Characterization of As-doped, *p*-type ZnO by x-ray absorption near-edge structure spectroscopy: Theory

Sukit Limpijumnong[a)]
National Synchrotron Research Center, Nakhon Ratchasima 30000, Thailand
and School of Physics, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

M. F. Smith
National Synchrotron Research Center, Nakhon Ratchasima 30000, Thailand

S. B. Zhang
National Renewable Energy Laboratory, Golden, Colorado 80401

Vaithianathan *et al.* [Appl. Phys. Lett. **88**, 112103 (2006)] measured x-ray absorption near-edge structure (XANES) of As-doped ZnO and analyzed it as evidence for As_O acceptors. However, upon carrying out first principles calculations, we found that the simulated XANES spectrum for As_O is very different from that observed. Instead, the simulated spectrum for $As_{Zn}-2V_{Zn}$ defect complex, which is predicted to be an acceptor [S. Limpijumnong *et al.*, Phys. Rev. Lett. **92**, 155504 (2004)], is far more consistent with the XANES data. The combination of our study, with the XANES of Vaithianathan *et al.* might be, until now, the strongest support for the $As_{Zn}-2V_{Zn}$ model. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2398895]

The challenge of doping *p*-type ZnO is currently attracting wide interest and serious investigation due to the potential for ZnO to be used as a wide gap material in optoelectronic devices.[1,2] Based on the basic idea that a hole can be created by substituting a group-VI oxygen anion with a group-V atom, several research groups have tried to dope ZnO using group-V elements, such as N,[3] P,[4] As,[5,6] and Sb,[7] with limited success. Among all group-V elements, only N has a comparable atomic radius to that of O. N is theoretically predicted to prefer to substitute for O and to have the lowest hole ionization energy in comparison with other group-V elements.[8] Nevertheless, the ionization energy of N_O is observed to be rather deep, i.e., $\sim 170-200$ meV (Ref. 3), resulting in a low hole concentration. Other group-V elements have an atomic radii which is much larger than O, making it difficult for them to substitute for O in ZnO. Indeed, first principles calculations show that larger group-V atoms (P, As, and Sb) prefer to substitute for Zn rather than O.[9,10] Even if they can somehow be forced to substitute for O, their ionization energies (in the order of 1000 meV) are much too large to result in any detectable holes.

In spite of such unpromising theoretical predictions, several recent experiments have shown success in doping *p*-type ZnO using large-size group-V elements $X=(P, As,$ and $Sb)$. Recently, based on first principles calculations, the puzzling *p* doping in these cases has been assigned to the $X_{Zn}-2V_{Zn}$ complexes, which have a calculated hole ionization energy of ~ 200 meV.[9,10] The formation of the $As_{Zn}-2V_{Zn}$ complex occurs because the As energetically prefers to substitute Zn (As_{Zn}) and subsequently induces and binds two Zn vacancies (V_{Zn}) to form an $As_{Zn}-2V_{Zn}$ complex, which is a moderately shallow single acceptor and likely responsible for *p*-type conductivity. Recently, there are several experiments that, in various aspects, support this complex model.[11–13] At this point, it is very beneficial to know whether the observed *p*-type conductivity is a result of the formation of $As_{Zn}-2V_{Zn}$ complex as theoretically predicted or a result of a well known, though theoretically unsupported, As_O model, so that the optimization of the doping procedure can be planned accordingly.

X-ray absorption spectroscopy (XAS) can selectively excite core electrons of a particular element (in this case, As) to unoccupied (and symmetry permitted) high energy states. XAS is generally used to obtain information about the arrangement of atoms in the locality of the absorbing atom and is made available by the high x-ray photon flux from synchrotron sources. It is a very powerful technique to directly gain information about the site and neighborhood of the As in ZnO.

