<table>
<thead>
<tr>
<th>Title</th>
<th>Conduction-Band Structures of Wurtzite ZnO Solid Solutions by First Principles Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Wang, Z. J.; Tanaka, I.</td>
</tr>
<tr>
<td>Citation</td>
<td>MATERIALS TRANSACTIONS (2009), 50(5): 1067-1070</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2009-05</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/109952">http://hdl.handle.net/2433/109952</a></td>
</tr>
<tr>
<td>Copyright</td>
<td>© 2009 The Japan Institute of Metals</td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
Conduction-Band Structures of Wurtzite ZnO Solid Solutions by First Principles Calculations

Z. J. Wang1,2,3 and I. Tanaka3,4

1National Laboratory of Superhard Materials, Jilin University, Changchun, Jilin, 130012, China
2Physics Department, Jilin University, Changchun, Jilin, 130026, P.R.China
3Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan
4Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

Solid solutions of Zn1−xMgO and Zn1−xMgO (0 ≤ x ≤ 1) with wurtzite structures are systematically investigated by first principles calculations with special interests on the dependence of energetics and electronic structures on the alloy structure. Alloying ZnO with CdO shows a linear trend in the lattice parameters when we choose energetically favorable alloy structures. On the other hand, they do not show such a linear trend when alloyed with MgO. Formation energy with reference to the end-member oxides of wurtzite structures is positive for Zn1−xMgO alloys, whereas it is slightly negative for Zn1−xMgO alloy. They are consistent with the experimental fact that highly concentrated solid solutions are easier to be formed in Zn1−xMgO alloys. The band gap shows a monotonous decrease in Zn1−xMgO and increase in Zn1−xMgO with the solute concentration. In Zn1−xMgO, Cd has an orbital component as large as that of Zn at the bottom of the conduction band. On the other hand, the contribution of Mg is much smaller in Zn1−xMgO. They are consistent with the changes in the band gap with the composition.

Keywords: zinc oxide, solid solution, semiconductor, electronic ceramics, dopant, band gap, first principles calculation

1. Introduction

ZnO is one of the most promising semiconductor materials for ultraviolet optoelectronic application due to its wide band gap of 3.4 eV and large exciton binding energy of 60 meV.1–3 Divalent metal oxides such as MgO and CdO are often used to alloy with ZnO as a common strategy for band-gap engineering and optical confinement.4–6 Zn1−xMgO and Zn1−xMgO alloys are well known that the addition of CdO in ZnO decreases the band gap whereas the contribution of MgO increases the band gap. Although both MgO and CdO occur in the cubic rocksalt structure under ordinary conditions, Zn1−xMgO and Zn1−xMgO alloys are accepted to form the wurtzite structure when x is small.4–7 Under meta-stable thin film growth conditions, the maximum concentration of Mg in wurtzite Zn1−xMgO is typically in the range of x = 0.4 to 0.6.8–10 On the other hand it is only about 0.15–15) for Cd in wurtzite Zn1−xMgO thin film, except for a few cases reporting success of higher solute concentrations under special process conditions.12

There have been a number of theoretical studies on the electronic structures and properties of ZnO, MgO and CdO3–18 and their pseudo-binary oxide-oxides.19–24 Very recently Fan and coworkers24) reported systematic first principles calculations of A2Zn1−xO alloys (A = Cu, Cd, Mg) with rocksalt and wurtzite structures. They examined all different alloy structures within a given supercell in order to know the dependence of the energetics, geometry and band-gap on the alloy structures and compositions. However, they did not explicitly investigate the conduction band structure of these alloys, which should play important roles in optoelectronic applications.

In this work, after confirmation of the dependence on the alloy structure of energetics and electronic structures in solid solutions of Zn1−xMgO, they examine the conduction band structures using first principles calculations.

2. Computational Methods

The calculations were made using the plane-wave basis projector augmented wave (PAW) method25) as implemented in the VASP code.26–28 Generalized gradient approximation (GGA) as parameterized by Perdew and Wang (PW91) was used.29) The plane-wave energy cutoff was chosen to be 500 eV. The Brillouin-zone (BZ) integrations in the electron density and the total energy were made using a set of 4 × 4 × 4 k-points of Monkhorst-Pack type30) for 16-atom Zn1−xMgO supercells. The cell volume and all the ionic positions were relaxed until the residual forces became less than 0.001 eV/Å.

