



Study on the intrinsic defects in tin oxide with first-principles method

Yu Sun^a, Tingyu Liu^{a,b,*}, Qiuxiang Chang^a, Changmin Ma^a

^a College of Science, University of Shanghai for Science and Technology, Shanghai 200093, China

^b Shanghai Key Lab of Modern Optical System University of Shanghai for Science and Technology, Shanghai 200093, China



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ABSTRACT

First-principles and thermodynamic methods are used to study the contribution of vibrational entropy to defect formation energy and the stability of the intrinsic point defects in SnO₂ crystal. According to thermodynamic calculation results, the contribution of vibrational entropy to defect formation energy is significant and should not be neglected, especially at high temperatures. The calculated results indicate that the oxygen vacancy is the major point defect in undoped SnO₂ crystal, which has a higher concentration than that of the other point defect. The property of negative-U is put forward in SnO₂ crystal. In order to determine the most stable defects much clearer under different conditions, the most stable intrinsic defect as a function of Fermi level, oxygen partial pressure and temperature are described in the three-dimensional defect formation enthalpy diagrams. The diagram visually provides the most stable point defects under different conditions.

1. Introduction

Transparent conducting oxides (TCOs) are the focus of people's attention because of its high electrical conductivity, low absorbance (less than 20% in the visible light range) and electrochemical stability [1]. They have been used in a wide range of areas such as gas-sensor technology, for solar cells, optical electronic device etc. [2–5]. The presence of point defects or doping may be generally the cause of conductivity in conducting oxides.

In recent years, people pay more and more attention to the research of the wide-band-gap semiconductor oxides. The most material for transparent electrodes is indium tin oxide (ITO) in the current market. However, the material of indium is rare and expensive. With the development of the application fields, it is necessary to search for new materials. Zinc oxide (ZnO) and tin oxide (SnO₂) are considered as the most suitable alternative materials. Compared with ZnO, SnO₂ has a wider band gap, a lower preparation temperature, and a more stable electrochemical stability. SnO₂, therefore, is a promising material that has been studied for many years. As we all know, SnO₂, with good optical properties, is a kind of TCO. The band gap of SnO₂ is 3.6 eV at room temperature [6,7]. Pure SnO₂ is theoretically an insulator because of its wide band gap. In fact, SnO₂, the same as other wide band gap oxides (ZnO, In₂O₃), is n-type semiconductor. The reason for the conductivity of SnO₂ may be that the tin ion is a multi-valence element, which is easy to produce oxygen vacancy or tin interstitial in the lattice and these point defects can be easily excited electronic at room temperature [8]. There are many reports about

the electronic structure and optical properties of tin oxide [9–13]. In fact, tin oxide crystals will often introduce many intrinsic defects in preparation, and the intrinsic defects can capture or scatter carriers, which affect the carrier transport. However, reason for conductivity is rarely reported, and the calculation of defect formation energy (DFE) is relatively few. Only in recent years, a few papers are reported referring to point defects in SnO₂. For example, Kumar and Anderson et al. calculated the defect formation energies and studied the reason of conductivity in the bulk SnO₂ [14]. In experiment, the system conditions are so limited that makes the simulation of atomic level more important. It is therefore necessary to make a further study on the intrinsic defects of tin oxide, and to elucidate the effect of different defects on carrier transport.

A systematic report about the stability and the contribution of vibrational entropy to defect formation energy in SnO₂ crystal is made with a range of Fermi level and system conditions (temperatures and oxygen partial pressure). First-principles and thermodynamic have been applied to study the formation of point defects in SnO₂ crystal. The result presents the necessity of considering vibrational entropy, especially under high temperatures. The stability of intrinsic defects is shown in three-dimension figure.

2. Computational methods

Tin oxide (SnO₂) with the rutile structure belongs to tetragonal system and has the space group of P42/mnm (D_{4h}¹⁴) [13]. The primitive unit

* Corresponding author. College of Science, University of Shanghai for Science and Technology, Shanghai 200093, China.

E-mail address: liutyxj@163.com (T. Liu).

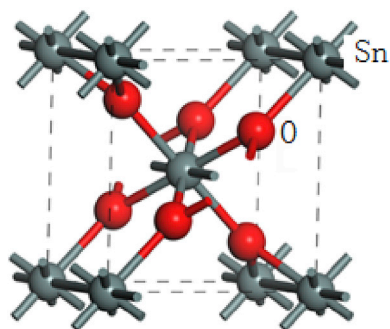


Fig. 1. Scheme of the perfect SnO₂ crystal.

cell of perfect SnO₂ contains two SnO₂ formula units, in which each tin ion is located in the center of octahedron of oxygen. The structure of the perfect SnO₂ crystal as shown in Fig. 1.

Density functional theory (DFT) calculations are all performed using Vienna ab initio simulation package (VASP) [15,16]. Electron-ion interactions are treated using projector augmented wave (PAW) method [17,18]. The generalized gradient approximation (GGA) in the parameterization by Perdew, Burke and Ernzerhof (PBE) [19] was selected to express the exchange-correlation potential. The tin (5s²5p²) and oxygen (2s²2p⁴) were treated as valence electrons. The cutoff energy was 496 eV in the plane-wave expansion and a 2 × 2 × 2 k-point mesh was sampled in the Brillouin zone. The lattice parameters a = 4.713 Å, c = 3.180 Å are in agreement with experimental values [20] of a = 4.738 Å, c = 3.188 Å. In addition, a 2 × 2 × 3 unit cell was applied to build a super cell for the perfect bulk SnO₂ calculations [8], where defective systems are simulated by adding (or removing) a host atom to (or from) a 72-atoms perfect super cell with periodic boundary conditions. The convergence of the main calculated parameters has been tested before calculations.