XAS can be divided into two regions: the x-ray absorption near-edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS). The XANES region corresponds to the excitation of a core electron to unoccupied bound states or low lying continuum states, typically covering up to 40–50 eV above the absorption edge, whereas the EXAFS region covers the higher energy regime and extends typically to ~ 1000 eV above the edge.[14] In the EXAFS region, the highly energetic excited electron may be treated as a nearly free electron, and its interaction with surrounding atoms included perturbatively. Information about the arrangement of atoms is obtained by analyzing possible scattering processes of the excited electron from nearby ions. This (multiple) scattering theory is rather well developed and can be conveniently used to analyze and interpret EXAFS spectra and thus determine the local atomic arrangement. This fact makes EXAFS the preferred, and more generally used, probe of local structure. However, EXAFS requires a much higher concentration of absorbing atoms than XANES. In many cases of interest, especially those involving samples with dilute impurities like the case at hand, only XANES data can generally be obtained.

In the XANES region, core electrons are promoted into symmetry-allowed unoccupied bound states or low lying continuum states, which are unoccupied defect states and conduction band states in semiconductors. While these states

a)Electronic mail: sukit@sut.ac.th
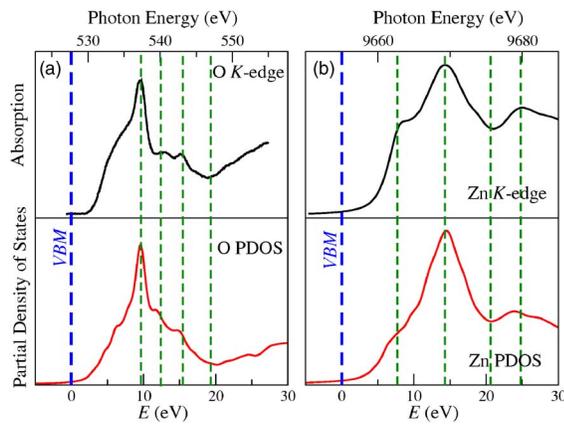
FIG. 1. (Color online) (a) (Top) the O K-edge XANES spectrum of bulk ZnO taken from Ref. 1. (Bottom) our calculated O-site and angular-momentum ($l=1$) projected PDOSs of bulk ZnO. (b) (Top) the Zn K-edge XANES spectrum of bulk ZnO taken from Ref. 18. (Bottom) calculated Zn-site and angular-momentum ($l=1$) projected PDOS. The PDOS are broadened by a Lorentzian [full width at half maximum (FWHM)=1.0 +0.05($E-E_F$) eV for O PDOS and FWHM=1.0+0.1($E-E_F$) eV for Zn PDOS] to account for the lifetime broadening of both initial and final states.

are sensitive to the arrangement of atoms around the absorbing atom (so that photon absorption involving these states relates sensitively on detailed local structure), deciphering out the atomic arrangement from XANES is not trivial. To our knowledge, there is no direct way to convert XANES into atomic arrangement. One must compare the observed signal with simulations based on various models of atomic configuration and seek the best match.

For a given atomic configuration, the XANES spectrum can be simulated from the electronic band structures, calculated up to a few tens of eV above the Fermi level E_F. The x-ray absorbance $\mu(\omega)$ is given by Fermi's golden rule as

$$\mu \propto \sum_f |\langle f|\mathsf{D}|i\rangle|^2 \delta(E_i - E_f + \omega), \qquad (1)$$

where $|i\rangle$, $|f\rangle$, E_i, and E_f are the initial and final states and their energies, respectively, ω and D are the photon frequency and dipole operator. For K-edge XANES, the initial state of the photoelectron is 1s, i.e., $|i\rangle=|1s\rangle$, so the dipole-allowed final states have the symmetry of atomic p states ($l=1$). Also, since the initial state is localized at the absorbing atom, only the final state wave function in the vicinity of the absorber is relevant. It thus turns out that the angular-momentum and site projected partial densities of empty states (PDOSs), with some broadening, resemble the XANES absorption spectra,[15] and has been used frequently to compare with experimental data.[16] For simplicity, we calculate the density of final states using the ground state electron occupation.