Figure 1 shows the structure of the 16-atom supercell used in the present study, which corresponds to 2 × 2 × 1 of the conventional wurtzite cell. The numbered atoms are Zn, Cd, and Mg, and the dark atoms are O. All different alloy models within the 16-atom supercell are shown in Table 1. All of them were employed for the first principles calculations.

3. Results and Discussion

Lattice parameters for wurtzite ZnO by the present calculation were a = 0.328 nm, c = 0.529 nm and u = 0.380. They are in reasonable agreements with those by experiments,31) i.e., a = 0.324 nm, c = 0.519 nm and u = 0.382. Lattice parameters of wurtzite CdO were obtained to be a = 0.368 nm, c = 0.581 nm and u = 0.384. They were a = 0.331 nm, c = 0.51 nm and u = 0.387 for wurtzite MgO.

Figure 2 shows the lattice constants of Zn1−xMgO and Zn1−xMgO alloys for all different alloy structures and compositions. The alloy structures corresponding to the lowest total energies for a given composition are highlighted by solid marks. The solid marks in Zn1−xMgO clearly show that both a and c lattice constants have nearly linear relationship with the Cd concentration. In other words, they follow the Vegard’s law, which is in good agreement with the
experiment results.\(^{12}\) On the other hand in Zn\(_{1-x}\)Mg\(_x\)O, the lattice parameters do not show such linear trends. (Note that the scale of the vertical axis is expanded for Zn\(_{1-x}\)Mg\(_x\)O.) The overall trend of the present results is similar to those in Ref. 24), although some differences can be seen between them. This may be partly ascribed to the use of different exchange-correlation functionals for the calculations and some other computational details. The local density approximation (LDA) is used in Ref. 24), whereas GGA is employed in the present study.

In order to study the stability of Zn\(_{1-x}\)Cd\(_x\)O and Zn\(_{1-x}\)Mg\(_x\)O alloys, the formation energies of all alloy configurations were computed. The results are shown in Fig. 3. Note that three wurtzite crystals, ZnO, MgO and CdO were used as references of the formation energy. Wide scattering of the formation energy with solute configuration is noteworthy for Zn\(_{1-x}\)Cd\(_x\)O. Solid marks correspond to the alloy configuration with the lowest formation energy for a given composition. Formation energy is positive for Zn\(_{1-x}\)Cd\(_x\)O alloys, whereas it is slightly negative for Zn\(_{1-x}\)Mg\(_x\)O alloys. They are consistent with the experimental fact that highly concentrated solid solutions are easier to be formed in Zn\(_{1-x}\)Mg\(_x\)O. The present results agree with those in Ref. 24).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sites occupied by M</th>
<th>Space group</th>
<th>Number of M-M pairs in the cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(_8)O(_8)</td>
<td>null</td>
<td>P(_6)(_3)mc</td>
<td>0</td>
</tr>
<tr>
<td>Zn(_7)M(_1)O(_8)</td>
<td>1, 8</td>
<td>P(_3)m1</td>
<td>0</td>
</tr>
<tr>
<td>Zn(_6)M(_2)O(_8)</td>
<td>1, 5</td>
<td>Cmc(_2)</td>
<td>1</td>
</tr>
<tr>
<td>Zn(_5)M(_3)O(_8)</td>
<td>1, 2</td>
<td>P(_n)</td>
<td>1</td>
</tr>
<tr>
<td>Zn(_4)M(_4)O(_8)</td>
<td>1, 2, 3, 4</td>
<td>P(_3)m1</td>
<td>6</td>
</tr>
<tr>
<td>Zn(_3)M(_5)O(_8)</td>
<td>1, 4, 5, 6</td>
<td>Pmc(_2)</td>
<td>4</td>
</tr>
<tr>
<td>Zn(_2)M(_6)O(_8)</td>
<td>1, 2, 3, 5</td>
<td>P(_3)m1</td>
<td>3</td>
</tr>
<tr>
<td>Zn(_1)M(_7)O(_8)</td>
<td>1, 2, 4, 5</td>
<td>C(_c)</td>
<td>2</td>
</tr>
<tr>
<td>M(_8)O(_8)</td>
<td>all</td>
<td>P(_6)(_3)mc</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 1 The 16-atom supercell of a wurtzite structure. Eight cation sites are labeled. The conventional unit cell is shown by thin lines.

Fig. 2 Theoretical lattice constants of wurtzite ZnO alloys with different solute arrangements. Solid marks correspond to the model showing lowest energy at given solute concentration.

