Substitutional diatomic molecules NO, NC, CO, N$_2$, and O$_2$: Their vibrational frequencies and effects on *p* doping of ZnO

Sukit Limpijumnong[a)]
National Renewable Energy Laboratory, Golden, Colorado 80401 and School of Physics, Suranaree University of Technology and National Synchrotron Research Center, Nakhon Ratchasima 30000, Thailand

Xiaonan Li, Su-Huai Wei, and S. B. Zhang
National Renewable Energy Laboratory, Golden, Colorado 80401

First-principles calculations show that AB defects substituting on an O site in ZnO where A, B =N, O, or C are an important class of defects whose physical properties cannot be described by the usual split interstitials but rather by substitutional diatomic molecules. The molecular natures of the (AB)$_O$ defects are reflected in their vibrational frequencies which are redshifted from those of the corresponding free molecules but only by about 10%. These calculated results agree with the frequency range recently observed by IR measurement on N-doped ZnO. Moreover, most (AB)$_O$ defects are donors in *p*-type samples. The (NC)$_O$ and (N$_2$)$_O$ defects have sufficiently low energies to convert substituional N$_O$ acceptors into donors, thereby hindering the efforts of doping ZnO *p* type. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1931823]

Recent experimental investigations on chemical vapor deposition grown nitrogen-doped ZnO[1–4] revealed that these samples contain not only a large amount of H, but also C, as well as an excess of N in unwanted forms. This, combined with the difficulty of achieving *p*-type ZnO, suggests that these defects may play important roles in compensating or passivating the N acceptors. Moreover, IR absorption measurements on N-doped ZnO showed several peaks in the range of 1800–2000 cm^{-1}, which are surprisingly close to the IR frequencies of free diatomic molecules but significantly higher than the phonon frequencies of the ZnO host. Recent x-ray photoelectron spectroscopy (XPS) experiments found strong signals from the C–N and N–N bonds, which are characteristic of those in free diatomic molecules. In a recent theory work,[5] charge distribution near a substitutional N$_2$ also showed the sign of a substitutional molecule.

In this work, we investigate systematically first-row C, N, and O impurities in ZnO forming the so-called split interstitials such as (NC)$_O$ and (N$_2$)$_O$. First-principles calculations show that these complexes have electronic and structural properties, which are inconsistent with the traditional split-interstitials picture[6] but in good agreement with a substitutional diatomic molecule (SDM) picture. In particular, the calculated diatomic bond length, wave functions, and stretch frequencies closely resemble those of free molecules, in qualitative agreement with experiments. The strong tendency of forming such molecules at least in the cases of (NC)$_O$ and (N$_2$)$_O$ also causes the conversion of the N$_O$ acceptors into unwanted donors that further compensate the remaining acceptors in ZnO.

Our calculations are performed using the density functional theory with the local density approximation (LDA) and ultrasoft pseudopotentials,[7] as implemented in the VASP codes.[8] The Zn 3*d* electrons are treated as valence electrons. The cutoff energy for the plane wave basis set is 300 eV. The calculated heat of formation of 3.58 eV agrees with the ex-

perimental value of 3.60 eV. We use a supercell with 36 atoms for the defect study.[9] Results for (N$_2$)$_O$ are tested using a 96-atom cell to ensure the convergence to be ±0.2 eV. For charged defects, a jellium background was used. Since LDA severely underestimates the band gap, we have instead examined the electronic properties at the $2 \times 2 \times 2$ Monkhorst-Pack special *k* points, which are used for the Brillouin zone integration. The band gap at the special *k* points is 2.5 eV. All the atoms are relaxed by minimization of force to less than 0.05 eV/Å.

The defect formation energy is defined as[10]

$$\Delta E_f = E_{\text{tot}}(D,q) - E_{\text{tot}}(0) + \sum \Delta n_X \mu_X + qE_F,$$

where $E_{\text{tot}}(D,q)$ is the total energy of the supercell with defect D in charge state q; $E_{\text{tot}}(0)$ is the total energy of the supercell without the defect; Δn_X is the number of species X (= Zn, O, N, and C) being removed from a defect-free cell to its respective reservoir with chemical potential μ_X to form the defect cell. The upper limits for μ_{Zn}, μ_O, μ_N, and μ_C are the calculated energies of metallic Zn, gaseous O$_2$ and N$_2$, and diamond. For mathematical simplicity, however, we express here the chemical potentials relative to their respective elemental natural phases. This redefines the μ_X so that $\mu_X \leq 0$. To keep ZnO thermodynamically stable, it is also required that $\mu_{\text{Zn}} + \mu_O = \mu_{\text{ZnO}} = -3.58$ eV. E_F is the electron Fermi level with respect to the valence band maximum (VBM) averaged at the special *k* points, as described in Refs. 11 and 12.