We find that partial densities of states generated from our first principles calculations bear a resemblance to XANES data. For example, our calculated PDOSs projected on the O and Zn atoms [Figs. 1(a) and 1(b), respectively] in bulk ZnO are in good qualitative agreement with the O K-edge (Ref. 17) and Zn K-edge XANES spectra.[18] In the figures, dominant corresponding features in the XANES spectra and PDOS are paired by thin dashed lines. The fact that the PDOS of both host atoms agrees well with the XANES data gives us strong confidence that this theoretical approach is reliable over a wide range of photon energy. Hence, the local
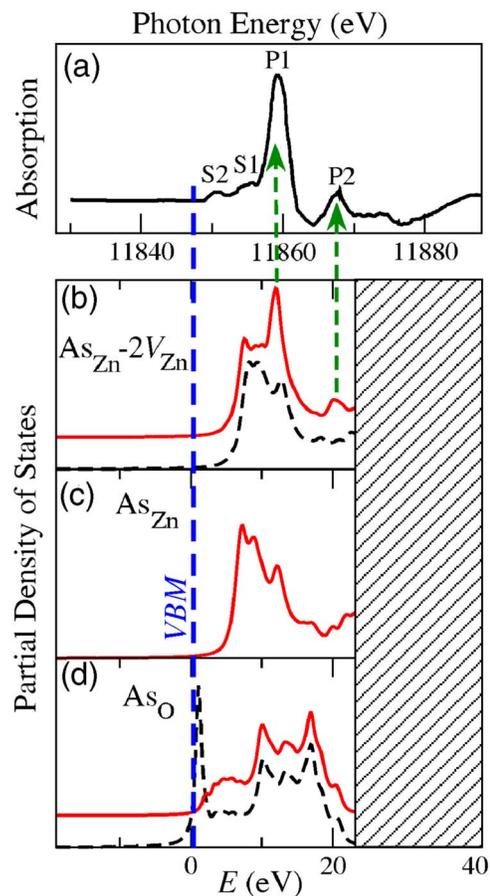
FIG. 2. (Color online) (a) As K-edge XANES spectrum of p-type ZnO:As taken from Ref. 1. [(b)–(d)] Calculated As-site and angular-momentum ($l=1$) projected PDOSs for $As_{Zn}-2V_{Zn}$, As_{Zn}, and As_O, respectively. For As_{Zn}, only PDOS for (3+)-charge state is shown. For $As_{Zn}-2V_{Zn}$ and As_O, PDOS for both neutral and (1−)-charge states are shown using dashed and solid curves, respectively (when plotted together, solid curves are offset from the dashed curves for clarity). All PDOSs are broadened by a Lorentzian with FWHM=1 eV.

structure of an As defect can be equally well determined by comparing the As PDOS with the As K-edge XANES spectra.

Figure 2(a) shows the As K-edge XANES measured from As-doped p-type ZnO by Vaithianathan et al.[17] In their letter, they interpreted their XANES results in favor of an As substituting an O (As_O) and concluded that As_O is the acceptor responsible for the observed p-type conductivity. Here, we will show, based on first principles calculations, that the XANES result in Ref. 17 is actually far more consistent with $As_{Zn}-2V_{Zn}$ complex and quite clearly inconsistent with As_O.

We have previously calculated As defects in ZnO (Ref. 9) using first principles methods based on a supercell approach (with cell size up to 96 atoms). Here, to compare with the As K-edge XANES spectrum, we use converged electron wave functions to calculate, for each defect configuration, the site and angular-momentum projected PDOS for the As atom (with a radius=1.4 Å and an angular momentum $l=1$). Sufficient unoccupied states (approximately 400 bands) are included in the calculations to generate the PDOS to ~25 eV above the valence band maximum (VBM).

