Asia Display / IDW `01, Oct. 16-19, 2001, Nagoya, Oct. 18, PH1-2 Invited

Codoping Method to Realize Low-Resistivity *p*-Type ZnO Thin Films

T. Yamamoto

Department of Electronic and Photonic System Engineering, Kochi University of Technology,
185 Miyanokuchi, Tosayamada-cho, Kami-gun, Kochi 782-8501, Japan

ABSTRACT

Zinc oxide (ZnO) exhibits an asymmetry in its ability to be doped *n*-type or *p*-type. We have reviewed out theoretical prediction concerning the control of the conduction type and subsequent confirmation of the applicability of co-doping to produce *p*-type ZnO for the fabrication of short-wavelength light-emitting devices.

INTRODUCTION

Transparent, electrically conductive *n*-type ZnO films have been investigated more recently, to be very promising as a transparent conducting oxide (TCO) thin film. Developing altematives to indium tin oxide (In_2O_3: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. Dilute acids and ammonium chloride are used to etch ZnO. One application in which ZnO is used as TCO and antireflection coating is in solar cells such as amorphous-silicon (a-Si) and Cu(InGa)Se_2-based solar cells.[1] 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 can be obtained in its low growth temperature. So it may be preferred for the solar cells above.

ZnO with a wide direct band gap of 3.3 eV has also attracted attention because of it possible application in short-wavelength light emitting devices.[3,4] In order to develop such optoelectronic devices, one important issue that should be resolved is the fabrication of low-resistivity *p*-type doped ZnO, as well as other wide-band-gap semiconductors such as ZnSe and GaN. ZnO, however, has proven to be difficult to doped as *p*-type: ZnO exhibits an asymmetry in its ability to be doped *n*-type or *p*-type, which is called to be the "*unipolarity*". 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 [5-8]. The basic idea of the codoping is based on our experiences on successful control of surface properties of polymers and magnetic properties of iron nitrides by doping the other transition elements for the fabrication of hard magnetism. [8] Subsequent confirmation of the applicability of the codoping to produce *p*-type ZnO was conducted by Osaka`s group [9].

The fabrication of *p*-type ZnO 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 $\leqq$ 200°C).

In this paper, first, we mention the "*unipolarity*" doping problem in ZnO crystals, based on the results of *ab initio* electronic band structure calculations and basic concepts of our codoping method. Second, we investigate the electronic structures of ZnO doped with only N species (ZnO:N) or codoped with Ga and 2N (ZnO:(Ga, 2N)) to clarify the effects of the codoping on the N-impurity states around the top of the valence band. Last, we discuss the control of the carrier concentration.

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 [10-12] and on the augmented spherical wave (ASW) formalism for the solution of effective single-particle equations [13]. 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 employs 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. (1) For *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. (2) For p-type ZnO doped with N alone, 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 doped with N concentration of $6.5 \times 10^{20} cm^{-3}$, we replace one of the 64 sites of O atoms by the acceptor site. (3) 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

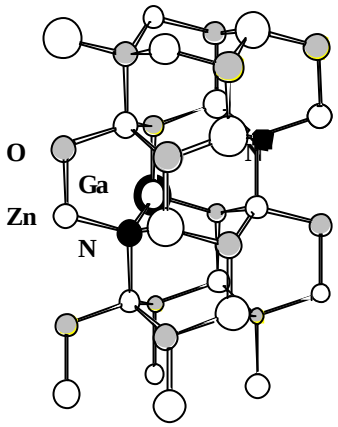

Fig. 1. Crystal structure of a supercell for ZnO: (2N, Ga).

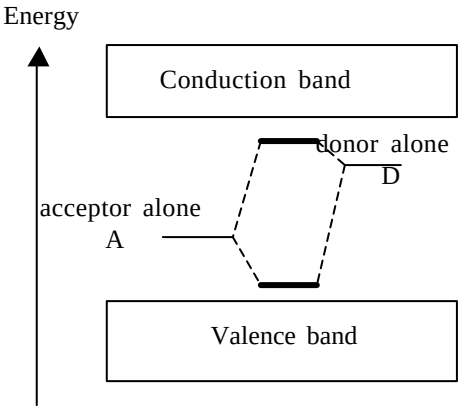

Fig. 2. Schematic energy diagram for *p*-type codoped semiconductors. The acceptor (A) level is lowered and the donor (D) level is raised with the formation of acceptor-donor-acceptor complexes upon codoping.

N atom site. We determined the crystal structure of ZnO:(N, III) by minimizing total enegy: The total energy calculations show that the formation of a pair of the N and III element which occupy the nearest neighbor sites is energetically favorable. (4) 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, which is shown in Fig. 1.

