Probing deactivations in Nitrogen doped ZnO by vibrational signatures: A first principles study

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Abstract

Based on first principles calculations, we investigate two probable types of deactivation mechanisms that hinder current efforts of doping ZnO p-type. (i) Passivation by Hydrogen. H prefers to bind with N_O at the anti-bonding site and form N_O–H complexes with a binding energy of about 1 eV. (ii) Passivation by the formation of substitutional diatomic molecules (SDM). Carbon impurities and excess N strongly prefer to passivate N_O and form low-energy SDM on the Oxygen site, $(NC)_O$ or $(N_2)_O$, both of which are donors with several-eV binding energies. Our calculated vibrational frequencies of N_O–H complexes and SDMs are consistent with the frequencies recently observed by IR measurement on N-doped ZnO, which is not p-type.
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1. Introduction

Recent SIMs results on nitrogen-doped ZnO grown by chemical vapor deposition technique show a substantial amount of H, C and N in unwanted forms [1–4]. These impurities are likely to play important roles in compensating or passivating N acceptors, making it difficult to dope ZnO p-type. Recent IR measurements on N-doped ZnO, which is not p-type, revealed several peaks associated with H, including a peak at $3020 \, cm^{-1}$ which is consistent with the N–H stretch vibration frequency. In addition, the spectrum in the lower frequency range contains several peaks in the range of $1800–2000 \, cm^{-1}$, which are close to the frequencies of diatomic molecules.

Based on first principles calculations, we found two types of defect complexes that are likely to form. While isolated H is predicted to exclusively be a donor in ZnO [5,6], it can also passivate N_O acceptors and form an electrically inactive N_O–H complex (Fig. 1) [3]. For the second type of complex, C impurities and excess N atoms prefer to passivate N_O acceptors and form a "substitutional diatomic molecule" (SDM), which is a strongly bound NC or N_2 molecule substituted on an oxygen site $[(NC)_O$ or $(N_2)_O]$ (Fig. 2) [7,8]. The $(NC)_O$ or $(N_2)_O$ SDMs are single and double donors, respectively. These SDMs have electronic and structural properties similar to free diatomic molecules. The calculated local vibrational modes (LVM) of these defects are in good agreement with the peaks recently observed by FTIR measurement on N-doped ZnO. These results suggest that, in addition to H, one should be careful with a C impurity that can turn an existing N acceptor (N_O) into an $(NC)_O$ SDM, which is a donor. In addition, excessive N incorporation could lead to an unwanted $(N_2)_O$ SDM, which is a double donor, instead of the desired N_O.

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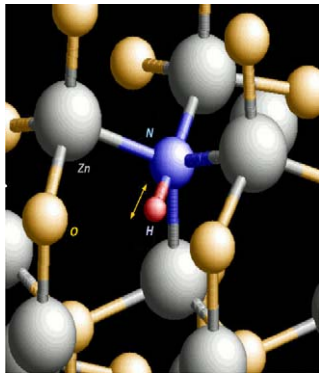*E-mail address:* sukit@sut.ac.th (S. Limpijumnong).

Fig. 1. Atomic structure of the N_O–H complex. Large sphere is Zn and small sphere is O. Impurities N and H are labeled.
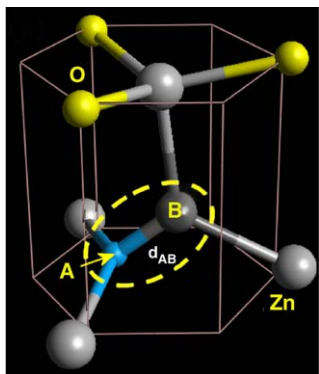

Fig. 2. Atomic structure of the substitutional diatomic molecule, where the encircled AB dimer replaces an O atom in ZnO. For $(N_2)_O$ SDM, $A = B = N$. For $(NC)_O$ SDM, $A = N$ and $B = C$. The large sphere is Zn and the small sphere is O.

2. Theoretical approach

2.1. Total-energy and formation energy calculations

Our first principles calculations are based on the pseudopotential planewave method with density-functional theory in the local-density approximation. The Vanderbilt-type ultra-soft pseudopotential [9], as implemented in the VASP codes [10], is used. The use of ultrasoft versions of the pseudopotentials allows relatively low energy cutoffs (300 eV) to be used for the planewave basis set. The Zn 3d electrons are treated as valence electrons. The calculated heat of formation for ZnO of 3.58 eV agrees with the experimental value of 3.60 eV.

