). It shows that adding H to V_{Zn}-N_O results in filling the lowest hole by the H electron, leaving the two higher spin-down states empty. These states reconstruct as two nearly degenerate states in the gap, indicated by arrows in Fig. 3(c). This explains the deep acceptor nature of V_{Zn}-N_O-H.

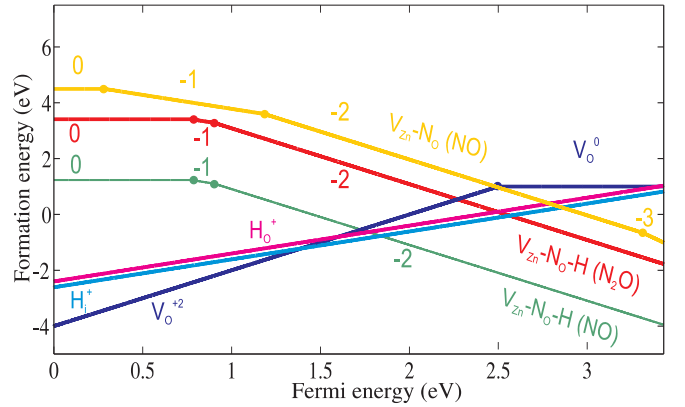**Fig. 2** Calculated formation energies as a function of Fermi energy for the complex V_{Zn}-N_O-H in ZnO in O-poor condition for two different conditions for nitrogen (NO and N_2O), together with the formation energies of some individual defects such as V_O, N_O, H_i, H_O and also the V_{Zn} − N_O complex in ZnO.

It is also necessary to consider the formation energy of the above complexes in relation to the formation energy of other defects[24]. For instance, although V_{Zn}-N_O is a relatively shallow acceptor, its formation energy is high compared to the formation energy of compensating defects like the O vacancy, H interstitial or H substitutional. These have rather low formation energies and are likely to form[25–27]. The formation energies for these defects are also shown in Fig. 2, indeed indicating that they behave as hole "killer" defects. This result is in contrast with the claim by Liu and co-workers that the V_{Zn}-N_O
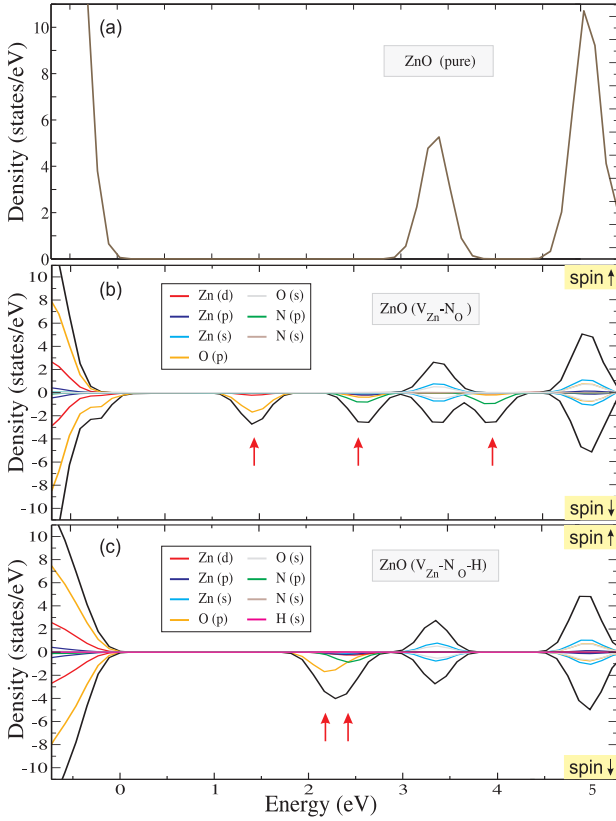
Fig. 3 Density of states at Γ point: (a) Total for the pure ZnO (b) Partial for spin up and spin down of the V_{Zn}-N_O complex (c) Partial for spin up and spin down of the V_{Zn}-N_O-H complex. VBMs are aligned at 0 eV.

complex is free from compensation due to spontaneous intrinsic donors[5]. They attributed to the V_{Zn}-N_O complex the origin of the *p*-type conductivity in the ZnO p-n junction achieved by Tsukazaki *et al.*[2] This might well be the case, but the reported *p*-type behavior is unstable, as later discussed by the same group[28]. In this perspective, it is of interest to note that the formation energy of the V_{Zn}-N_O-H complex is about 0.57 eV lower than the sum of the formation energies of the V_{Zn}-N_O complex and the H_i defect separately. This shows that adding the H to the V_{Zn}-N_O complex results in a complex with lower formation energy, tending to stabilize it and making it easier to form. This is a step in the right direction, but unfortunately at the same time the acceptor level becomes deep, as shown above.

4 Conclusions

To summarize, we have studied by first principles calculations the complex V_{Zn}-N_O-H in ZnO using DFT with the HSE06 functional. We first show that this complex will indeed tend to form, as its formation energy is lower than the sum of the formation energies of the isolated dopants. We further show that the presence of H is important, in that it results in a complex of lower formation energy compared to the H-free complex, V_{Zn}-N_O. However, having H in the system adds one more electron to the complex and fills an empty state which turns it from a shallow into a deep acceptor. Moreover, the formation energy values depend highly on the chemical potentials of the species and even for the optimal experimental conditions that we considered in our calculations, the obtained formation energies are still high with respect to the formation energy of native compensating donor defects. Thus, the stabilizing effect of the H is thus not strong enough. Our results indicate that the V_{Zn}-N_O-H complex itself cannot be the cause of the significant *p*-type behavior observed in experiment. Instead, the annealing process could lead to the formation of the shallow acceptor V_{Zn}-N_O complex, resulting in the observed conductivity. In any case, because of their high formation energy compared to that of compensating defects, it is very unlikely that these complexes can act as a lasting source of any conductivity in ZnO under standard conditions.

5 Acknowledgments

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