First, let us consider split interstitial in the "traditional" picture: namely, a complex embedded in a local *sp*^{3} environment. For example, the C$_2$ split interstitial in diamond where each carbon atom is threefold coordinated.[6] One can expect that the pair form single bonds with surrounding host atoms. Alternatively, one can view the complex according to the molecular orbital theory, in which the energy levels of free molecules are *ssσ*, *ssσ**, *ppπ* (doublet) *ppσ*, *ppπ** (doublet), and *ppσ** in the order of increasing energy. When embedded in ZnO, the *ssσ*, *ssσ**, *ppπ*, and *ppσ* states are all in the
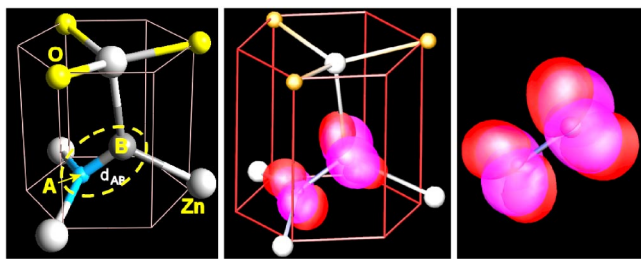
[a)]Electronic mail: sukit@sut.ac.th

FIG. 1. (Color online). (a) Atomic structure of an $(AB)_O$ defect, $A=N$, B $=C$, where the encircled AB dimer replaces an O atom. Large sphere is Zn and small sphere is O. (b) Charge density of the $pp\pi^*$ states of the $(NC)_O$ defect. The two states should be degenerate in a free dimer as shown in (c) but the degeneracy is lifted by ZnO crystal field.

TABLE I. Calculate bond length, stretch frequencies, and formation energy of the $(AB)_O$ defects at $E_F=0$, $\mu_{Zn}=\mu_N=\mu_C=0$. d_{free} is the bond length of free molecules.

Defect $(AB)_O$	Charge q	d_{A-B} (Å)	d_{free} (Å)	ω (cm^{-1})	ΔE_f (eV)
$(O_2)_O$	0	1.46	1.23	1051	5.1
$(NO)_O$	2+	1.23		1462	2.5
	1+	1.29		1357	3.1
	0	1.36		1173	4.4
	1−	1.48	1.17	967	6.1
$(CO)_O$	2+	1.16		1894	1.8
	1+	1.22		1652	3.5
	0	1.27	1.14	1373	5.7
$(N_2)_O$	2+	1.14		2108	−1.5
	1+	1.20		1852	0.4
	0	1.28	1.11	1537	2.5
$(NC)_O$	1+	1.18	1.17	1995	0.4

valence band as expected and are hence doubly occupied. If we do an electron counting for $(NC)_O$, for example, we have 5 doubly occupied states with 11 available electrons, 2 from 4 Zn neighbors in Fig. 1(a), 5 from N, and 4 from C. This leaves $(11-10)=1$ electron to occupy the higher $pp\pi^*$ (doublet) states above the VBM as shown in Fig. 2.

The calculated wave functions in Fig. 1(b) are almost copies of the $pp\pi^*$ states for the free dimer in Fig. 1(c). Most strikingly, the charge contour in Fig. 1(b) is for the entire supercell, suggesting that these doublet states are highly localized. Indeed, the dispersion in k space due to cell–cell interaction through the ZnO host is small, only 0.2 eV for these states. Thus, there is little coupling between the $pp\pi^*$ states and the surrounding Zn atoms. This shows clearly that the SDM model is a better description of the $(NC)_O$ complex. Due to the crystal field of ZnO, however, the double degenerate $pp\pi^*$ states of the free molecule is replaced by two nondegenerate, spatially orthogonal states.

