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P7-10

A Theoretical Study on Influence of Oxygen Vacancies on the Electronic Properties of Indium Oxide and Indium Tin Oxide

Chen Lv[1], Xiaojing Wang[1], Agalya Govindasamy[1], Hideyuki Tsuboi[1], Michihisa Koyama[1], Akira Endou[2], Momoji Kubo[1, 3], Ewa Broclawik[4] and Akira Miyamoto[1, 4, *]

[1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan.
[2]Institute of Fluid Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.
[3]PRESTO, Japan Science and Technology, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.
[4]New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan.
*Fax: +81-22-795-7233, Phone: +81-22-795-7235, e-mail: miyamoto@aki.che.tohoku.ac.jp

1. Introduction

Interest in transparent conductors can be tracked back to the beginning of twentieth century [1] when the transparent and conductive properties of cadmium oxide film was first reported. Ever since there has been a growing technological interest in materials with these unique properties, as evidenced by not only their increased numbers but also the large variety of techniques that have been developed for their deposition. Recently, with the rapid development of organic light-emitting devices (OLED), many researches have focused on the most favored transparent conducting oxides, such as indium tin oxide (ITO). ITO can be regarded as one of the most suitable anode materials of OLED because of its high electronic conductivity, high transparency in visible range and high reflectivity [2]. Although ITO is prepared as a thin film for most commercial and research purposes, the understanding of the bulk properties of ITO is still important. Information concerning bulk properties is critical to understand the properties of the thin films of ITO. It is difficult, however, to determine band structure of ITO by experiment. Only a few experimental and theoretical studies on the band structure of n-type bulk ITO have been reported [3]. Moreover, less work has been done to investigate the influence of oxygen deficiencies on band structure and conductivity of ITO and its parent material indium oxide (In_2O_3).

In the present study, we combine our original accelerated quantum chemical molecular dynamics program "Colors" and the density functional theory (DFT) method to investigate the geometry, electronic properties, band structure and density of states for In_2O_3 and ITO with oxygen vacancies. Furthermore, the influences of oxygen vacancies, tin-doping site and tin content on the electronic properties, band structure and conductivity of In_2O_3 and ITO were investigated by both DFT and our accelerated quantum chemical molecular dynamics method.

2. Computational Methods

The accelerated quantum chemical molecular dynamics program "Colors" [4], which is based on our original tight-binding approximation, was used for the present simulation. It realized 5000 times acceleration compared to the traditional first-principles molecular dynamics method. In order to validate the accuracy of our original accelerated quantum chemical molecular dynamics program "Colors", first-principles DFT calculations were performed by DMol[3] program under the periodic boundary condition. The basis set of double numerical plus polarization functions (DNP) were used. Effective core potentials were used for indium and tin below the 4d and 5s orbitals, respectively. The calculations were performed using the Vosko-Wilk-Nusair local correlation functional (LDA). The thermal smearing was applied to orbital occupation to accelerate SCF convergence of band calculations.

3. Results and Discussion

The calculated bulk structures of $In_{32}O_{47}$ and $In_{30}Sn_2O_{47}$ were constructed by removing oxygen anions from the structure of the cubic bixbyite indium oxide that is very useful for understanding the properties of ITO. Fig. 1 depicts the geometries of the $In_{32}O_{47}$ and $In_{30}Sn_2O_{47}$ (In_2O_3 with 10% SnO_2 dopant) calculated by DFT under the periodic boundary conditions. In the models, the properties of indium oxide and ITO with oxygen vacancy were calculated by using "Colors" program. The position of oxygen vacancy was determined randomly. For indium oxide with oxygen vacancy, the band gap energy of 3.63 eV was obtained, while for ITO with oxygen vacancy, the band gap energy of 3.83 eV calculated by "Colors" program is 0.06 eV larger than that of ITO without oxygen

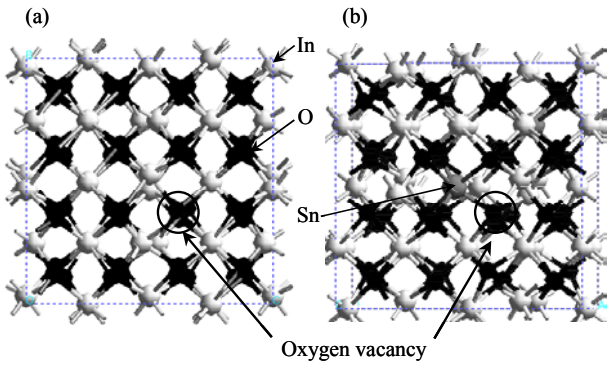

Fig. 1 The structure of (a) $In_{32}O_{47}$ (b) $In_{30}Sn_2O_{47}$. The white sphere represents indium atom, the dark gray one is tin atom and the black one is oxygen atom.

vacancy [5]. Fig. 2 shows the calculated partial density of states (PDOS) of oxygen and indium for (a) $In_{32}O_{48}$ and (b) $In_{32}O_{47}$. From the PDOS for $In_{32}O_{47}$, it was observed that similarly to indium oxide, O 2p orbital mainly contributes to the top of valence band, while the bottom of conduction band consists of In 5s. In variance to indium oxide, a new feature called donor level appeared between the top of valence band and bottom of conduction band. The analysis of the PDOS shows that this level originates mainly from anti-bonding states between In 5s and O 2p states.

