

Tin Doping Mechanism in Indium Oxide by MD Simulation

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In order to investigate Sn substitution sites and interstitial O atoms in tin-doped indium oxide, molecular dynamics (MD) simulations were carried out. There are two kinds of cation sites in In_2O_3 , namely b-site and d-site. NTP-MD simulations under the condition of 300 K and 0 GPa were performed with two kinds of cells substituted by Sn atoms at each site. The excess oxygen atom accompanied with Sn doping was also taken into consideration. According to the calculations of Sn potential energies in each site, it was revealed that Sn atoms were substituted for b-sites rather than for d-sites. It was also revealed that the interstitial excess oxygen atoms tend to be connected with the Sn atoms substituted for the d-sites Sn rather than for the b-site. These MD simulation results well agreed with the experimental results.

Key words : ITD, MD, Simulation, Doping mechanism, Substitution site

I. Introduction

Tin doped indium oxide (ITO) shows a high transmittance of more than 80% in the visible region of light between the wavelengths corresponding to the absorption edge in the ultraviolet and the plasma wavelength in the infrared.¹⁾ ITO is an n-type semiconductor with a band gap of approximately 3.8 eV. It has a high carrier density of the order of 10^{20} cm^{-3} and hence a low resistivity of the order of $10^{-4} \text{ ohm}\cdot\text{cm}$. Because of these electrical and optical properties, ITO has been used in a variety of optoelectronic devices, such as liquid crystal displays and solar cells. Many studies on the relationship between fabrication process and the properties have been performed in an effort to produce high quality films, because the electrical and optical properties of the films strongly depend on the preparation methods used.

Numerous investigations on the microscopic structure and the mechanism of the conductivity of ITO have also been performed.^{1,2)} In_2O_3 has a cubic bixbyite structure that includes 80 atoms per unit cell. The bixbyite structure is similar to the fluorite structure except that every fourth anion is missing. It includes two kinds of non-equivalent sites of indium. Some of the indium atoms (8/32) occupy the center of the trigonally distorted oxygen octahedra (b-sites) and the rest (24/32) of the indium atoms occupy the center of the more distorted octahedra (d-sites).³⁾ Mössbauer results suggest that Sn(IV) atoms substituted for In at b-sites rather than d-sites.^{4,5)} The results of extend X-ray absorption fine structure (EXAFS) suggest that Sn atoms induce disorder in the indium oxide structure.^{6,7)} The oxygen concentration in ITO films on

glass substrates fabricated by reactive ion sputtering was determined by Rutherford backscattering (RBS) analysis and it has been concluded that the ratio of O/In varied from 0.4 to 1.5 depending on the preparation conditions and the depth from the film surface.⁸⁾ Free carriers in the ITO are considered to be supplied from oxygen vacancies and substitutional Sn.^{1,2,9)}

The molecular orbital calculations of ITO have been performed and these studies investigated the relationship between electronic states and conductivity.¹⁰⁾ However, the research on atomic configurations with Sn doping has not yet been performed. Since Sn atoms are considered to be substituted for In atoms in ITO, O atoms around the Sn atoms have to be relaxed with the Sn substitution. Also, from the viewpoint of charge balance, excess oxygen atoms have to be introduced into the lattice doping of Sn. In this study, molecular dynamics (MD) simulations were carried out in order to investigate the Sn doping mechanism from the relaxed structure. The MD cell of ITO was constructed to investigate the behavior of both substitutional Sn atoms and interstitial O atoms introduced with Sn doping. The configurations around the Sn atoms substituted at each site were simulated and the potential energies of the Sn atoms were calculated. On the basis of MD results, we discussed about the relationship between Sn content and conductivity in ITO.