UNIPOLARITY

The main contribution to the binding energy of crystals with wurtzite structure that is favored by more ionic compounds is electrostatic and is called the Madelung energy. In order to clarify the stability of the lattice of *n*- or *p*-type doped ZnO, we summarize the differences in the calculated Madelung energy between undoped and the *n*- or *p*-type doped ZnO in Table I. It shows that while *n*-type doping using the group III elements (III=B, Al, Ga, and In), a Zn-substituting species, or F species, an O-substituting species, causes a decrease in the Madelung energy, *p*-type doping using N or As, an O-substituting species, or Li, a Zn-substituting species, gives rise to an increase in the Madelung energy, resulting the instability of the ionic charge distributions within the *p*-type doped crystals. Table I indicates the occurrence of a doping problem called "*unipolarity*", whereby both high-conductivity *n*- and *p*-type ZnO crystals are difficult to fabricate.

Table I. Calculated Differences in the Madelung energies between undoped ZnO and *n*- or *p*-type doped ZnO. units:eV.

n-type
B:-3.91, Al:-6.44, Ga:-13.72, In:-9.73, F:-1.86
p-type
Li: +13.56, N:+0.79, As:+12.61

BASIC CONCEPTS OF CODOPING METHOD

We summarize the basic concepts of our codoping method.[5-8] The codoping method using acceptors (A) and donors (D) as a reactive codopant, in a ratio of A:D=2:1, contributes (i) to enhance the incorporation of the acceptors because the strong attractive interactions between the acceptor and donor dopants overcomes the repulsive interactions between the acceptors, (ii) to lower the energy levels of the acceptors and raise them of the donors in the band gap due to the the strong attractive interactions between the acceptor and donor as reactive codopants, as shown in Fig.2, (iii) to increase the carrier mobility due to the short-range dipole-like scattering mechanism, and (iv) to reduce the Madelung energy. Thus, a 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. It should be noted that the donor is not the *p*-type killer but a good by-player that activates acceptors, i.e., the reactive codopant.

RESULTS AND DISCUSSION

n-type doping of the group III elements, Al, Ga and In, forms the broad impurity bands originated in the large radius of the donor orbital.[5] As a result, the electron has the small effective mass, which gives the rather low impurity ionization energies in ZnO. Moreover, from *ab initio* electric calculations, we find that the repulsive interactions between the same donor species are very weak compared with those between the N acceptors [5], so that the incorporated donors are very stable in highly *n*-type doped ZnO crystals.

According to the modified Bohr theory of the hydrogen atom, the dielectric constant has the most important effect on the acceptor energy because it enters

as the square, whereas the effective mass enters only as the first power. Noting that AlN, GaN and InN has the same wurtzite structure with ZnO and their dielectric constants are larger than that of ZnO, the group III elements above are eminently suitable for use as reactive codopants with N acceptors.

Here we focus on N species as acceptors because an increase in the Madelung energy for ZnO:N is rather small compared with ZnO:Li or ZnO:As from Table I.

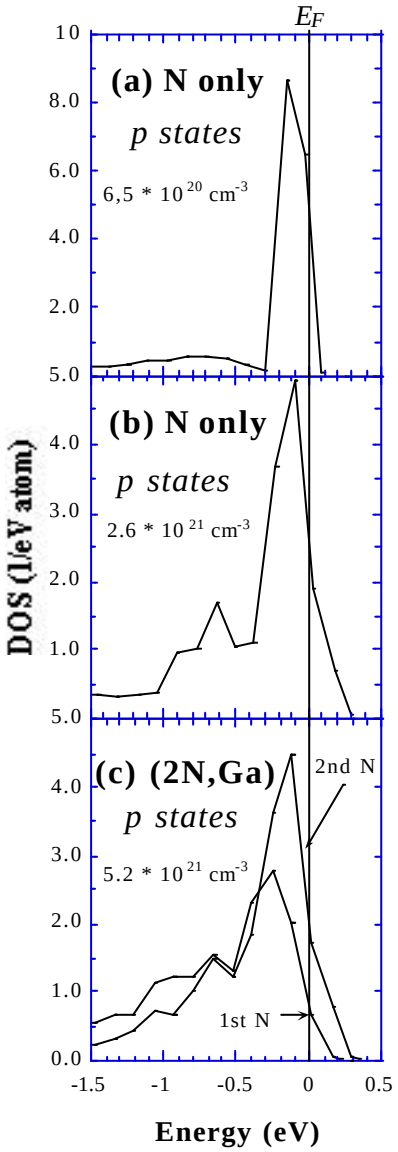

Fig. 3. Site-decomposed DOSs for (a) and (b) ZnO:N and (c) ZnO:(2N, Ga). For (c), 1st N curve indicates that the DOS at the N sites close to the Ga site; 2nd N curve indicates the DOS at the sites of next-nearest-neighbor N atoms (see Fig. 1). For an explanation, see text.