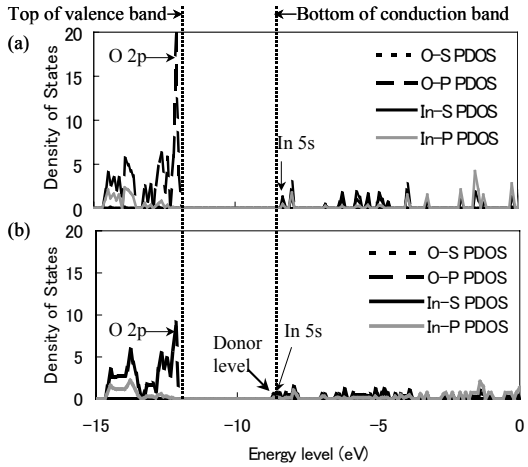

Fig. 2. PDOS for oxygen and indium of (a) $In_{32}O_{48}$ and (b) $In_{32}O_{47}$.

Moreover, Fig. 3 depicts the PDOS for oxygen, indium and tin of (a) ITO without oxygen vacancy and (b) ITO with oxygen vacancy. Comparing the PDOS of Fig. 3(a) with that of Fig. 3(b), one can observe that overall features of PDOS corresponding to the top of valence band and the bottom of the conduction band of ITO are almost conserved except for the appearance of two new levels just below the conduction band. Similarly to their parent material indium oxide, for both ITO with oxygen vacancy and without oxygen vacancy the top of valence band mainly composed of O 2p. Compared to ITO without oxygen vacancy, however, the top of valence band shifts to lower energy level. While the levels at the bottom of conduction band are mostly composed of unoccupied anti-bonding molecular orbitals of Sn 5s and O 2p origin. The two new levels show the same characteristic as the bottom of conduction band, i.e., these two levels are also anti-bonding molecular orbitals of Sn 5s and O 2p. The above results show that these new impurity levels are occupied excess electrons produced by Sn-doping and oxygen vacancy. The existence of these levels will increase the conductivities of ITO. From the analysis of orbital occupation, degenerate singly occupied orbitals of tin origin and doubly occupied vacancy level were found. The donor level (II) shown in Fig. 3 (b) is the overlap bands caused by two doped-Sn atoms, while the existence of oxygen vacancy leads to the appearance of the new donor level (I). From Fig. 3, it can be observed easily that donor level (II) lie closer to the bottom of conduction bands than donor level (I). This result demonstrates that tin is more efficient for increasing the conductivities of ITO.

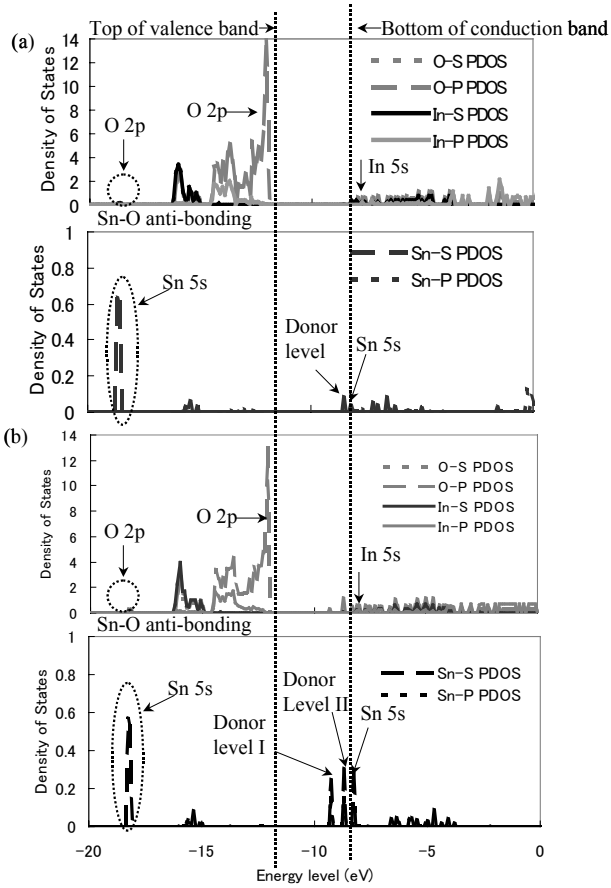

Fig. 3. PDOS for oxygen, indium and tin of (a) $In_{30}Sn_2O_{48}$ and (b) $In_{30}Sn_2O_{47}$

4. Conclusions

In the present study, our original accelerated quantum chemical molecular dynamics program "Colors" was used to challenge the study on influence of Sn impurities and oxygen vacancy on the electronic structure of ITO. As a result, it was clarified that due to the existence of the substituted Sn atom and oxygen vacancy, the impurity states are formed leading to the increase of conductivities of ITO.

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