The calculated bond lengths compare favorably with those of the corresponding free molecules, also. Note, however, that as a substitutional impurity, each $(AB)_O$ accepts two electrons from its Zn neighbors. Thus, we should compare neutral free molecules with SDMs of $(2+)$ charge state to keep the same orbital occupation. Table I shows that for $(N_2)_O^{2+}$, the bond length, $d_{N-N}=1.14$ Å, is only 3% longer than the triple bond of free N_2 of 1.11 Å. In contrast, the sum of single-bond atomic radii yields 1.50 Å, which is 32% longer. For $(CO)_O^{2+}$, d_{C-O} is longer than that of free CO by only 2%. For $(NO)_O^{2+}$, d_{N-O} is 5% longer. An elongation is generally expected due to the screening of the ZnO host.

To calculate stretch frequencies, we employed the approach used in Ref. 13. Our calculated results for the free molecules are in reasonable agreement with the measured values: $1485(cm^{-1})$ versus 1580.2 for O_2, 1819 versus

1904.2 for NO, 2197 versus 2358.6 for N_2, 2132 versus 2169.8 for CO, and 2052 versus 2068.6 for NC. To calculate the frequency ω for the SDMs in ZnO, in principle, one should solve the dynamic matrix with coupling to at least a few shells of neighboring atoms. However, we found that the coupling to the ZnO host is very weak, which is a reminiscence of the substitutional molecules: for example for $(N_2)_O$, the coupling results in a shift in ω less than 2 cm^{-1}. Because of this, in the calculation we keep the host atoms fixed, which allows us to include also the anharmonic effect. Table I, column 5 shows ω scaled by the ratio between experiment and theory for free molecules (given by the previous results) to reduce systematic errors in the results. The frequencies of the SDMs are reasonably close to those of the free molecules.

Because the $pp\pi^*$ molecular orbitals are antibonding orbitals, its occupation will lead to an increase in the AB bond length. We can see from Table I that adding electrons to the $pp\pi^*$ states always causes an increase in the AB bond length, resulting in weaker bonds and a reduction in ω. For example for $(N_2)_O$, the bondlength increases from 1.14 Å for $q=2+$, to 1.20 Å for $q=+$, and to 1.28 Å for $q=0$. Accordingly, the frequency decreases from 2108, to 1852, and eventually to 1537 cm^{-1}. Because of the Coulomb repulsion between electrons, energy levels in Fig. 2 will shift when occupation changes. For example, in the case of $(O_2)_O$, the removal of any electron from the gap state in Fig. 2 would lower the level to below the VBM, thus making the neutral state the only stable state.

The formation energies of the SDM impurities (ΔE_f) are tabulated in Table I. Figure 3 shows the E_F dependence of ΔE_f for $(CO)_O$, $(NC)_O$, $(NO)_O$, $(N_2)_O$, and N_O. Our results for N_O agree to within 0.2 eV with those in Refs. 5, 14, and 15. For $(N_2)_O$, our results agree to within 0.3 eV with Ref. 15. Isolated interstitial N_i and C_i are unstable against spontaneous formation of $(NO)_O$ and $(CO)_O$ so they are ignored. In the presence of N_O, $(NO)_O$, and $(CO)_O$ are also unstable against the formation of $(N_2)_O$ and $(NC)_O$. On the other hand, both $(N_2)_O$ and $(NC)_O$ have lower formation energy than that of isolated N_O in p-type ZnO. Hence, their formation will severely reduce the concentration of N_O acceptors.
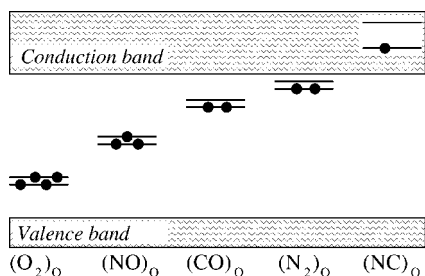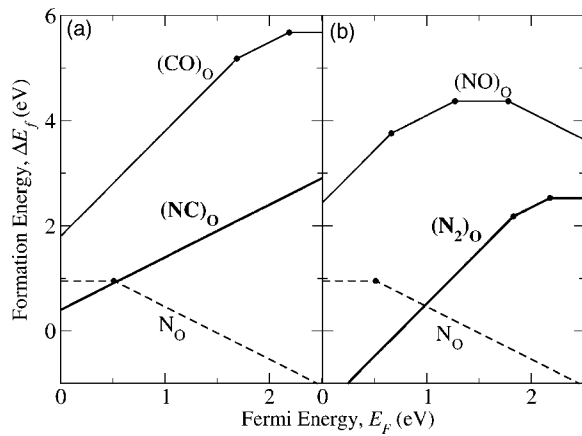

FIG. 2. Calculated energy levels of the $pp\pi^*$ states for charge neutral defects with respect to the band gap of ZnO calculated by the special k-point average. Solid dots show the electron occupations.

