Electronic Structure of Group III Elements Doped into ZnO by Using Molecular Orbital Calculation

Moriyasu Nonaka,* Shigenori Matsushima,† Masataka Mizuno,†† and Kenkichiro Kobayashi†††
Department of Earth Resources Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581
†*Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology, Kita-Kyushu 802-0985*
††*Department of Materials Science and Engineering, Osaka University, 2-1 Yamadaoka, Suita 565-0871*
†††*Department of Materials Science, Shizuoka University, 3-5-1 Jyohoku, Hamamatsu 432-8011*

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The electronic structures of ZnO doped with group III elements (B, Al, Ga and In) are calculated by using the discrete variational Xα method of clusters. For ZnO doped with group III elements, new states originating from group III elements appear in the band gap. The depth energy of impurity-related states is the shallowest for Al and is the deepest for B.

ZnO film has been used as a transparent electrode in a CIS ($CuInSe_2$) solar cell,[1] as well as Sn-doped indium oxide (ITO). Minami et al.[2] have attempted to decrease the electric resistance of ZnO films by doping of group III elements such as B, Al, Ga and In, because the electric resistance of ZnO film was higher than that of ITO. They reported that the carrier concentration of ZnO film was enhanced by doping of Al, Ga and In, whereas a remarkable increase of the carrier concentration was not attained by B-doping. Such a doping efficiency may be governed by several factors, e.g., the solubility limits of impurities, the incorporation of intrinsic defects, the depth energy of impurity levels, and so on. In particular, the energy levels of impurity-related gap states are of importance because a number of carrier is proportional to a factor of $\exp(-E_d/kT)$, where E_d is the depth energy of impurity levels. However, there was little theoretical consideration on the electronic structure of ZnO doped with the group III elements. In this paper, we calculate the electronic structure of M-doped ZnO crystals (M: B, Al, Ga, and In) by means of the discrete variational (DV) Xα method[3] and elucidate the doping efficiency of the group III elements.

ZnO crystal has the wurzite-type structure, and its space group is $P6_3mc$. The lattice constants of ZnO are $a = 0.3250$ nm and $c = 0.5207$ nm.[4] For the MO calculation by the non-relativistic DV-Xα method,[3] we employ clusters composed of 114 ions, $[Zn_{39}O_{75}]^{72-}$ and $[MZn_{38}O_{75}]^{71-}$, where M is the group III elements: B, Al, Ga, and In. In the cluster $[MZn_{38}O_{75}]^{71-}$, an impurity ion, M, is substituting for the central Zn ion and the structural relaxation is not taken into account. The cluster is embedded in the Madelung potential generated by point charges situated outside the cluster. The electronic structure of the model cluster is self-consistently calculated by numerical atomic basis functions. In the calculation, we consider 1s to 4p orbitals of Zn and 1s to 2p orbitals of O.

Figure 1 shows the energy level diagrams for $[Zn_{13}O_{29}]^{32-}$ and $[Zn_{39}O_{75}]^{72-}$ clusters. The highest occupied MO (HOMO) is adjusted to zero point on the energy axis. The band gap between HOMO and the lowest unoccupied MO (LUMO) is 5.59 eV and 4.79 eV for each cluster. The band gap energy is overestimated for the small cluster $[Zn_{13}O_{29}]^{32-}$. The overestimation is slightly

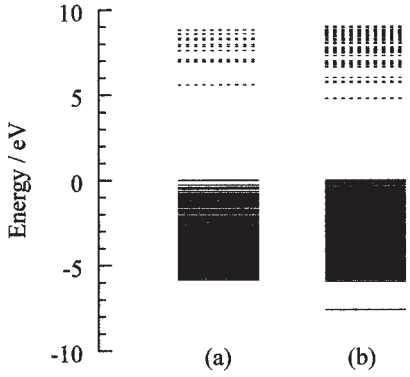

Figure 1. Energy level diagrams for (a) $[Zn_{13}O_{29}]^{32-}$ and (b) $[Zn_{39}O_{75}]^{72-}$ clusters.

released for the large cluster $[Zn_{39}O_{75}]^{72-}$. In principle, a theoretical value approaches an experimental value (3.3 eV),[5] as the size of cluster increases.[6] As will be discussed later, the calculation of the $[Zn_{39}O_{25}]^{72-}$ cluster is satisfactory for qualitative discussion. Thus, we perform the calculation of the $[Zn_{39}O_{75}]^{72-}$ cluster.

Figure 2(a) shows the total (TDOS) and the partial (PDOS) densities of states for the $[Zn_{39}O_{75}]^{72-}$ cluster. All the curves are drawn by the treatment in which the discrete energy eigenvalues are broaden by the Gaussian functions with 0.5 eV full width at half maximum. The upper valence band is mainly constructed from O 2p orbitals and the lower one mainly from Zn 3d. There exists no distinct DOS peak at the top of the valence band arising from a lone-electron pair of O. On the other hand, the conduction band is composed of vacant Zn 4s and O 2p orbitals. ZnO is expected to have an appreciable electron mobility because spatially spread Zn 4s orbitals are dominant at the bottom of the conduction band. For comparison, the DOS obtained by the scalar-relativistic full potential linearized augmented plane wave (FLAPW) method[7] is shown in Figure 2(b). The exchange and correlation interactions are treated within the local density approximation (LDA).[8] In the calculation of electronic structure, approximately 470 plane waves are used. The atomic spheres (radii) of Zn and O atoms are 1.8 and 1.6 a.u., respectively. The k point sampling is chosen to be 16 irreducible points within the Brillouin zone. The DOS curves in Figure 2(a) show a tendency similar to that obtained by FLAPW method. Therefore, the cluster model $[Zn_{39}O_{75}]^{72-}$ is proper for the calculation of electronic structure of ZnO crystal. The net charge is +1.03e for Zn and −1.07e for O, respectively. In addition, the bond overlap population between Zn and O is estimated to be of 0.25 from a

