

**E-3-1 (Invited)****Materials Design for the Development of ZnO-Based Devices**

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**1. Introduction**

*n*-type semiconductor Zinc Oxide (ZnO) is very promising as a transparent conducting oxide (TCO) thin film. Developing alternatives to indium tin oxide ( $\text{In}_2\text{O}_3:\text{Sn}$ , ITO) is desirable because of the high cost and scarcity of indium. ZnO is lower in cost and also easier to etch than ITO is, so it may replace ITO as a front electrode in some future displays, such as flat-panel displays. In forming amorphous-silicon solar cells on a transparent conductor (TC) superstrates, the TC is exposed to a plasma containing hydrogen atoms. ZnO is much more resistant to hydrogen-plasma reduction and may be preferred for applications such as amorphous-silicon solar cells.

On the other hand, the theoretical prediction for the realization of *p*-type ZnO by codoping Ga and N in the ratios of N:Ga=2:1 was proposed by us [1-4]. Subsequent confirmation of the applicability of the codoping to produce *p*-type ZnO was conducted by Osaka's group [5]. The fabrication of *p*-type ZnO with a direct band gap of 3.3 eV is driving the development of ZnO technology; ZnO will be an important material in short-wavelength light emitting devices because ZnO is lower in cost and can be deposited successfully at low temperatures (typically  $\leq 200^\circ\text{C}$ ).

In this paper, first, we investigate the electronic structure of ZnO doped with only N species (ZnO:N) or codoped with Ga and 2N (ZnO:(Ga, 2N)) in order to clarify the effects of the codoping on the N-impurity states around the top of the valence band. Second, we discuss the influence of *n*- or *p*-type doping on the lattice energy, Madelung energy, of ZnO. Last, we discuss the control of the carrier concentration.

**2. Methodology**

The results of our band structure calculations for ZnO crystals were based on the local-density approximation (LDA) treatment of electronic exchange and correlation [6-8] and on the augmented spherical wave (ASW) formalism for the solution of effective single-particle equations [9]. For the calculations, the atomic sphere approximation (ASA) with a correction term was adopted. For undoped ZnO crystals, Brillouin zone integration was carried out for 84-*k* points in an irreducible wedge and for 24-*k* points for doped and codoped ZnO crystals. For valence electrons, we employ outermost *s*, *p* and *d* orbitals for Zn atoms and *s* and *p* orbitals for the other atoms. The Madelung energy, which reflects long-range electrostatic interaction in the system, was assumed to be restricted to a sum over monopoles. We studied the crystal structures of

doped and codoped ZnO with periodic boundary conditions by generating supercells that contain the object of interest. More details are given elsewhere [1].

**3. Results and discussion***Electronic structures of ZnO:N and ZnO:(Ga, 2N)*

We show the N-site-decomposed density of states (DOS) for (a) and (b) ZnO:N and (c) ZnO:(Ga, 2N) in Fig. 1. The concentrations of N acceptors for Fig. 1(a), 1(b) and 1(c) are  $5.7 \times 10^{20}\text{cm}^{-3}$ ,  $2.6 \times 10^{21}\text{cm}^{-3}$ , and  $5.2 \times 10^{21}\text{cm}^{-3}$ , respectively. Energy is measured relative to the Fermi level ( $E_F$ ).

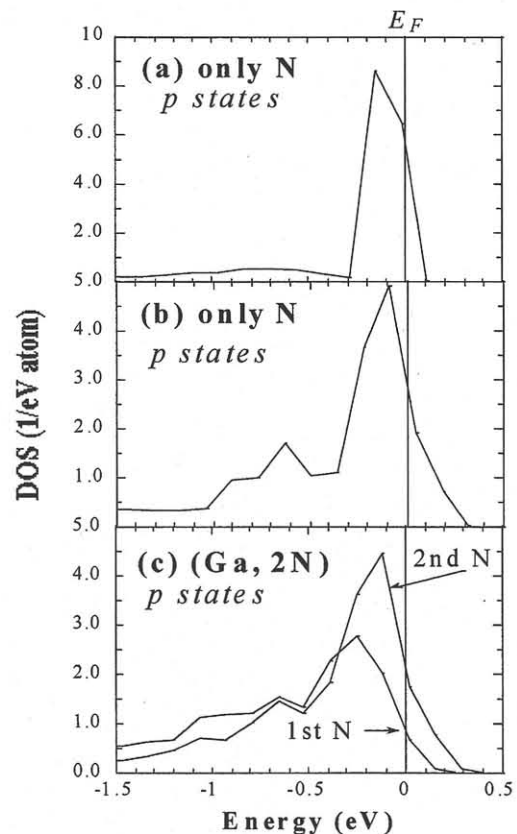


Fig. 1 Site-decomposed DOS for (a) and (b) ZnO:N and (c) ZnO:(Ga, 2N). 1st N curve indicates the DOS at the N atom sites close to the Ga site; 2nd N curve indicates the DOS at the sites of next-nearest-neighbor N atoms.