FIG. 3. Formation of (a) $(NC)_O$ from isolated NO and $(CO)_O$ and (b) $(N_2)_O$ from N_O and $(NO)_O$. The chemical potentials are set at $\mu_{Zn}=\mu_N=\mu_C=0$.

Also, the SDMs are donors, therefore compensating any remaining N_O acceptors.

The situation could be more severe when higher N concentration, [N], than the equilibrium value is incorporated via nonequilibrium growth methods because high [N] implies higher chemical potential μ_N. Note that the formation energy of the $(N_2)_O$ complex decreases twice as fast as that of N_O when one raises μ_N. 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 control the growth temperature to be low enough to suppress $(N_2)_O$. Also, one should be cautioned about carbon impurities in p-type ZnO. Carbon can form not only double donor C_{Zn}, by substituting Zn, but also single donor $(NC)_O$, which has low formation energy when E_F is low. Hence, beside controlling the concentration of $(N_2)_O$ by kinetic means, one also has to suppress C_{Zn} and $(NC)_O$ in order to get high enough hole concentrations.

Recent XPS experiment has 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. The calculated frequencies for $(N_2)_O^{2+}$ and $(NC)_O^{2+}$, 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 ones.[2] Also, the calculated frequency of 1894 cm^{-1} for $(CO)_O^{2+}$ is consistent

with experiment but the calculated formation energy is higher than $(NC)_O$. Although we do not have a definitive answer why $(CO)_O$ should coexist with $(NC)_O$, we realize that the probability for an interstitial C_i to find an O site should be significantly larger than to find an N_O site.

In conclusion, first principles total energy calculations show that first-row impurities, C, N, and O, can form substitutional diatomic molecules on the oxygen site in ZnO. Both the electronic and structural properties of the SDMs are consistent with those of free molecules but in contrast to those of conventional split interstitials. The calculated vibrational frequencies are in qualitative agreement with recent IR experiment. Our calculations further show that all these SDMs are donors in p-type ZnO. In particular, $(NC)_O$ and $(N_2)_O$ could have low formation energies. These results should shed new lights on how to improve the fabrication of high quality p-type ZnO by nitrogen.

[1]S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, J. Vac. Sci. Technol. B **22**, 932 (2004).
[2]B. M. Keyes, L. M. Gedvilas, X. Li, and T. J. Coutts, J. Cryst. Growth (submitted).
[3]X. Li, B. M. Keyes, S. E. Asher, S. B. Zhang, S.-H. Wei, T. J. Coutts, S. Limpijumnong, and C. G. Van de Walle, Appl. Phys. Lett. **86**, 122107 (2005).
[4]C. L. Perkins, S.-H. Lee, X. Li, S. E. Asher, and T. J. Coutts, J. Appl. Phys. **97**, 034907 (2005).
[5]E.-C. Lee, Y.-S. Kim, Y.-G. Jin, and K. J. Chang, Phys. Rev. B **64**, 085120 (2001).
[6]S. Uhlmann, T. Frauenheim, and U. Stephan, Phys. Rev. B **51**, 4541 (1995).
[7]D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[8]G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[9]S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).
[10]S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
[11]S. B. Zhang, J. Phys.: Condens. Matter **14**, R881 (2002).
[12]S.-H. Wei, Comput. Mater. Sci. **30**, 337 (2004).
[13]S. Limpijumnong, J. E. Northrup, and C. G. Van de Walle, Phys. Rev. B **68**, 075206 (2003).
[14]L. G. Wang and A. Zunger, Phys. Rev. Lett. **90**, 256401 (2003).
[15]Y. Yan, S. B. Zhang, and S. T. Pantelides, Phys. Rev. Lett. **86**, 5723 (2001).