CONTROL OF VALENCE STATES FOR ZnO and ZnS WITH A WIDE-BAND GAP 
BY A CODOPING METHOD

T. Yamamoto
Department of Electronic and Photonic Systems Engineering, Kochi University of Technology,
185 Miyanokuchi, Tosayamada-cho, Kami-gun, Kochi 782-8502, JAPAN

ABSTRACT

We have investigated the electronic structures of $p$- or $n$-type doped ZnO and ZnS based on the basis of the analysis of the results obtained by ab initio electronic band structure calculations. We find the doping problems of the two materials. They at highly N-doping levels have the narrow impurity bands at the top of the valence band, where holes are very localized by repulsion effects. As a solution to the doping problems described above, we proposed a codoping method: The deliberate codoping of the donors with N acceptors is essential for the enhancement of N-acceptor incorporation and delocalization of the N-impurity states with the electrostatic energy gain in $p$-type highly doped ZnO and ZnS.

INTRODUCTION

Both ZnO with a wide direct band gap ($E_g$) of 3.3 eV and ZnS with a direct $E_g$ of 3.68 eV at room temperature have attracted attention because of their possible application in short-wavelength light emitting devices [1,2]. Thin films made from ZnO or ZnS are attractive on account that they are cheap and abundant raw materials. ZnO can be deposited successfully at low temperatures (typically $\sim 200$ $^{\circ}$C).

In order to develop ZnO- or ZnS-based optoelectronic devices, one important issue that must be resolved is the fabrication of low-resistivity $p$-type doped materials, as well as other wide-band-gap semiconductors, such as GaN. The two materials described above, however, has proven to be difficult to be doped as $p$-type. The theoretical prediction for the realization of $p$-type ZnO by codoping of Ga donors with N acceptors was proposed by us [1-3]. For the fabrication of $p$-type ZnS, codoping of In donors with N acceptors was found to be very effective based on the analysis of calculated results of ab initio electronic band structure calculations [4,5]. Subsequent confirmation of the applicability of the codoping to produce $p$-type ZnO and ZnS was sought by Joseph et al. and Kishimoto et al., respectively [6,7].

The most important factor determining the radius of an impurity orbital is the dielectric constant of the medium. Wide-band-gap semiconductors, ZnO and ZnS, have low dielectric constants, and hence the two materials have very contracted impurity orbitals. In such systems, therefore, much larger concentrations of acceptors are required before their orbitals can overlap sufficiently for good conduction to occur. For our codoping method, it is key that non random configuration, such as acceptor (A)-donor (D)-acceptor (A) trimers that occupy the nearest neighbor sites or trimers-like complexes in codoped materials is postulated to enhance the incorporation of acceptors into materials and produce the required reduced ionization energy of acceptor impurities in materials doped with the acceptors alone, as shown in Fig. 1 [2]. ZnO has wurtzite structure, which is favored by more ionic compounds, while ZnS has zinc-blende structure. Does the difference in the crystal structures between ZnO and ZnS described above
Figure 1. Derivation of the acceptor and donor levels in the band gap. (a) isolated acceptor (A) and donor (D); (b) the acceptor and donor in the interaction between them; (c) inclusion of bandwidths arising from acceptor-orbital overlap, or, lowered acceptor levels through delocalization due to the formation of A-D-A complexes (see right-hand figure) upon codoping.

cause the difference in the configuration of the A-D-A complexes and, as a result, in acceptor-impurity states around the top of the valence band?

The aim of this paper is to give answers to the question described above, based on the analysis of results obtained by \textit{ab initio} electronic band structure calculations.

\section*{METHODOLOGY}

The results of our band structure calculations for ZnO and ZnS crystals were based on the local-density approximation (LDA) treatment of electronic exchange and correlation \cite{8-10} and on the augmented spherical wave (ASW) formalism for the solution of effective single-particle equations \cite{11}. For the calculations, the atomic sphere approximation (ASA) with a correction term was adopted. For undoped ZnO and ZnS crystals, Brillouin zone integration was carried out for 84-k points in an irreducible wedge and for 24-k points for doped and codoped crystals. For valence electrons, we employ outermost s, p and d orbitals for Zn atoms and outermost 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 both ZnO and ZnS with periodic boundary conditions by generating supercells that contain the object of interest.