2.1. Defect calculations

The defect formation energy is an important parameter, which can reflect its equilibrium concentration according to defect formation energy. Considering the vibrational entropy, the formation energy of a defect can be expressed as follows [21–23]:

$$\Delta G_f(i, q, T, p) \cong E^{\text{total}}(i, q) - E^{\text{total}}(\text{perfect}) + n_i \mu_i(T, p) + q(E_{\text{VBM}} + E_F + \Delta V) - T \Delta S_{\text{vib}}^q(T) \quad (1)$$

where $\Delta G_f(i, q, T, p)$ is the defect formation energy. $E^{\text{total}}(i, q)$ is the relaxed total energy of supercell including the defect a of charge state q obtained from the DFT calculations, and $E^{\text{total}}(\text{perfect})$ is the relaxed total energy of the corresponding ideal supercell crystal also obtained from DFT calculations. Here the value of n_i is the atomic number, which is removed from the super cell ($n_i > 0$) or added in the super cell ($n_i < 0$). $\mu_i(T, p)$ is the chemical potential of the defect atom [18]. E_{VBM} is the value of the valence band maximum (VBM), and E_F is the Fermi level referenced to E_{VBM} . ΔV is the difference of average electrostatic potential between the defective and perfect crystal super cells. The term of $\Delta S_{\text{vib}}^q(T)$ is the difference of vibrational entropy between defect and perfect crystal super cells. For charged defects, the total energy was corrected to $O(L^{-3})$, where L is the supercell size.

2.2. Vibrational entropy calculations

Point defects in the crystal are not fixed, and are easily influenced by the surrounding environment. Previously, the influence of vibrational entropy on the DFEs always was ignored. In this work, the values of vibrational entropy were calculated. The effect on DFEs was discussed in Section 3.1. Here, the vibrational entropy is given as [24]:

$$S_{\text{vib}}(T) = R \ln Z_{\text{vib}} + RT \left(\frac{\partial \ln Z_{\text{vib}}}{\partial T} \right) \quad (2)$$

$$Z_{\text{vib}} = \sum_k \omega_k \sum_{\text{all}} \left(1 - \exp \left(-\frac{h\nu}{kT} \right) \right)^{-1} \quad (3)$$

Here, S_{vib} is the vibrational entropy. Z_{vib} denotes the partition function of vibrational entropy. h and R are the Boltzmann constant, Planck's constant and perfect gas constant, respectively. ν is the vibrational frequency. T is temperature.

The reasonable vibrational entropy can be obtained by using General Utility Lattice Program (GULP) program by choosing suitable calculation parameters [24]. The GULP is used to calculate the lattice vibrational entropy with a core and shell model. The interaction among ions is described as [24,25]:

$$U_{ij} = \frac{Z_i Z_j e^2}{r} + A \exp \left(\frac{-r}{\rho} \right) - \frac{C}{r^6} \quad (4)$$

Here, the first term is a long range Coulomb interaction potential, which contains 90% of the energy. Z_i represents the effective charge of the i th atom, and r is the distance between i and j atoms. The remaining two terms are the short range Buckingham potential of the two bodies, which are the linear combination of the Born-Mayer equation and Van Der Waals energy, respectively. The potential parameters used in the calculations are listed in Table 1.

In order to examine the reliability of fitting parameters, both calculated results and experimental results were listed in Table 2. The maximum error between the results and the experimental values is less than 5%. The results show that the parameters used in the calculation of the Buckingham potential are feasible and the results are reliable.

3. Results and discussion

3.1. Vibrational entropy

In this paper, the difference of vibrational entropy between defect (oxygen vacancy, tin vacancy, oxygen interstitial, tin interstitial) and perfect crystal super cells was calculated as implemented in the GULP program. The result of the difference of vibrational entropy between defect and perfect crystal super cells as a function of temperatures was shown in Fig. 2.

In Fig. 2, when the temperature is less than 300 K, the contribution of vibrational entropy to point defects is not obvious, which can be neglected. With the increasing of temperatures, the vibrational entropy should be considered especially for tin interstitial under high

Table 1
Empirical potential parameters of SnO₂ crystal.

Buckingham	A(eV)	$\rho(\text{\AA})$	C(eV·Å ⁶)
Sn _{shel} - O _{shel}	938.7	0.3813	0.0
O _{shel} - O _{shel}	22764.3	0.1490	43.0
		Charge	Spring
Sn	Core	0.010	191.50
	Shell	3.990	
O	Core	1.000	117.8
	Shell	3.000	

Table 2
Comparison of calculated and experimental structural parameters in SnO₂ crystal.

Lattice Parameters	Calculated	Experimental [15]	Relative error (%)
a (nm)	0.4676	0.4738	-1.30
c (nm)	0.3333	0.3188	4.55
Volume (10 ⁻³ nm ³)	72.8999	71.5663	1.86

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