To study defects, we use a supercell approach with a supercell containing at least 36 atoms. Test calculations for the $(N_2)_O$ and N_O–H complexes are performed with a larger 96-atom cell to ensure that the convergence is within ± 0.2 eV. For charged defects, a jellium background was used. Since LDA substantially underestimates the ZnO band gap, we have instead examined the electronic properties at the $2 \times 2 \times 2$ Monkhorst-Pack special k

points, which are also used for the Brillouin zone integration. The band gap at the special k points is 2.5 eV. All atoms in the cell are allowed to relax until the magnitude of the residue force on each atom is <0.05 eV/Å. The defect formation energy (ΔH_f) which has been described in detail elsewhere (for example, Refs. [11,12]), can be defined as

$$\Delta H_f = E_{tot}(D, q) - E_{tot}(0) + \Delta n_{Zn}\mu_{Zn} + \Delta n_O\mu_O + \Delta n_X\mu_X + qE_F, \tag{1}$$

where $E_{tot}(D,q)$ and $E_{tot}(0)$ are the total energies from first principles calculations of the supercell with and without the defect, D, and $X (= H, N, C)$ represents impurity elements. Quantities Δn_A and μ_A are the number of species $A (= Zn, O, H, N, C)$ removed from a defect-free cell to its respective reservoir to form the defect cell and the corresponding reservoir chemical potential. The chemical potentials μ_{Zn}, μ_O, μ_H, μ_N and μ_C have upper limits at their respective natural phases, i.e. the energies of metallic Zn, gaseous O_2, H_2, N_2 and solid-state C, which are offset to zero in the present study. To keep the ZnO thermodynamically stable, it is also required that $\mu_{Zn} + \mu_O = \mu_{ZnO,calc} = -3.58$ eV. This imposes an additional constraint that μ_O be in the range -3.58 eV $\leqslant \mu_O \leqslant 0$ and redefines $\mu_{Zn} = -3.58$ eV$-\mu_O$. Unless noted otherwise, all calculations in this paper are done in the Zn-rich limit, i.e. $\mu_{Zn} = 0$. In Eq. (1), q and E_F are the defect charge state and Fermi level with respect to the VBM.

2.2. Vibration frequency calculations

We use the so-called frozen phonon calculation approach. After the defect is relaxed to the lowest energy configuration, we dislocate the vibrating atom (for example H atom in the N–H LVM case) along the vibrating direction in a small step at a time (typical step is 0.05 Å). For each step, the calculated total energy is recorded. The potential energy curve is constructed from the plot of total energy versus the vibrating distance.

In the case of N_O–H complex, it is a good approximation to dislocate only the H atom to construct the potential energy curve. This is because H is much lighter than other atoms. However, when calculating the N–H stretch frequency the reduced mass of N and H atoms must be used. Due to its light mass, the H atom vibrates with a large amplitude, i.e. ~10% of the bond distance in the ground state and 20% in the first excited state. Therefore, it is important to include anharmonic effects in the LVM calculation [13,14].

In the case of SDMs, the situation is somewhat different. N and C have a comparable mass that is over ten times heavier than H, leading to a much smaller zero-point vibration amplitude. Since the amplitude of the vibration is small, the anharmonicity in N–C and N–N vibrations are much smaller than that of the H–N vibration. For example, including anharmonicity in the calculation only leads to a

change in the LVM of a free N_2 molecule by $< 20 \, \text{cm}^{-1}$ out of a total frequency of about $2000 \, \text{cm}^{-1}$ [14]. In calculating the LVM of SDMs, both atoms in the dimer are simultaneously dislocated with the same amplitude in opposite directions. Other atoms in the supercell are fixed.