For \textit{n}-type ZnO doped with group III elements (III=B, Al, Ga or In), we replace one of the 16 sites of Zn atoms by a donor site in model supercells. For \textit{p}-type ZnO doped with N alone (ZnO:N), we calculated two cases: (a) For ZnO doped with N concentration of $2.6 \times 10^{21}$ cm$^{-3}$, we replace one of the 16 sites of O atoms by an acceptor site; (b) For ZnO codoped with N and the group III elements in a ratio of N:III=1:1, (ZnO:(N, III)), we replace one of the 16 sites of the Zn atoms by the donor site and one of the 16 sites of the O atoms by the N atom site. We determined the crystal structure of ZnO:(N, III) by minimizing total energy: The total energy calculations show that the formation of a pair of the N and III element that occupy the nearest
neighbor sites is energetically favorable. For ZnO:(2N, III), we replace one of the remaining 15 sites of the O atoms by the N atom site for ZnO:(N, III) determined above. We determined the crystal structure of ZnO:(2N, III) under the same condition as that for ZnO:(N, III).

For ZnS:N, we replaced one of the 32 sites of S atoms with a N site. For ZnS:(In, N), we replaced one of the 32 sites of S atoms with a N site and one of the 32 sites of Zn atoms with an In site. First, we calculated the total energy for all cases to be considered for ZnS:(In, N). Then, we determined the crystal structure of the material under the condition that the total energy is minimized. We find that an In\textsubscript{Zn}-N\textsubscript{S} pair that occupies nearest-neighbor sites in the crystal is formed. For ZnS:(In, 2N), we replaced one of the remaining 31 sites of S with another N site for ZnS:(In, N), as mentioned above. Under the same total energy condition as that of ZnS:(In, N), we determined the crystal structure for ZnS:(In, 2N). The total energy calculations indicate that the formation of the trimer, N\textsubscript{S}-In\textsubscript{Zn}-N\textsubscript{S}, that occupies the nearest-neighbor sites, is energetically favorable. The difference in the total energy between the crystal structure having the lowest total energy and the one having the second-lowest total energy, such as the In\textsubscript{Zn}-N\textsubscript{S} pair and another N which occupy the second-nearest neighbor sites from the In sites, is 832 meV.

RESULTS AND DISCUSSION

We show N-site-decomposed density of states (DOSs) for (a) ZnO:N, (b) ZnS:N and (c) ZnTe:N as a reference in figure 2, where \( p \) states at N sites are illustrated.

![Figure 2. N-site-decomposed DOS for (a) ZnO:N, (b) ZnS:N and (c) ZnTe:N](image_url)
Energy is measured relative to the Fermi energy ($E_F$).

Figure 2 show the formation of a N-impurity band due to the overlap of the N-acceptor orbitals for the three materials. For ZnTe, Baron et al. succeeded in the fabrication of $p$-type ZnTe doped with high concentrations of holes in the order of $10^{20}$ cm$^{-3}$ [12]. For ZnO:N, we find that there increases the N-impurity bandwidth as there increases the concentration of N acceptors in the material. Holes generated around the top of the valence band in the narrow bands for ZnO and ZnS are very localized by repulsion effects, as compared to those of ZnTe:N in figure 2(c). As a result, for ZnO and ZnS, there occurs a sharp DOS peak to locate near the top of the valence band due to the repulsion potential; the center of gravity of $p$ states at N sites in the two materials shifts toward higher energy regions.

We find narrow N-impurity band for ZnO:N as compared to ZnS:N from figures 2(a) and 2(b). This mainly originates in crystal structure, wurtzite structure, due to the characteristics of chemical bonds of the host material: Wurtzite structure is favored by more ionic compound, ZnO, whereas zinc-blende structure by more covalent compounds, ZnS. The differences in electronegativity, given by Pauling, between Zn and anion species for ZnO, ZnS and ZnTe are 1.79, 0.93 and 0.45, respectively. The dielectric constants of ZnO, ZnS and ZnTe are 8.59, 8.32 and 10.1, respectively. Considering that the width of the impurity bands comes from the overlap of the impurity orbitals, figures 2(a) and 2(b) suggest that the Bohr radius of the N acceptors in ZnO:N is very small compared with that in ZnS:N. Based on the Bohr theory of the hydrogen atom, being modified to take into account both the dielectric constant of the medium and the effective mass of a hole, this means the large effective mass of the hole, which is a consequence of the narrow band, resulting in large acceptor ionization energy of ZnO:N. For N-doped ZnS having lower dielectric constant than that of ZnO, Svob et al. reported the energy levels of the N acceptors to be slightly deep, about 0.19 eV, above the valence band [13].

