A First Principles Analysis of Electronic Structure of $InGaZnO_4$ with Modified Becke-Johnson Exchange Potential

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1 Introduction

Recently transparent conductive oxides (TCO) or transparent amorphous oxide semiconductors (TAOS) have been gathering much attention, since they are applicable to the thin-film transistors, thin-film light-emitting diodes, large scale liquid crystal displays, and other wide range of information and communication technology (ICT) related devices. Amorphous In-Ga-Zn-O (a-IGZO) is representative of TAOS and especially attracting attention. a-IGZO is well known for high electron mobility, wide band gap etc., and these properties are similar to crystalline IGZO (c-IGZO). It is also known that because density of states (DOS) of oxygen occupy the conduction band minimum (CBM) and valence band maximum (VBM), DOS can be strongly influenced by oxygen defect. Additionally, a-IGZO thin film transistor (TFT) can be made on a resin substrate at room temperature. Therefore, a-IGZO is expected to be applied to flexible devices.

In a first principles analysis of electronic structure based on density functional theory (DFT), exchange-correlation potential such as local density approximation (LDA) or generalized gradient approximation (GGA) tends to underestimate bandgap of semiconductors. In order to improve this issue, advanced methods such as the GW approximation or L(S)DA+U have been proposed. The GW approximation shows good reproducibility of experimental data, but it requires a huge computational effort. Moreover, the calculation of IGZO needs supercell methods which require much computational time. In our study, we calculate electronic structure with Modified Becke-Johnson (MBJ) potential [1] instead of the GW approximation. MBJ potential has a high precision which is similar in degree of the GW with a low computational time. We analyze bulk c-$InGaZnO_4$ as a first step and compare MBJ results of bulk c-$InGaZnO_4$ with those of GGA.

2 Models and Calcilation

We choose c-$InGaZnO_4$ as the calculation object because of the simple composition ratio 1:1:1:4. c-$InGaZnO_4$ has a rhombohedral unitcell and hexagonal lattice (a=b=3.295Å, c=26.071Å, α=β=90°, γ=120° [2]). This unitcell is $YbFe_2O_4$-type structure and belongs to the space group 166($R\bar{3}m$). Figure 1.(a) shows the $2 \times 2 \times 1$ supercell of $InGaZnO_4$ whose atomic positions are cited from Ref. [3]. This supercell has a layered structure composed of $InO_{1.5}$ layers and $ZnGaO_{1.5}$ layers, respectively. We calculate bulk c-$InGaZnO_4$ using a first principles calculation package WIEN2k [4], which is using density functional theory (DFT) based on the full-potential (linearized) augmented plane-wave ((L)APW)+local orbitals (lo) method (F(L)APW+lo). In practice, we calculate new monoclinic structure (a=26.071Å, a=5.707Å, c=3.295Å, α=β=γ=90°) suggested by WIEN2k shown in Fig.1.(b). Note: The new model belongs to the space group 10(P2/m), and axes of coordinate are changed because of unique axis c in 10(P2/m).

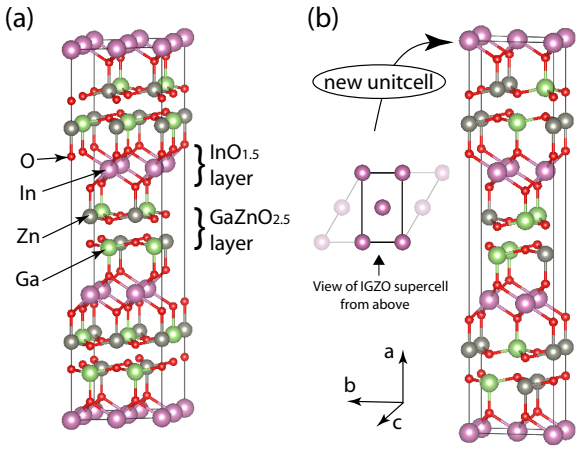

Fig. 1. (a)The supercell model of $InGaZnO_4$ which contains $(InGaZnO_4)_{12}$, (b)New model suggested by WIEN2k which contains $(InGaZnO_4)_6$.

In the calculations, at first we optimize internal structural parameters with PBE-GGA using the calculated forces on the nuclei. As regards volume optimization using total Energy, because the original structure is close to relaxed and the structure is relaxed in which case volume increases about 3%, we do not optimize throughout this paper. As for the MBJ potential, MBJ exchange potential and LSDA correlation potential (PW92) are used(see Ref.[1]). MBJ exchange potential is a modified potential of original Becke-Johnson exchange potential in order to fit bandgaps of typical semiconductors. We choose this MBJ potential and PBE-GGA for the exchange-correlation potential and compare the results of two, with the calculation condition, 500 k-point in the 1st BZ, muffin-tin radius: $R_{mt}^{In} = 2.02$ bohr^{-1}, $R_{mt}^{Ga} = 1.76$ bohr^{-1}, $R_{mt}^{Zn} = 1.96$ bohr^{-1}, $R_{mt}^{O} = 1.74$ bohr^{-1}, RKMAX=6.0, energy to separate core and valence states: −7.5Ry.

3 Results and Discussion

Fig. 2. shows band structure and density of states of bulk c-$InGaZnO_4$ with the results of GGA. Fig. 3. shows these with results of MBJ. In those figures, we define the high-symmetric point as M(0,1/2,0), K(0,1/2,1/2), Z(0,0,1/2), A(1/2,0,0), respectively. The bandgaps of

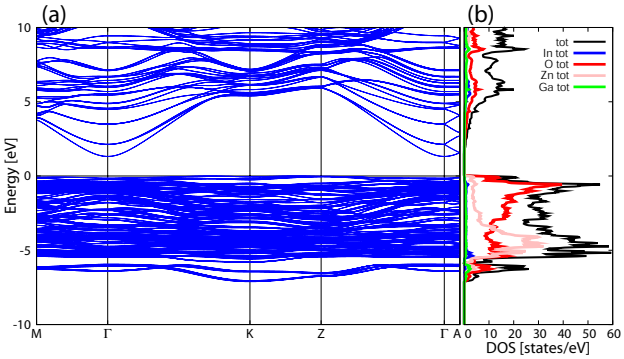

Fig. 2. (a)Electronic structure and (b) DOS calculated with GGA.

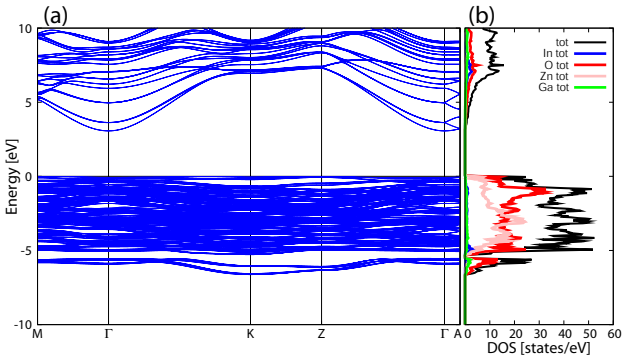

Fig. 3. (a)Electronic structure and (b) DOS calculated with MBJ.

GGA and MBJ are 1.32eV and 3.07eV, which are respectively underestimated by 62% and 12% compared to the experimental optical bandgap of 3.5eV [5]. It should be noted that the underestimation of bandgap is significantly improved with using the MBJ potential. While, there is no big difference of DOS between GGA and MBJ. Figure 4 shows an enlarged view of partial DOS with MBJ. The s state of indium (In(s)), s and p states of oxygen (O(s,p)) at the CBM, and Zn(d), O(p) at the VBM are fairly large, especially oxygen occupy both the CBM and VBM. Table I. shows the effective masses of electron from Γ point. These values are calculated by fitting from -5% to 5% of the CBM in the 1st BZ(e.g. from $-0.05(\pi/a)$ to $0.05(\pi/a)$) to $E = \hbar^2 k^2/2m^*$. It is found that c-$InGaZnO_4$ has the isotropic effective mass of an electron: GGA $0.21m_0$ and MBJ $0.33m_0$. It is noteworthy that the result from the present MBJ $0.33m_0$ is quite comparable to the experimental value of $0.32m_0$ [6].

4 Conclusion

We have performed a first principles calculation with modified Becke-Johnson (MBJ) potential for bulk c-$InGaZnO_4$. As a result, it is found that the underestimations of the bandgap and the effective mass of electron are considerably improved by using MBJ potential in a first principles calculation for c-$InGaZnO_4$ and results from MBJ were close to experimental values. Such high precision values are obtained within as much as 10 times computational time of the GGA calculation. It is also found that states of oxygen significantly occupy the CBM and VBM.

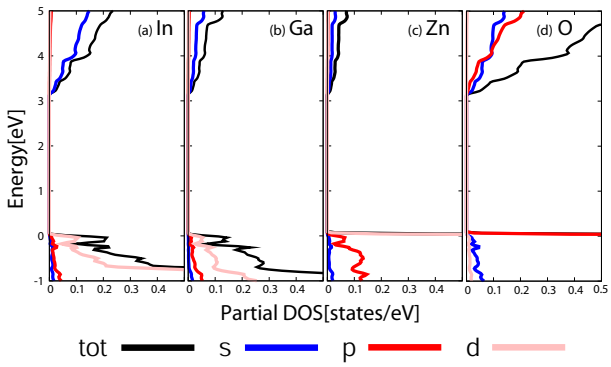

Fig. 4. Enlarged partial DOS of (a)In (b)Ga (c)Zn and (d)O calculated with MBJ.

Acknowledgments

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Table I. The effective mass of electron along each directions from Γ point.

	effective mass (m^*/m_0)	
directions	GGA	MBJ
Γ → M ([010])	0.209	0.333
Γ → K ([011])	0.208	0.326
Γ → Z ([001])	0.207	0.322
Γ → A ([100])	0.196	0.341

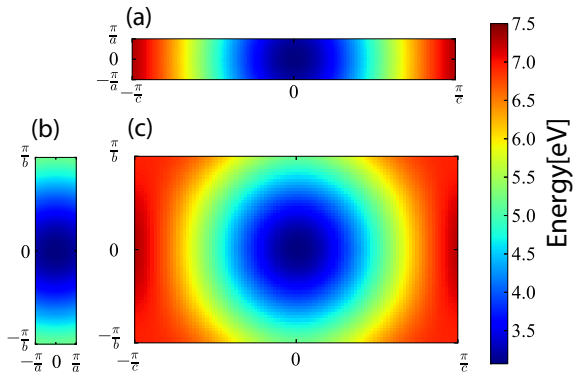

Fig. 5. Energy contours of the CBM in the 1st BZ. (a) a^*c^* plane, (b) a^*b^* plane, (c) b^*c^* plane, respectively.