3. Results and discussions

3.1. Passivation by hydrogen

Using the definition of the formation energy given above, we calculated the formation energies of an isolated interstitial H, a nitrogen acceptor N_O, and a N_O–H complex in ZnO. An isolated interstitial H is exclusively a donor in ZnO and always exists in the form of H^+. For an isolated H^+ location, there are four low-energy sites surrounding an O atom with the so-called $BC_{\parallel}$ site being the site with the lowest energy [6,15]. The other three sites have slightly higher energies (approximately within 0.2 eV). An isolated N_O is an acceptor. Currently the exact location of the ionization energy of N_O is still under debate [3]. Over almost the entire Fermi energy range, the isolated N_O is stable in a $(1-)$-charge state whereas an isolated interstitial H atom is always stable in a $(1+)$-charge state. The two defects, therefore, have a Coulomb attraction and have a strong tendency to form a N_O–H defect complex. The formation energy of H^+ (at $BC_{\parallel}$ site) and N_O are plotted (dashed lines) as a function of Fermi level in Fig. 3 with the sum of the two formation energies shown as dotted lines. In the same figure, we also plot the formation energy of the N_O–H complex (thick solid line). The binding energy of the N_O–H complex is 0.95 eV, i.e. the difference in energy between the dotted and solid line. For the N_O–H defect complex, the $AB_{N\perp}$ configuration (Fig. 1) has the lowest

Fig. 3. Formation energy of an interstitial H, N_O (dashed lines) and a N_O–H complex (solid line) in ZnO as a function of electron Fermi energy. The dotted line shows the sum of the formation energies of an isolated interstitial hydrogen and an isolated N_O. The Zn-rich condition, N_2 and H_2 phase precipitation limits were assumed. The energy difference between the dotted line and the solid line is the binding energy of the N_O–H complex.

formation energy. The AB_N configurations are energetically more stable than the BC by about 0.2–0.3 eV, making the likelihood of forming BC configurations negligible. The difference in formation energy between the two AB_N configurations is within the computational error bar. Both AB_N configurations have a similar N–H stretch mode frequency, with an average value of $2927 \, \text{cm}^{-1}$. The anharmonic contributions are rather large, i.e. approximately 8%. Both BC configurations also have a similar N–H stretch mode frequency, with an average value of $3319 \, \text{cm}^{-1}$, which is clearly higher than those of the AB_N configurations. The anharmonic contributions are less than half of those for the AB_N cases. The smaller anharmonic contribution in BC in comparison with AB_N agrees with the usual trend found for an isolated H in ZnO [6] as well as in the GaN system [13]. To estimate the systematic error of our calculation, we calculated the known stretch-mode frequency of a free ammonia (NH_3) molecule. We obtained the symmetric stretch LVM of $3194 \, \text{cm}^{-1}$ which is $143 \, \text{cm}^{-1}$ smaller than the known experimental value ($3337 \, \text{cm}^{-1}$). Assuming that our calculated LVM of the N–H bond in ZnO is underestimated by similar amount, our adjusted value for AB_N of $2927 + 143 = 3070 \, \text{cm}^{-1}$ is in reasonable agreement with the recently observed peak at $3020 \, \text{cm}^{-1}$ [3].

3.2. Passivation by the formation of substitutional diatomic molecules

The diatomic molecule is one of the most common forms for first row elements, namely, C, N, and O, because these small atoms tend to form strong triple bonds with each other. Recently, similar complexes, such as N_2 and NC inclusions in GaAs have been studied both theoretically and experimentally [16,17]. In the case of ZnO, the $(N_2)_O$ and $(NC)_O$ SDM are found to have bonding and anti-bonding characteristics very similar to their free molecules confirmed by the detailed investigation of the electronic wavefunctions [7,8]. Here, we will focus only on the energetic and the LVM of the complexes.