The calculated PDOSs for As_{Zn} and As_O are shown in Fig. 2 along with the XANES spectrum taken from Ref. 17. We align the onset of energy-dependent absorption in the XANES with the VBM of the calculated PDOS. Under

p-type conditions (i.e., when the Fermi energy is located near the VBM), the only relevant charge state for As_{Zn} (which is a donor) is 3+ whereas the relevant charge states for $As_{Zn}-2V_{Zn}$ and As_O are neutral and $(1-)$-charge states. The PDOS for As_O in both charge states are almost identical except that a prominent sharp peak at 1 eV above VBM in the PDOS for the neutral charge state is absent in the $(1-)$-charge state. This peak is a deep localized As_O acceptor level which becomes occupied in the $(1-)$-charge state. The PDOSs for $As_{Zn}-2V_{Zn}$ in neutral and $(1-)$-charge states are, however, notably different. The PDOS for neutral $As_{Zn}-2V_{Zn}$ [dashed curve in Fig. 2(b)] is nearly identical to that for As_{Zn}^{3+} [Fig. 2(c)] but clearly differs from that for $(As_{Zn}-2V_{Zn})^{1-}$. The ratio between the concentration of $As_{Zn}-2V_{Zn}$ (or As_O) defects in $(1-)$-charge states (active acceptors) to the concentration of the same defects in neutral charge states (inactive acceptors) depends on the ionization energy and the Fermi energy of the sample. Since the samples of this type are highly compensated and generally show only weak p characteristics, it is likely that majority of the $As_{Zn}-2V_{Zn}$ are in the $(1-)$-charge state, i.e., either compensated by donors or being active. On the other hand, if As_O is formed (calculations show that As_O is energetically unfavorable), they will be mainly in the neutral charge state in p-type ZnO because calculations show that As_O is a very deep acceptor.[9]

We see from Fig. 2 that the PDOS of $As_{Zn}-2V_{Zn}$ in the $(1-)$-charge state is far more consistent with the measured XANES than that of As_O. Indeed, whereas there appears to be little correspondence between features of the As_O PDOS and the XANES data, the $As_{Zn}-2V_{Zn}$ PDOS correctly accounts for several qualitative features in the measured spectrum. First, the main XANES peak (P1) at 11 859 eV is approximately 11 eV above the onset of absorption. The corresponding peak of $As_{Zn}-2V_{Zn}$ is about 12 eV above the VBM. Second, P1 is followed by a sharp drop, and then a slow increase to a much smaller second peak (P2) at around 11 868 eV, with $E(P2)-E(P1) \approx 9$ eV. An identical feature is observed in the PDOS of $As_{Zn}-2V_{Zn}$ with a peak separation ≈ 8 eV. Third, there is a shoulder peak (S1) at about 3 eV below P1, which is also consistent with the shoulder in the PDOS of $As_{Zn}-2V_{Zn}$. The origin of the S1 can be traced back to isolated As_{Zn}, as Fig. 2(c) shows the main feature in the PDOS of As_{Zn} is in this energy range. The dominant PDOS peak for neutral charge As_O is only 1 eV above the VBM (and is thus inside the ZnO band gap), with other peaks being relatively insignificant. In Fig. 2(a) a small shoulder (S2) at 2 eV above the onset of absorption has been observed, which has no correspondence in the $As_{Zn}-2V_{Zn}$ PDOS. This S2 feature could originate from As_O and thus give evidence that some As_O defects are present in the sample. However, the small height of S2 relative to the other features in the data would suggest that the concentration of As_O is much less than that of $As_{Zn}-2V_{Zn}$. To summarize, in contradiction to the assignment in Ref. 17, first principles results support the assignment of the measured XANES spectrum to the $As_{Zn}-2V_{Zn}$ complex.