II. Experimental Procedure

All MD simulations were carried out with a computer-software MASPHYC (Fujitsu Co., Ltd.). Periodic boundary conditions were used for MD cells. The integration time

step was 1 fs and the total simulation time was 5 ps (equal to 5000 steps). The Coulomb interaction forces for each atom were calculated using the Ewald method. The effective charges of In, Sn and O atom are defined as +1.8, +2.4 and -1.2, respectively. Born-Mayer-Huggins (BMH) type potential was used (equation 1). Each pair i - j of atoms separated by a distance r_{ij} was assigned a potential energy as follows, where Z is the charge and A_{ij} and B_{ij} are adjustable parameters:

$$\phi_{ij}(r_{ij}) = k \frac{Z_i Z_j}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) \quad (1)$$

1. Determination of potential parameters

The MD simulations were carried out under the conditions of constant temperature and volume (NVT ensemble) to optimize potential parameters. The MD cells of In_2O_3 and SnO_2 crystal structure as an initial configuration consisted of 640 ($2a \times 2b \times 2c$) and 1050 ($5a \times 5b \times 7c$) particles, respectively. When the mean pressure during last 1 ps was approximately equal to 0 GPa under the condition of 300 K (NVT ensemble), the potential parameter set was determined. The MD simulations using the parameters were performed with the same cells under the condition of constant temperature and pressure (NPT ensemble), and the mean lattice constants during last 1 ps were compared with the experimental ones.

2. MD simulations of ITO

When Sn atoms were substituted for In atoms of In_2O_3 lattice, O atoms were introduced in the lattice in order to compensate for the total charge of the system. As two

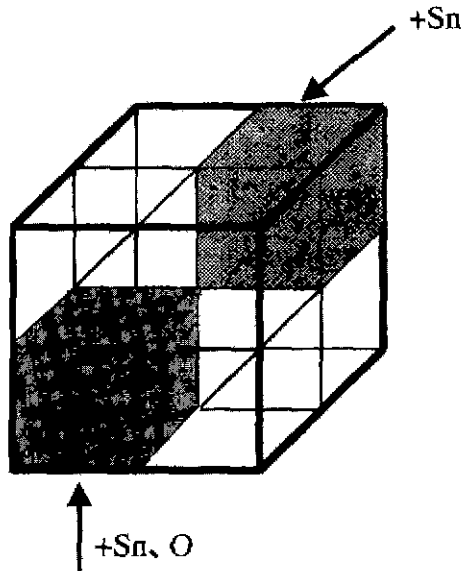


Fig. 1. Schematic representation of a MD cell of ITO: (A) the cell included one Sn atom substituted for one In atom; (B) the cell had one Sn atom substituted at the same In site and one interstitial O atom was introduced; Other six cells were identical to the In_2O_3 unit cell.

Sn atoms were substituted for two In atoms per unit cell, one excess O atom was introduced into the cell. Neutron diffraction study suggested that the excess O atoms occupied the $(1/8, 1/8, 1/8)$ site.¹¹ MD cells of ITO shown in Fig. 1 were constructed. The cell was composed of eight In_2O_3 unit cells. One of the unit cells included one Sn atom substituted for one In atom. Another unit cell had one Sn atom substituted at the same In site and one interstitial O atom was introduced, as consequence only this cell consisted of 81 atoms. Other six cells were identical to the In_2O_3 unit cell. Hence the MD cell of ITO consisted of 641 particles. The MD simulations were carried out under the conditions of constant temperature and pressure.

III. Results

1. Determination of potential parameters

a) SnO_2

The B_{ij} parameters of O-O were varied from 2.5 to 5.0 and NVT-MD simulations were carried out with the SnO_2 cell at 300 K. The potential parameters of Sn-O were determined corresponding to each O-O parameter. Using the obtained parameters, NPT-MD simulations of SnO_2 were done under the condition of 300 K and 0 GPa, and the lattice constants were averaged over last 1 ps. The calculated lattice constants versus the O-O parameters are summarized in Fig. 2. At $B_{O-O}=2.71$, the difference between the calculated and the experimental lattice constant almost became zero. Therefore the parameters of Sn and O were determined at $B_{O-O}=2.71$.