From above findings, N-impurity bands of the two materials are needed to change from narrow bands to broad bands in order to obtain the reduced acceptor binding energy. It is our codoping method that solves the issue described above.

We show the crystal structures of ZnO:(2N, III=Al, Ga and In) in Fig.3. We find the formations of complexes, including the N-III pair, that occupies nearest-neighbor sites, and a more distant N, located at the next-nearest-neighbor site in a layer close to the layer including the N-Ga pair, due to the strong repulsive interaction between the N acceptors. On the other hand, the stable configuration of 2N in the III-free ZnO:2N in the supercell having the same size cannot be found under the condition that total energy is minimized. On the other hand, for ZnS, total energy calculations show that the formation of NS-In$_{Zn}$ (Ga$_{Zn}$)-NS complexes that occupy
the nearest neighbor sites (see right-hand figure in figure 1) is energetically favorable. The difference in the configuration of complexes constituting 2N acceptors and a codopant between ZnO and ZnS is due to the degree of contraction of N-acceptor orbitals. The above findings suggest smaller Bohr radius of N acceptors in ZnO:N than that in ZnS:N.

We show N-site-decomposed DOS for (a) ZnO:(2N, Ga), (b) ZnS:(2N, In) and (c) ZnTe:N as a reference in figure 4, where $p$ states at N sites are illustrated. Energy is measured relative to $E_F$. For ZnO:(2N, Ga), $p$ states only at N sites close to the Ga-Zn sites are shown in figure 4(a).

Making a comparison between figure 2 and figure 4, we find a change from narrow N-impurity bands for ZnO:N or ZnS:N to broad ones for $p$-type codoped materials due to the strong hybridization between $p$ states at the N sites and $p$ states at the reactive-donors site. We verify the drastic change for $p$-type ZnS with NS-In$_{2}$N$_{5}$ trimers as compared to $p$-type ZnO with the trimers-like complexes (see figure 3). This change in the two materials leads to the enhancement of the Bohr radius of N-acceptor orbitals, resulting in the reduced acceptor binding energy.

We note that sharp DOS peaks, indicated by arrows in figures 4(a) and 4(b), shift toward lower energy regions. This means the stabilization of the ionic charge distributions in the two materials by the codoping method. Considering that the main contribution to the binding energy of crystals of wide-band-gap semiconductors that is favored by more ionic compounds is electrostatic energy, it is very easy to understand that the codoping method will suppress the self-compensation by the formation of intrinsic defects, such as anion vacancies, induced by $p$-type doping.

![Figure 4. N-site-decomposed DOS for (a) ZnO:(2N, Ga), (b) ZnS:(2N, In) and (c) ZnTe:N](image)
CONCLUSIONS

We investigate the electronic structures of ZnO with wurtzite structures and ZnS with zinc-blende structures on the basis of the analysis of the results obtained by ab initio electronic band structure calculations. The two materials have low dielectric constants, and hence very contracted N impurity orbitals. For more ionic compound, ZnO:N, we find very localized N-impurity states. The codoping of donors with N acceptors causes a drastic change from localized N-impurity states for only N-doped materials to the delocalized ones for p-type codoped materials with the enhancement of the incorporation of the N acceptors.

ACKNOWLEDGMENTS

The author would like to express sincere thanks to Prof. Hiroshi Katayama-Yoshida of Osaka University, Prof. Seishi Iida, vice president, of Nagaoka University of Technology, Dr. Sadao Ibe, general manager, and Dr. Yasuhiro Ueshima, general manager, of Asahi Kasei corporation for their fruitful discussion and Dr. Jürgen Sticht for his technical support. We have ESOCS code by accelrys. The present research was made possible by a grant of a regional consortium from New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES
