Transactions of the Materials Research Society of Japan. Vol. 20

First-principles study on the electronic structure of indium tin oxide

H.Odaka(a), S.Iwata(a), S.Ohnish(b), Y.Shigesato(a), I.Yasui(a), Y.Hashi(c), Y.Kawazoe(d)
(a) The University of Tokyo (b) NEC fundamental Research Labs. (c) Hitachi Tohoku Software
(d) Tohoku University

(Abstract)

First-principles study on the electronic structure of indium tin oxides (ITO) is presented. A new software called Castep(1) was used to investigate the electronic structure of ITO: the density of state was calculated for pure In2O3 and substitutional point defect of In by Sn respectively. The feasibility of electronic structure calculation treatment is discussed: the pseudopotential model and the treatment of partial occupancies for levels close to Fermi energy.

1. Introduction

Indium tin oxide (ITO) is a highly degenerate wide-gape semiconductor. Because of its high transmissivity to visual light and low electrical resistivity, thin-film ITO is used in many optical applications. With recent demands for large size and high quality display panel, ITO films are required to have extremely low resisitivity for both type of the displays. It is necessary to understand the electronic conducting mechanism form the viewpoint of electronic structure, because it reduces to the one of the most important conception to make the lower resisitivity films.

In this study we demonstrated an attempt of first-principles electronic structure calculation for pure In2O3 and substitutional point defect of In by Sn. Discussion is foucused on the feasibility of first-principles calculation treatment. Since we have assumed no charge compensation in this study, the change of electronic structure from semiconductor to metal arises from introducing the substitutional point defect of In by Sn, i.e. we can expect that the point defect system will be metallic with one of the low-lying states half-filled. To treat such a phase transition of electronic structure, Castep introduced the scheme of partial occupancies for levels close to Fermi energy. We checked the reliability of this scheme by calculating the electronic structure of pure In2O3 and substitutional point defect of In by Sn. The ability of treating phase transition of electronic structure plays one of the most important roles in analyzing the electronic structure of point defects.

2. Method

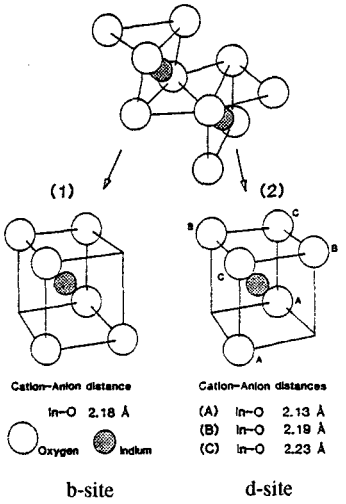
The Castep is a first-principles electronic structure calculation program. The theoretical basis of this program is density functional theory(2) (DFT) with local density approximation(3) (LDA). The ion-electron interaction is described using a pseudopotential concept. Potential for O, In and Sn atom have been generated using the optimization scheme(4) of Lin et al. This optimization ensure that the potentials are transferable and sufficient soft. To accelerate computational speed, pesudopotential is rewritten by separable Kleinman-Bylander form(5) and the real space implementation scheme(6) is introduced. Electronic structure in ground state is obtained by minimizing the total energy. The electronic wavefunction is expanded using plane-wave basis set, and the expansion coefficients are varied so as to minimize the total energy. This minimization can be achieved by using band-by-band technique(1), where each wave function is optimized independently. For integration of over the Brillouin zone, special k-points method(7) is used. Partial occupancies for levels close to Fermi energy is introduced for metallic system(8).

3. Results and Discussion

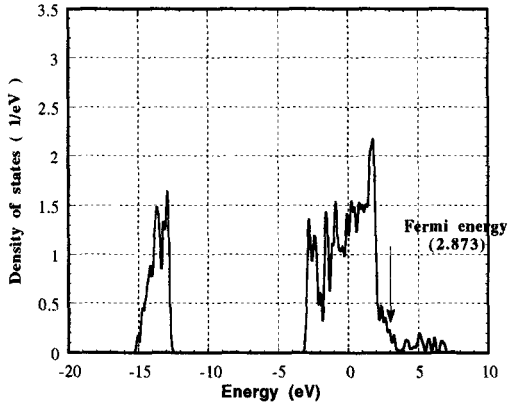
In2O3 is the host crystal of ITO: it takes bixbyite type crystal structure at atmospheric pressure. There are two non equivalent crystallographic sites of indium atom as shown in (Fig.1). In this study we call these two site b-site and d-site respectively. To model ITO, an indium atom in conventional unit cell was chosen and substituted by a tin atom. We performed electronic structure calculations for two type of systems: pure In2O3 crystal; indium tin oxide in which a b-site indium is substituted by Sn. A plane wave basis corresponding to an energy cutoff of 500 eV (~13000 plane waves) was treated. The scheme of partial occupancies for levels close to Fermi energy was employed: after four extra bands were added and artificial electronic temperature(5 eV) was introduced by assuming gaussian-like smearing of each energy level, the smearing width was periodically halved during the calculation and was reduced to 0.1 eV finally. Calculated density of state for both systems are shown in (Fig.2) and (Fig.3), respectively. We found that the electronic structure of pure In2O3 converged to metallic state, which was not coincide with experimental fact. To investigate this reason, we recalculated the electronic structure of pure In2O3 with full occupancies: we treated only valence band electron. Calculated density of state is shown in (Fig.4), which converged correct semiconductor-like density of state. We found that the problem of wrong convergence did not depend on the pesudopotential model but depended on the treatment of partial occupation.

4. Summary and conclusion

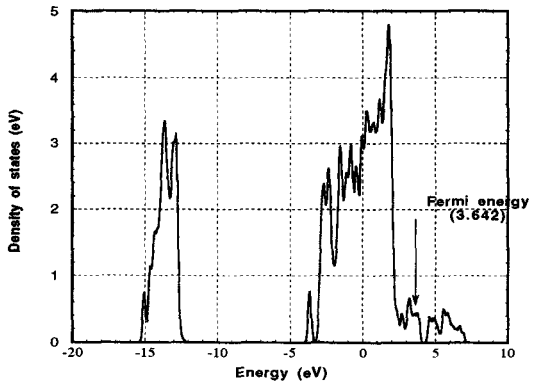
We performed first-principles calculation on the electronic structure of ITO. The converged electronic structure was found to be sensitive for the treatment of partial occupation even to pure In2O3 crystal. To analyze the electronic structure of points defect of ITO, we must determine suitable partial occupation condition.



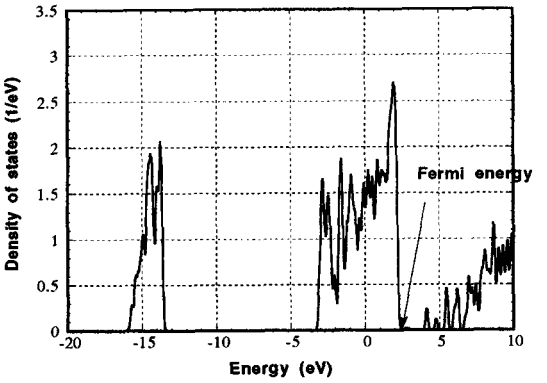
(Fig.1) Bixbyte type crystal structure of In2O3



(Fig.2) Density of states of In2O3: the scheme of partial occupancies was introduced.



(Fig.3) Density of states of indium tin oxide in which a b-site indium was substituted by Sn: the scheme of partial occupancies was introduced



(Fig.4) Density of states of In2O3: only valence electron was treated in the calculation procedure.

References

1. Payne, M. C. et al., Rev. Mod. Phys., 64,1045 (1992)
2. Hohenberg, P., and W.Kohn, Phys. Rev. 136, 864B (1964)
   Kohn, W., and L. J. Sham, Phys. Rev. 140, 1133A (1965)
3. Kohn, W., and L. J. Sham, Phys. Rev. 140, 1133A (1965)
4. Lin, J. S. et al., Phys. Rev. B47 4147 (1993)
5. Kleinman, L., and D. M. Bylander, Phys. Rev. Lett. 4, 1425 (1982)
6. King-Smith, R. D., M. C. Payne, and M, J-S Lin, Phys. Rev. B44. 13063 (1991)
7. Monkhorst, H. J., and J. D. Pack, Phys. Rev. B13, 5188. (1991)
8. de Vita, A., Ph. D. Thesis, Keele Univ., UK (1992)