Note that Vaithianathan *et al.*[17] interpreted their results in favor of As_O based on an argument about the As oxidation states without any rigorous theory. While XANES peak po-

sitions may occasionally be used to probe the oxidation state of an atom in an organic matrix, such a practice is unlikely to work for crystalline ZnO. In an organic matrix, hybridization between atomic orbitals results in discrete molecular orbitals, so to a large extent each atom maintains its characteristic ionization signature in the XANES spectra. The situation in crystalline materials is, however, qualitatively different since the electronic states must be described in terms of a band structure of itinerating electrons. In such a picture, the valence $4p$ states of a substituting As strongly intermix with the host states and hence lose their original ionization signature. The only exception may be when the final states are deep inside the band gap, e.g., in the case of As_O, but the maximum energy separation between the peaks cannot exceed the band gap of 3.4 eV for ZnO.

Based on first principles methods, XANES spectra for As at different sites in ZnO have been simulated. This sheds new light on the interpretation of previous XANES experiments on As-doped p-type ZnO by Vaithianathan *et al.*[17] Our results show that the measured XANES is not consistent with As substituting O as previously assigned. Instead, it is far more consistent with the complex acceptor involving As substituting Zn, i.e., $As_{Zn}-2V_{Zn}$.

[1] D. C. Look, Mater. Sci. Eng., B **80**, 383 (2001).
[2] C. Jagadish and S. J. Pearton, *Zinc Oxide Bulk, Thin Films and Nanostructures* (Elsevier, Oxford, 2006).
[3] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[4] K. Kim, H. Kim, D. Hwang, J. Lim, and S. Park, Appl. Phys. Lett. **83**, 63 (2003).
[5] C. Morhain, M. Teisseire, S. Vézian, F. Vigué, F. Raymond, P. Lorenzini, J. Guion, G. Neu, and J.-P. Faurie, Phys. Status Solidi B **229**, 881 (2002).
[6] Y. R. Ryu, T. S. Lee, and H. W. White, Appl. Phys. Lett. **83**, 87 (2003).
[7] T. Aoki, Y. Shimizu, A. Miyake, A. Nakamura, Y. Nakanishi, and Y. Hatanaka, Phys. Status Solidi B **229**, 911 (2002).
[8] C. H. Park, S. B. Zhang, and S.-H. Wei, Phys. Rev. B **66**, 073202 (2002).
[9] S. Limpijumnong, S. B. Zhang, S.-H. Wei, and C. H. Park, Phys. Rev. Lett. **92**, 155504 (2004).
[10] W.-J. Lee, J. Kang, and K. J. Chang, Phys. Rev. B **73**, 024117 (2006); Physica B **376–377**, 699 (2006).
[11] U. Wahl, E. Rita, J. G. Correia, A. C. Marques, E. Alves, and J. C. Soares, Phys. Rev. Lett. **95**, 215503 (2005).
[12] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, Appl. Phys. Lett. **87**, 252102 (2005).
[13] G. Braunstein, A. Muraviev, H. Saxena, N. Dhere, V. Richter, and R. Kalish, Appl. Phys. Lett. **87**, 192103 (2005).
[14] D. C. Koningsberger and R. Prins, *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (Wiley, New York, 1988).
[15] P. Ravindran, A. Kjekshus, H. Fjellvåg, A. Delin, and O. Eriksson, Phys. Rev. B **65**, 064445 (2002).
[16] T. Mizoguchi, I. Tanaka, S. Yoshioka, M. Kunisu, T. Yamamoto, and W. Y. Ching, Phys. Rev. B **70**, 045103 (2004).
[17] V. Vaithianathan, B.-T. Lee, C.-H. Chang, K. Asokan, and S. S. Kim, Appl. Phys. Lett. **88**, 112103 (2006).
[18] S. Larcheri, C. Armellini, F. Rocca, A. Kuzmin, R. Kalendarev, G. Dalba, R. Graziola, J. Purans, D. Pailharey, and F. Jandard, Superlattices Microstruct. **39**, 267 (2006).