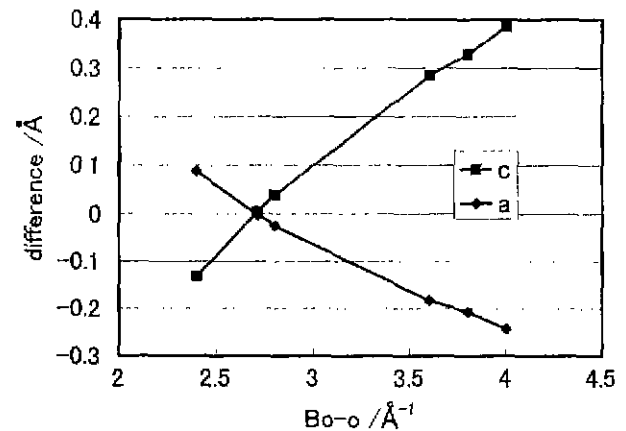


Fig. 2. Potential parameter B_{O-O} versus difference between the observed and calculated SnO_2 lattice constant.

Table 1. Pair Potential Parameters A_{ij} and B_{ij} of Eq. (1)

	A_{ij}/J	$B_{ij}/\text{\AA}^{-1}$
In-O	6.8331E-16	4.2785
O-O	6.1703E-17	2.7100
In-In	4.7268E-15	5.0000
In-Sn	4.2693E-15	5.0000
Sn-O	8.7220E-15	5.6647
Sn-Sn	3.8811E-15	5.0000

Table 2. Lattice Parameters of In_2O_3 , Calculated by the NTP-MD Simulations (T=300K, P=0 GPa)

	a	b	c	α	β	γ
In_2O_3	10.118	10.118	10.118	90.000	90.000	90.000
MD	10.118	10.119	10.118	90.015	80.994	90.000

Table 3. Mean Bond Distances of In-O at Each In Site(unit Å)

b-site MD	In_2O_3	d-site MD	In_2O_3
2.182	2.192	2.114	2.120
2.180	2.192	2.115	2.121
2.183	2.192	2.201	2.191
2.180	2.191	2.203	2.193
2.181	2.191	2.222	2.209
2.184	2.191	2.222	2.210

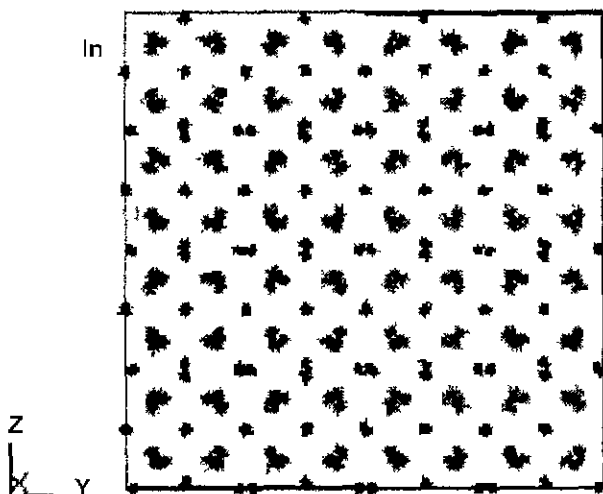
b) In_2O_3

By the method identical to the SnO_2 potential determination, NTV-MD simulations were performed with the In_2O_3 cell at 300 K. The potential parameters of In-O were determined and summarized in Table 1. With the obtained parameters, NTP-MD simulations of In_2O_3 was done under the condition of 300K and 0 GPa, and the lattice constants were averaged over last 1000 steps and listed in Table 2. The crystal structure of In_2O_3 is almost reproduced. Table 3 summarizes the mean In-O distances calculated from the simulated configuration. The trajectory during the simulation was illustrated in Fig. 3.

2. MD simulations of ITO

Using the ITO MD cells which had the Sn atom substituted for the In atom at b-site or d-site, the NTP-MD simulations were carried out with the parameters listed in Table 1 under the condition of 300 K and 0 GPa. No atoms including interstitial O atom jumped to other sites during simulation.

