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Structures of wurtzite ZnO solid solutions with MgO and CdO by first principles calculations

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Formation of solid solutions or alloys is a common strategy for band-gap engineering of semiconductors. Divalent metal oxides such as MgO and CdO are often used to alloy with ZnO. Although both MgO and CdO occur in the cubic rocksalt structure under ordinarily conditions, $Zn_{1-x}Mg_xO$ and $Zn_{1-x}Cd_xO$ alloys are known to form the wurtzite structure when x is small. It is generally accepted that the addition of CdO in ZnO decreases the band gap whereas that of MgO increases the band gap. However, the arrangements of solute atoms, especially their effects on atomic/electronic structures of the alloys, are not clarified yet. In the present study, we show first principles results on these issues employing all different alloy structures within the 16-atom supercell of wurtzite ZnO crystal. All calculations were made by the PAW method as implemented in the VASP code[1]. GGA (PW91) functional, plane wave cutoff of 500 eV and 4×4×4 mesh for k-point sampling were used.

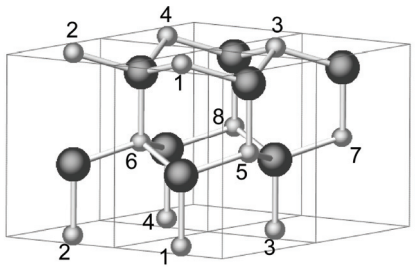

Fig.1 The 16-atom supercell of a wurtzite structure. Eight cation sites are labeled. The conventional unit cell is shown by thin lines.

Table1 All different alloy models within the 16-atom supercell. Calculations were made imposing the space group given below.

Composition	Sites occupied by M	Space group	Number of M-M pairs in the cell
Zn_8O_8	null	$P6_3mc$	0
$Zn_7M_1O_8$	8	$P3m1$	0
$Zn_6M_2O_8$	1, 8	$P6_3mc$	1
	1, 5	$Cmc2_1$	1
	1, 2	Pm	1
$Zn_5M_3O_8$	1, 2, 3	$P3m1$	3
	1, 4, 5	Cm	1
	1, 2, 5	Cm	2
$Zn_4M_4O_8$	1, 2, 3, 4	$P3m1$	6
	1, 4, 5, 8	$Pmc2_1$	2
	1, 2, 5, 6	$Pmn2_1$	4
	1, 2, 3, 5	$P3m1$	3
	1, 2, 5, 7	Cc	3
	1, 2, 4, 5	Cm	2
$Zn_3M_5O_8$	4, 5, 6, 7, 8	$P3m1$	3
	2, 3, 6, 7, 8	Cm	4
	3, 4, 6, 7, 8	Cm	5
$Zn_2M_6O_8$	2, 3, 4, 5, 6, 7,	$P6_3mc$	6
	2, 3, 4, 6, 7, 8	$Cmc2_1$	7
	3, 4, 5, 6, 7, 8	Pm	6
$Zn_1M_7O_8$	1, 2, 3, 4, 5, 7, 8	$P3m1$	9
M_8O_8	all	$P6_3mc$	12

Theoretical formation energies of alloys with two end member-oxides as references are shown in Fig.2. Solution of Mg shows negative formation energies, whereas that of Cd is positive. Wide scattering of formation energy with solute configuration is noteworthy especially when M=Cd. GGA band gaps are summarized in Fig. 3. Results with negative band-gaps are hereafter omitted from the plot. Although the absolute values of the energy gap are significantly underestimated due to the usual error of GGA, their dependences on solute concentration well agree to experimental data available in literature[2,3]. In order to quantify the

electronic structures at the bottom of the conduction band, fractions of cationic s-orbitals at the lowest unoccupied state at k=0 (Γ-point) are examined. The fraction of Cd5s and Mg3s increases and that of Zn4s decreases linearly with the increase of the M-concentration (Fig.4). The bottom of the conduction band gradually changes from Zn4s to Cd5s/Mg3s characters with the M concentration.

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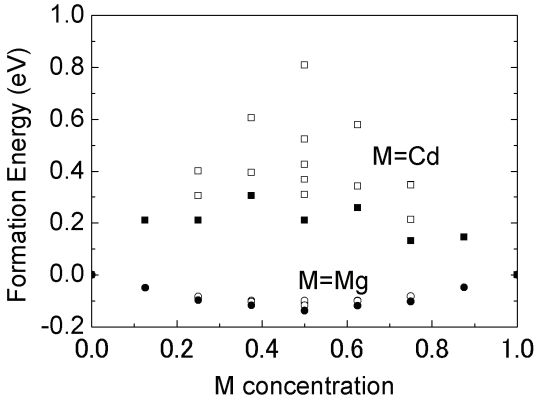

Fig.2 Theoretical formation energy of wurtzite ZnO alloys with different solute arrangements. Full marks correspond to the model showing lowest energy at given solute concentration.

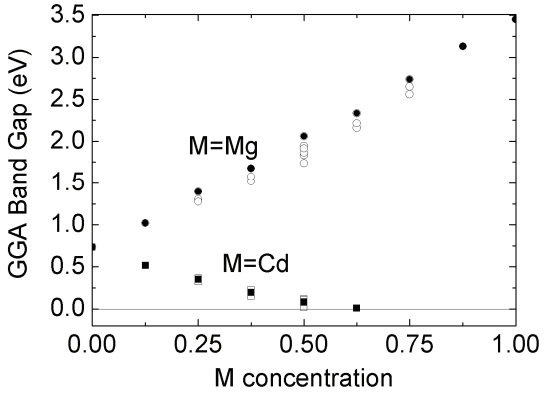

Fig.3 GGA band-gap of wurtzite ZnO alloys with different solute arrangements. Marks denote the same meaning hereafter as Fig.2.

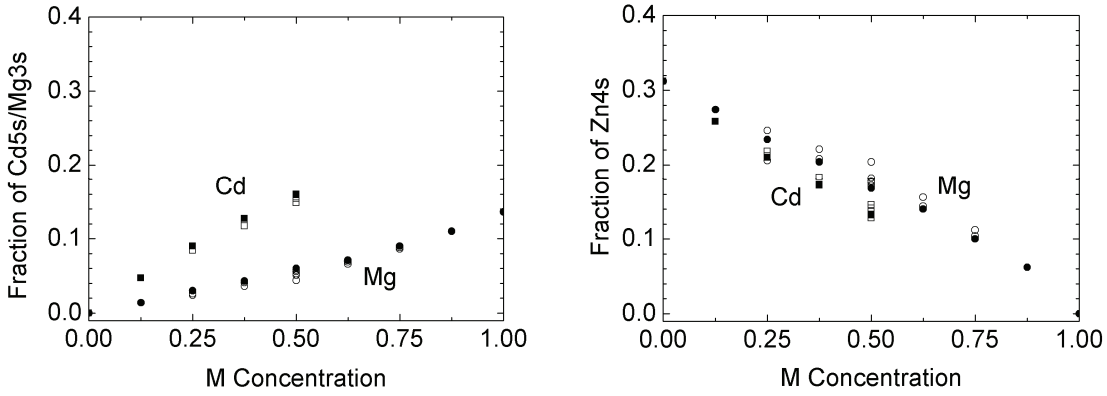

Fig.4 Orbital population of the state at the bottom of the conduction band at the Γ-point (k=0).

References
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