Fig. 4 shows the E_F dependence of the formation energy (ΔH_f) in the Zn-rich, N-rich, and C-rich conditions ($\mu_{Zn} = \mu_N = \mu_C = 0$) for $(CO)_O$, $(NC)_O$, $(NO)_O$, and $(N_2)_O$. Since the isolated interstitials N_i and C_i have very high formation energies, they tend to immediately bind with the closest lattice O, forming $(NO)_O$ and $(CO)_O$. However, in the presence of N_O, $(NO)_O$ and $(CO)_O$ are unstable against the formation of $(N_2)_O$ and $(NC)_O$. The binding energies are typically several eV due in part to Coulomb attraction between oppositely charged impurities and in part to the combination of two impurities into one. This can significantly reduce the formation energy because, for example, when $N_O + (NO)_O \rightarrow (N_2)_O + O_O$, one less oxygen site is disturbed by the impurities after the reaction. In the right panel of Fig. 4, the formation energy of N_O and $(NO)_O$ are shown as the dashed line and the thin solid line with the sum of the two as the dotted line. The sum is to be
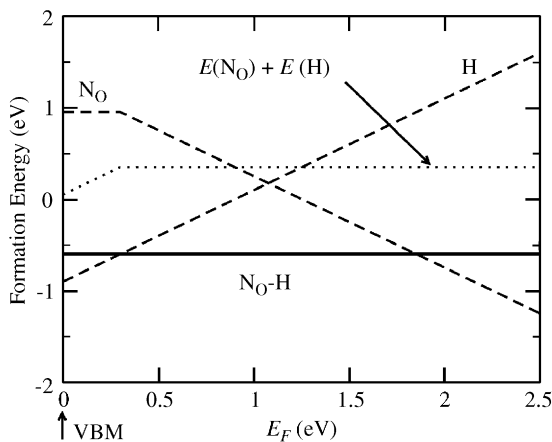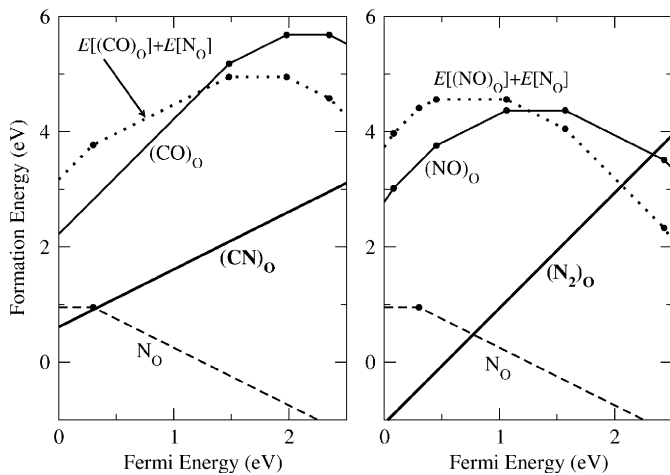
Fig. 4. Formation of (left panel) $(NC)_O$ from isolated N_O and $(CO)_O$ and (right panel) $(N_2)_O$ from N_O and $(NO)_O$. The Zn-rich condition, N_2 and diamond phase precipitation limits were assumed.

compared with the thick solid line, which is the formation energy of $(N_2)_O$ defect. We can immediately see that the binding energy, which is the difference between the dotted line and the thick solid line, depends somewhat on the Fermi energy, but has a typical value of several eV. The binding energy is of similar magnitude for the case of $(NC)_O$, as shown in the left panel. This is especially true in the case of p-type ZnO, for which the binding energies are large enough to make both $(N_2)_O$ and $(NC)_O$ lower in energy than isolated N_O. It is therefore expected that the formation of $(N_2)_O$ and $(NC)_O$ will compete with the formation of N_O acceptors. Since these SDMs are donors in p-type samples, their formation further hinders p-type doping by compensating the already lowered N_O acceptors.

The situation could be worse when one tries to increase N concentration, [N], above the equilibrium value via non-equilibrium growth methods. Effectively, this is similar to increasing the nitrogen chemical potential μ_N. Although the formation energy of N_O decreases as one raises μ_N, the formation energy of the $(N_2)_O$ complex decreases twice as fast. In thermal equilibrium, this would end up increasing the concentration of the donor $(N_2)_O$ complex instead of the acceptor N_O. However, because the formation of $(N_2)_O$ from $N_O + (NO)_O$ involves the breakup of one SDM, the diffusion of N_i, and the formation of another SDM, one might be able to adjust the growth temperature to be low enough that $(N_2)_O$ is suppressed.

The calculated frequencies for $(N_2)_O^{2+}$ and $(NC)_O^+$, which are the most stable form for these complexes in p-type ZnO, are 2108 and 1995 cm^{-1}, respectively. These frequencies fall within 200 cm^{-1} of the experimentally observed values [2]. Moreover, recent XPS experiments have found strong signals of N–N and C–N bonds with similar characteristics to those of free diatomic molecules [4]. These observations strongly suggest the existence of $(N_2)_O$ and $(NC)_O$ in these samples.

4. Conclusion

First principles total energy calculations show that H, C, and N can passivate N_O acceptors in ZnO. H can passivate N_O and form N_O–H complexes with the binding energy of approximately 1 eV. C and excess N can passivate N_O and form low energy $(NC)_O$ and $(N_2)_O$ substitutional diatomic molecules (SDM) on the oxygen site in ZnO. The calculated vibrational frequencies are in qualitative agreement with recent IR experiments. Our calculations also show that both $(NC)_O$ and $(N_2)_O$ are donors in p-type ZnO. These results should shed new light on efforts to improve the fabrication of high quality p-type ZnO by nitrogen.

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