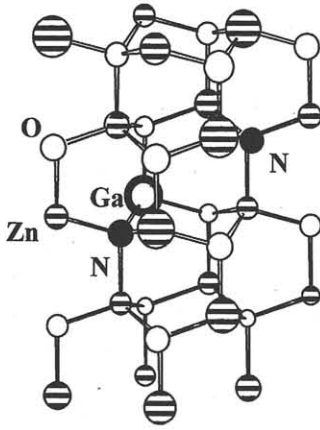


Fig. 2. Crystal structure of a supercell for ZnO codoped with 2N as acceptors and Ga as reactive donors.

Figures 1(a) and 1(b) show the formation of an N-impurity band due to the overlap of the N-acceptor orbitals; holes in the narrow bands are localized by repulsion effects. The width of the band comes from the overlap of orbitals and depends on their separation. The total energy calculations show that N atoms are well separated from each other by strong repulsive interactions while the group III elements, Al, Ga and In species, which exhibit as donors, occupy Zn sites at a small distance [1].

Then we propose materials design, a codoping method, using reactive codopants. The deliberate codoping of the donors is essential for the delocalization of the impurity states at the acceptors and the stabilization of the ionic charge distributions in *p*-type highly doped semiconductors. The donor is not the *p*-type killer but a good by-player who activates acceptors, i.e., the reactive codopant.

We show the crystal structure of supercells for ZnO:(Ga, 2N) crystals in Fig. 2. *Ab-initio* total energy calculations revealed that the formation of complexes, including the III-N pair, which occupy nearest-neighbor sites, and a more distant N, located at the next-nearest-neighbor site in a layer close to the layer including the III-N pair, due to the strong repulsive interaction between the N acceptors. Figure 1(c) for ZnO:(Ga, 2N) shows the formation of the complexes leads to a mixed state of a hole generated at the top of the valence band originating from the two N acceptors. As a result, we find a change from a narrow band in Fig. 1(b) to a broad N-impurity band in Fig. 1(c); the weight of the *p* states at the site of N atoms (1st N curve) close to the site of the reactive codopant, Ga, shifts towards lower-energy regions due to the charge transfer from the Ga to the N atoms. For *p*-type ZnO:(Ga, 2N), we predict a shallow acceptor with the low effective mass of holes, which is a consequence of the broad band.

#### Lattice energy

We summarize the difference in the lattice energy, Madelung energy, among undoped as a standard reference, *n*-type doped, *p*-type doped, and *p*-type codoped ZnO crystals in Table I.

Table I Calculated differences in the Madelung energy among undoped as a standard reference, *n*-type doped, *p*-type doped, and *p*-type codoped ZnO. Units: eV.

<i>n</i> -type	<i>p</i> -type
Al:-6.44, Ga:-13.72, In:-9.73,	N:+0.79,
<i>p</i> -type codoped	
(Al, 2N):-3.95, (Ga, 2N):-11.27, (In, 2N):-7.01	

Table I shows that *p*-type doping using N species causes an increase in the Madelung energy while *n*-type doping using Al, Ga or In species gives rise to a decrease in it. It should be noted that the ionic charge distribution in *p*-type codoped ZnO are stabilized as well as *n*-type doped ZnO.

Finally, we discuss the control of carrier concentration for *p*-type ZnO. From the calculations concerning the three codoped ZnO [1], the delocalization of states of the N close to the reactive donors is found to increase in the following order: ZnO:(In, 2N) < ZnO:(Al, 2N) < ZnO:(Ga, 2N). In order to control the carrier concentration in the semiconductor range, it is required to apply the triple-codoping method using two of the three reactive donors and N acceptors to ZnO crystals.

#### 4. Conclusions

We propose a materials design using the codoping method to control the conduction type and carrier concentrations for the development of ZnO-based devices.

#### Acknowledgments

We would like to express sincere thanks to Prof. Hiroshi Katayama-Yoshida of Osaka University for his fruitful discussion and Dr. Jürgen Sticht for his technical support. The present research was made possible by a grant from New Energy and Industrial Technology Development Organization (NEDO).

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