Fig. 3 Theoretical formation energy of wurtzite ZnO alloys with different solute arrangements. Marks denote the same meaning hereafter as Fig. 2.
The band structures of Zn$_{1-x}$M$_x$O (M = Cd, Mg) alloys were calculated along lines connecting high-symmetry points in the BZ. Our results show that both the top of the valence band and the bottom of the conduction band are located at the Γ point (k = 0), which indicates the presence of direct band gaps in all of the alloys examined in the present study. The band gaps of the Zn$_{1-x}$Cd$_x$O and Zn$_{1-x}$Mg$_x$O alloys are shown in Fig. 4. The band gap of undoped ZnO in the present study is 0.73 eV, which is significantly smaller than that by experiments. The band gap vanishes in CdO. Such errors are typical for first principles calculations with the GGA or LDA. For Zn$_{1-x}$Cd$_x$O alloys, negative band gaps are omitted from the plot. Although the absolute values of the gap are significantly underestimated, their dependences on solute concentration well agree with experimental data available in literature 10,12.

In order to quantify the electronic structures at the bottom of the conduction band, the fractions of cationic s-orbitals are examined. The fractions of Cd5s and Mg3s increase and that of Zn4s decreases nearly linearly with the increase of the M-concentration as shown in Fig. 5. The bottom of the conduction band gradually changes from Zn4s to Cd5s/Mg3s characters with the M concentration. The increment is larger in Cd doping as compared to the Mg doping. The changes in the conduction band structure can be well visualized by plotting the wave function at the bottom of the conduction band (Γ-point). Figure 6 compares the squared wave functions for ZnO, Zn$_{7/8}$Mg$_{1/8}$O and Zn$_{7/8}$Cd$_{1/8}$O. As for Zn$_{7/8}$M$_{1/8}$O (M = Cd, Mg), the alloy structure is determined uniquely within the 16-atoms supercell as can be learned from Table 1. The wave functions are plotted on the (0001) plane on which cations number 5 to 8 are periodically located (see Fig. 1). In Zn$_{7/8}$Cd$_{1/8}$O, Cd shows a contribution as large as that of Zn at the bottom of the conduction band. On the other hand, the contribution of Mg is much smaller in Zn$_{7/8}$Mg$_{1/8}$O. This is related to the change in the band gap due to the presence of the solute.

4. Conclusion

Solid solutions of wurtzite ZnO with MgO and CdO are systematically investigated by first principles calculations. Results can be summarized as follows:

(1) The lattice parameters of Zn$_{1-x}$Cd$_x$O alloys show a linear increase with the Cd concentration when we choose energetically favorable alloy structures. On the other hand, they do not show such a linear trend in Zn$_{1-x}$Mg$_x$O alloys.

(2) Formation energy with reference to the end-member oxides of wurtzite structures is positive for Zn$_{1-x}$Cd$_x$O alloys, whereas it is slightly negative for Zn$_{1-x}$Mg$_x$O alloy. They are consistent with the experimental fact that highly concentrated solid solutions are easier to be formed in Zn$_{1-x}$Mg$_x$O alloys.

(3) Band gap shows a monotonous increase in Zn$_{1-x}$Mg$_x$O and decrease in Zn$_{1-x}$Cd$_x$O with the solute concentration. Although the absolute values of the gap are significantly underestimated, their dependences on the solute concentration well agree with experimental data available in literature.

(4) In Zn$_{1-x}$Mg$_x$O, Mg makes a small contribution to the wave function at the bottom of the conduction band. On the other hand, the contribution of Cd is comparable to that of Zn in Zn$_{1-x}$Cd$_x$O. They are consistent with the changes in the band gap with the composition.

Acknowledgments

The authors would like to thank Fumiyasu Oba for his helpful discussion and Kazuaki Toyoura for technical assistance. This study was supported by Grant-in-Aid for Scientific Research on Priority Areas of Nano Materials Science for Atomic Scale Modification (No. 474) from Ministry of Education, Culture, Sports, Science and Tech-
Z. J. W and I. Tanaka

REFERENCES


Fig. 6 Squared wave function at the bottom of the conduction band at the Γ-point ($k = 0$) plotted on a (0001) plane. (a) Zn$_7$Mg$_1$O$_8$, (b) Zn$_9$O$_8$, and (c) Zn$_7$Cd$_1$O$_8$.