The average potential energy of each Sn atom was calculated from last 1000 steps and summarized in

**Fig. 3.** Trajectories of indium and oxygen atoms during NTP-MD simulation.**Table 4.** Calculated Energies of Sn Atoms Substituted for each In Site: 7-cod is a 7-fold Oxygen Coordinated Sn atoms; 6cod is a 6-fold Coordinated Sn Atom

	b-site/eV	d-site/eV
6cod	-56.690	-56.451
7cod (6+O _{interstitial})	-58.861	-59.232

Table 4. All In atoms in In_2O_3 are 6-fold oxygen-coordinated. In Table 4, the 6-fold coordinated Sn means the Sn atom was normally substituted for the In atom. The 7-fold coordinated Sn means the Sn atom was substituted for the In atom and, in addition, combined with the interstitial O atom introduced. According to Table 4, in the case of 6-fold coordination, the value of the Sn potential energy at b-site was lower than that at d-site. On the other hand, in the case of 7-fold coordination, the value of the Sn potential energy at d-site was lower than that at b-site.

IV. Discussion**1. Reproduction of bixbyite crystal structure**

There are two kinds of cation sites in In_2O_3 bixbyite structure. The bond distances between the cation at b-site and the nearest neighbor O atoms are equivalent, and the distances at d-site are non-equivalent. In general, the MD simulation only with pair potential is capable of reproducing isotropic configuration, but it has some difficulty in reproducing unisotropic structure. When the NTP-MD simulation was done with the potentials in Table 1, it was observed that all atoms vibrated at their own sites shown as the trajectory in Fig. 3. Moreover, the mean distances of In-O were calculated in Table 3. Because all differences between the calculated and observed distances were less than 0.015 Å, the calculated distances at both sites were well agreed with the experimental ones.

2. MD simulations of ITO

Mössbauer results suggest that, at low Sn content, Sn atoms are substituted at b-sites rather than d-sites, and that at high Sn content Sn atoms, at d-site and/or 7-fold coordinated Sn atoms increased with Sn content. According to MD simulation results in Table 4, the Sn atom at b-site was more stable than at d-site in the case of 6-fold coordination because the configuration at b-site is similar to that in SnO_2 crystal structure. It is supposed that the Sn atom is preferentially substituted for In atom at b-site. On the contrary, the Sn atom at d-site was more stable than at b-site in the case of 7-fold coordination by the interstitial O atom introduced. It is assumed that Sn atoms at d-site tend to combine with the interstitial O atom. The calculated mean Sn-O distances were listed in Table 5.

In 6-fold coordination, because of the substitutional solid

Table 5. Mean Bond Lengths of Sn-O Calculated from NTP-MD Simulations ($T=300$ K, $P=0$ GPa) (unit Å)

6 fold coordination			7-fold (6+O _{interstitial})		
In ₂ O ₃	b-site	In ₂ O ₃	d-site	b-site	d-site
2.191	2.043	2.119	2.023	2.138	2.043
2.191	2.043	2.121	2.024	2.178	2.042
2.191	2.057	2.191	2.051	2.141	2.228
2.192	2.053	2.193	2.043	2.142	2.283
2.192	2.043	2.209	2.087	2.142	2.111
2.192	2.043	2.210	2.073	2.134	2.191
interstitial				2.079	2.038

solution of the Sn(IV) atom whose ionic radius is smaller than In(III) atom, the mean Sn-O distances in both sites were shorter than those of In-O in In₂O₃. On that occasion their configurations were almost similar to that in In₂O₃.

Next, in 7-fold coordination, the bonds in d-sites were well relaxed and the bond between the Sn and the interstitial O was not able to be distinguished from other Sn-O bonds. On the contrary, in the case of b-site, the bond distance between the Sn atom and the interstitial O atom were shorter than those of other bonds. This configuration causes that the Sn atom substituted at b-site was less stable than at d-site in the case of 7-fold coordination.

Frank and Köstlin^{9,12)} examined the relationship between Sn content and conductivity in ITO films. In low Sn content, the conductivity of ITO increased linearly with Sn concentration. However, in high Sn content, the Sn doping efficiency dropped with increasing Sn concentration. MD simulation results suggest that the Sn atoms tend to be substituted at b-site and then they are little likely to combine with the interstitial O atoms. In this case, Sn doping efficiency was expected to be very high. Since it was reported that In₂O₃ and ITO have oxygen vacancies, in low Sn content the concentration of interstitial O atoms was supposed to be low. At that time the fraction of Sn atoms at b-site was assumed to be high and it was considered that the conductivity increases almost linearly with Sn content. Next, in high Sn content, the fraction of the Sn atoms at d-site increased with Sn content. Because the Sn atoms at d-site tend to be 7-fold coordinated, they were assumed to combine with the interstitial O atoms more easily. Since such Sn atoms did not play a role of donors, the doping efficiency was low in high Sn content. Although the relationship between the conductivity and Sn content in ITO are considerably complex, the results in this work provided a microstructural basis to explain the relationship consistently.