We show the N-site-decomposed density of states (DOSs) for (a) and (b) ZnO doped with N alone and (c) ZnO:(2N, Ga) in Fig. 3, where *p* states at N sites are illustrated. The concentrations of N acceptors for Fig. 3(a), 3(b) and 3(c) are 6.5×10^{20}cm^{-3}, 2.6×10^{21}cm^{-3}, and 5.2×10^{21}cm^{-3}, respectively. Energy is measured relative to the Fermi level (E_F).

Figures 3(a) and 3(b) show the formation of a N-impurity band due to the overlap of the N-acceptor orbitals; holes generated around the top of the valence band in the narrow bands are very localized by repulsion effects. Considering that the width of the impurity bands comes from the overlap of the impurity orbitals, the two figures show that the Bohr radius of the N acceptors is very small. Based on the modified Bohr theory, 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. Moreover, from Table I, N doping gives rise to an increase in the Madelung energy. Those hampers the use of N as a practical impurity.

For ZnO:(2N, Ga), we find the formations of complexes, including the N-Ga 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 N-Ga pair, due to the strong repulsive interaction between the N acceptors. For Ga-free ZnO:2N, we verified a large distance between the N acceptors in the supercell. [5] We summarize the differences in the Madelung energy among undoped ZnO as a standard, *p*-type ZnO:N and *p*-type codoped ZnO in Table II. It shows that the codoping method using the group III elements as reactive codopants with the N acceptors stabilize the ionic charge distributions of *p*-type codoped ZnO compared with *p*-type ZnO doped with the N acceptor alone. Thus, the codoping method enhances the incorporation of N atoms into ZnO crystals.

Next, Figure 3(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 N-impurity band in Fig. 3(b) to a broad N-impurity band in Fig. 3(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, which causes a significantly decrease in the Madelung energy (see Table II). For *p*-type ZnO:(2N, Ga), we predict a shallow acceptor with the low effective mass of holes, which is a consequence of the broad band.

Table II Calculated differences in the Madelung energy between undoped and *p*-type codoped ZnO. Units: eV.

(Al, 2N): -3.95, (Ga, 2N): -11.27, (In, 2N): -7.01

Finally, we discuss the control of carrier concentration for *p*-type ZnO. Based on the analysis of the calculated results concerning the *p*-type codoped ZnO:(2N, Al), (2N, Ga) or (2N, In), 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.

CONCLUSION

We propose a materials design using the codoping method to control the conduction type and carrier concentrations for the development of transparent conductive ZnO thin films and also ZnO-based electrical or optical devices for near future displays.

Acknowledgements

The author would like to express sincere thanks to Prof. Hiroshi Katayama-Yoshida of Osaka University, 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. The present research was made possible by a grant of regional consortium from New Energy and Industrial Technology Development Organization (NEDO).

References

[1] S. Mayer and K. L. Chopra, Sol. Energy Mater. **17**, 319(1988).

[2] H. N. Wanka, E. Lotter and M. B. Shubert, in Amorphous Silicon Technology-1994, edited by E. A. Shiff, M. Hack, A. Madan, M. Powell and A. Matsuda (Mater. Res. Soc. Symp. Proc. **336**, Pittburgh, 1994) p.657.

[3] P. Yu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma and Y. Segawa, *Proc. 23th. Int. Conf. Physics of Semiconductors, Berlin, 1996*, vol. 2, p. 1453.

[4] Y. Segawa, A. Ohtomo, M. Kawasaki, H. Koinuma, Z. K. Tang, P. Yu and G. K. L. Wong, phys. status solidi (b) **202**, 669 (1997).

[5] T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys. **38**, L166 (1999).

[6] T. Yamamoto and H. Katayama-Yoshida, Mater. Res. Soc. Proc. **623**, 223 (2000). MRS Spring Meeting, San Francisco, 2000. Invited.

[7] T. Yamamoto and H. Katayama-Yoshida, J. Cryst. Growth **214/215**, 552 (2000) .

[8] T. Yamamoto, NEW DIAMOND **17**,18 (2001) [in Japanese].

[9] M. Joseph, H. Tabata and T. Kawai, Jpn. J. Appl. Phys. **38**, L1205 (1999) .

[10] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[11] L. Hedin and B. I. Lundquist, J. Phys. C**4**, 3107 (1971).

[12] U. von Barth and L. Hedin, J. Phys. C**5**, 1629 (1972).

[13] A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. **B19**, 6094 (1979).