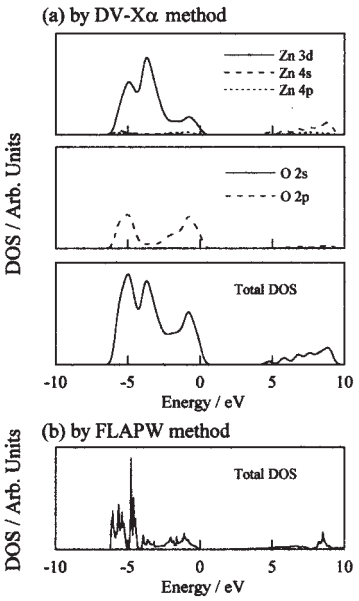

Figure 2. DOS curves for ZnO crystal by means of (a) DV-Xα method, $[Zn_{39}O_{75}]^{72-}$ cluster having been used and (b) FLAPW method.

sum of the overlap population of occupied orbitals. These results suggest that the Zn-O bond is partially covalent.

Figure 3 shows the TDOS and the PDOS for $[MZn_{38}O_{75}]^{71-}$ clusters (M: B, Al, Ga, In). As seen in Fig. 3, a doped M ion forms localized states in the band gap. The gap states originating from B, Al, Ga, and In are located at 2.51, 1.55, 2.06 and 1.68 eV below the bottom of the conduction band, respectively. One cannot accept straightforward the calculated values of the energy levels of the impurity-related gap states because of an inaccuracy of the band-gap energy. Qualitatively, among the group III elements, the B-related gap states are the deepest while the Al-related gap states are the shallowest. In other words, Al and In are effective donors compared with Ga and B. The theoretical prediction is consistent with the experimental results,[2] except for Ga. The discrepancy for Ga implies that in the doping process new intrinsic defects or impurity-defect complexes are incorporated into ZnO crystal. Further studies are in progress to obtain more information about the electronic structure of ZnO crystal containing intrinsic defects.

References and Notes

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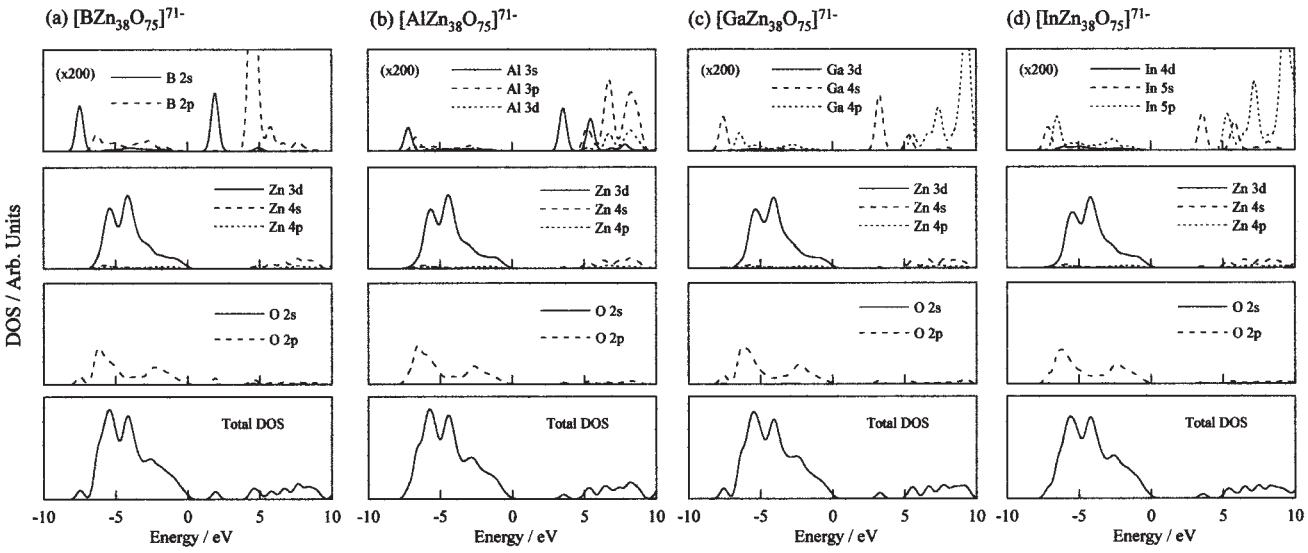

Figure 3. DOS curves for (a) $[BZn_{38}O_{75}]^{71-}$ (b) $[AlZn_{38}O_{75}]^{71-}$ (c) $[GaZn_{38}O_{75}]^{71-}$ (d) $[InZn_{38}O_{75}]^{71-}$ clusters.