V. Conclusions

In order to investigate Sn substitution sites and in-

terstitial O atoms in ITO, MD simulations were carried out with the optimized potentials against In₂O₃ and SnO₂. In 6-fold coordination Sn atoms tend to be substituted at b-sites rather than d-sites and in 7-fold coordination they were likely to be substituted at d-site. This result was in good agreement with Mössbauer results and was able to explain the relationship between Sn content and conductivity in ITO.

References

1. I. Hamberg and C. G. Granqvist, "Evaporated Sn-doped In₂O₃ Films: Basic Optical Properties and Applications to Energy-efficient windows," *J. Appl. Phys.*, **60**(11), R123-159 (1986).
2. J. C. C. Fan and J. B. Goodenough, "X-ray Photoemission Spectroscopy Studies of Sn-doped Indium-oxide Films," *J. Appl. Phys.*, **48**(8), 3524-3531 (1977).
3. M. Marezio, "Refinement of the Crystal Structure of In₂O₃ at two Wavelengths," *Acta Cryst.*, **20**, 723-728 (1966).
4. K. Nomura, Y. Ujihira, S. Tanaka and K. Matsumoto, "Characterization and Estimation of ITO (Indium-Tin-Oxide) by Mossbauer Spectroscopy," *Hyper-fine Interactions*, **42**, 1207-1210 (1988).
5. N. Yamada, Y. Shigesato, I. Yasui, H. Li, Y. Ujihira and K. Nomura, "Estimation of Chemical States and Carrier Density of Sn-doped In₂O₃ (ITO) by Mössbauer Spectroscopy," *Hyper-fine Interactions*, **112**, 213-216 (1998).
6. Ph. Parent, H. Dexpert, G. Tourillon and J. M. Grimol, "Structural Study of Tin-doped Indium Oxide Thin Films Using X-ray Absorption Spectroscopy and X-ray Diffraction. I Description of the Indium Site," *J. Electrochem. Soc.*, **139**(1), 276-281 (1992).
7. Ph. Parent, H. Dexpert, G. Tourillon and J. M. Grimol, "Structural Study of Tin-doped Indium Oxide Thin Films Using X-ray Absorption Spectroscopy and X-ray Diffraction. II. Tin Environment," *J. Electrochem. Soc.*, **139**(1), 282-285 (1992).
8. S. Honda, A. Tsujimoto, M. Watamori and K. Oura, "Depth Profiling of Oxygen Concentration of Indium Tin Oxide Films Fabricated by Reactive Sputtering," *Jpn. J. Appl. Phys. Part 2*, **33**, L1257-L1260 (1994).
9. G. Frank and H. Köstlin, "Electrical Properties and Defect Model of Tin-doped Indium Oxide Layers," *Appl. Phys. A*, **27**, 197-206 (1982).
10. M. Mizuno, T. Miyamoto, T. Ohnishi and H. Hayashi, "Effects of Tin Doping and Oxygen Vacancies on the Electronic States of Indium Oxide," *Jpn. J. Appl. Phys.*, **36**, 3408-3413 (1997).
11. N. Nadaud, M. Nanot, J. Jove and T. Roisnel, "Structural Study of Tin-doped Indium Oxide (ITO) Ceramics Using ¹¹⁹Sn Mössbauer Spectroscopy and Neutron Diffraction," *Key Eng. Mat.*, **132-136 Part II**, 1373-1376 (1997).
12. H. Köstlin, R. Jost and W. Lems, "Optical and Electrical Properties of Doped In₂O₃ Films," *Phys. Stat. Sol.*, **29**, 87-93 (1975).