

Density Functional Study of the Cluster Model of SnO₂(110) Surface Modified by Benzoic Acids

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ABSTRACT

The properties of the modified surface of SnO₂(110) with benzoic acid (Y-C₆H₄-COOH: Y is para position relative to -COOH group) derivatives were investigated using density functional theory. Zehner *et al.* mentioned that the modification of surface dipole moment made it possible to tune the work function of the system. The experiment of Ganzorig *et al.* showed that there was a linear relationship between the dipole moment of the binding molecule and the work function change of the system using the modified surface of indium-tin oxide (ITO) with some benzoic acid derivatives. To elucidate the relation between the dipole moment of the molecule and the work function change, we investigated the modified surface of SnO₂(110) using Sn₇O₁₄ cluster model which was embedded in the fixed point charges. On the modification of the surface, benzoic acid derivatives were bound to SnO₂ surface. By changing the terminal group of benzoic acid with H, Cl, F, CF₃ and CCl₃, the work function changed and the dipole moment of the binding molecules of the modified SnO₂(110) were evaluated. The results showed that there was a linear relationship between the dipole moment of the binding molecules and the work function change. From this relation, the average value of the dipole moments of Sn-OOC linkage at the surface was also evaluated.

Keywords: Benzoic Acid Derivatives; Dipole Moment; Work Function Change; Cluster Model; Modification of Surface

1. Introduction

The tuning of the work function of metal oxide is important in the research on the application field of the electronic devices [1]. The modification of the surface with self assembled monolayer (SAM) has been known as a method to change the work function of the metal oxide substrates [2,3]. One of such metal oxide substrates is tin oxide (SnO₂), which has been used for gas sensors, transparent conductors, and catalysts [4]. The (110) surface of SnO₂ is the thermodynamically most stable face compared to other low index faces of tin dioxide and has been investigated not only experimentally [5-8] but also theoretically the properties of its surface [9-15]. Many researchers studied molecular adsorption and oxygen vacancies of tin dioxide surface theoretically [16,17] to interpret how tin dioxide surfaces sense gases [18] and conduct electric current [19]. In this work, we studied the

work function change of the SnO₂(110) surface using the density functional theory (DFT) with the cluster model of SnO₂(110) where surface was modified by various benzoic acid derivatives.

If SAM is conceptualized as parallel charged sheets, the work function change ($\Delta\Phi$) can be expressed by the following equation [20]

$$\Delta\Phi = -\frac{N\mu_{\perp}}{k\epsilon_0} \quad (1)$$

where N is the density of the molecules on the surface; μ_{\perp} is the component of the dipole moment of SAM normal to the surface; k is the dielectric constant of the dipole layer; and ϵ_0 is the permittivity of vacuum. By assuming the chemisorbed SAMs are modeled as two dipole sheets with different dielectric constants, Zehner *et al.* derived the Equation (2) for work function change ($\Delta\Phi$) of the chemisorptions of SAM from a series of

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arene-thiol adsorbates on the gold [20].

$$\Delta\Phi = -N \left[\frac{\mu_{\perp,mono}}{\epsilon_0 k_{mono}} + \frac{\mu_{Au-S}}{\epsilon_0 k_{Au-S}} \right] \quad (2)$$

where $\mu_{\perp,mono}$ is the dipole moment of the chemisorbed molecule normal to the surface plane, and μ_{Au-S} , k_{Au-S} , and k_{mono} are the dipole moment of Au-S bond, dielectric constant of Au-S bond, and dielectric constant of monolayer, respectively. They were determined independently according to Zehner *et al.* [20]. If we apply this equation to the system of SnO₂ surface modified by benzoic acid molecules, the following equation can be formed

$$\Delta\Phi = -N \left[\frac{\mu_{\perp,mono}}{\epsilon_0 k_{mono}} + \frac{\mu_{Sn-OOC}}{\epsilon_0 k_{Sn-OOC}} \right] \quad (3)$$

where $\mu_{\perp,mono}$ is the dipole moment of the modified monolayer component normal to SnO₂(110) surface, and μ_{Sn-OOC} and k_{Sn-OOC} are the dipole moment and the dielectric constant of Sn-OOC bonds, respectively. As there are no existing experimental values of surface density (N) and the work function change ($\Delta\Phi$) of the modified SnO₂(110) surface with benzoic acid derivatives, it is difficult to evaluate the work function change by these dipole moments from Equation (3) directly. Therefore, we substituted left side of Equation (3) to the right side of Equation (1), then, we derived the following equation

$$\mu_{\perp} = \frac{k}{k_{mono}} \mu_{\perp,mono} + \frac{k}{k_{Sn-OOC}} \mu_{Sn-OOC} \quad (4)$$

If we assume the coefficient (k/k_{mono}) of the first term and the whole second term of the right side of Equation (4) are constants, we can expect the linear relationship between μ_{\perp} and $\mu_{\perp,mono}$. The main aim of this work is to check the relationship between them by using the first principle method. The results showed that the relation between dipole moment of μ_{\perp} and $\mu_{\perp,mono}$ was linear.

2. Calculation Method

2.1. Calculation Procedure

DFT calculation was performed with Becke's hybrid three parameters approach [21,22] and Lee-Yang-Parr exchange-correlation functional (B3LYP), [23] which is implemented in Gaussian03 package program, [24] was used. Basis set for Sn atom was chosen by a relativistic effective core potential (ECP) [25] with double zeta function (LanL2DZ) which treats 1s² to 4p⁶ electrons are frozen and 5s²5p² electrons are explicitly included in the valence. For H, C, O, F and Cl atoms, basis set of 6-31G were used [26]. During the optimization, the atoms of the cluster of Sn₇O₁₄ were frozen and their geometric positions were the same as crystal geometry [27].

2.2. Calculation Model

The surface of SnO₂(110) was modeled as a cluster of Sn₇O₁₄ embedded in point charges (PCs) according to the model of Melle-Franco and Pacchioni (Figure 1) [28]. In this figure, PCs are illustrated by wire model with +2 and -1 electrons substituted in positions of Sn and O atoms in the bulk geometry of SnO₂, respectively [27]. This cluster model corresponds to the stoichiometric surface structure of SnO₂(110).

The binding structure of the benzoic derivative Y-C₆H₄-COOH (Y: H, F, Cl, CCl₃, CF₃) on the SnO₂ surface was modeled and shown in Figure 2.

Calatayud *et al.* [29] calculated the methanol adsorption on SnO₂(110) surface. They modeled the cleavage of the methanol O-H bond and the resulting fragments of H and CH₃O were bounded to the bridging oxygen (O_b) and 5-fold tin (Sn₅) atoms, respectively. According to their model, we modeled the cleavage of benzoic acid COO-H bond and the resulting fragments of H and COO were bound to the same bridging oxygen (O_b) as Calatayud *et al.* model [29] and 5-fold tin (Sn₅) atoms to make the system with singlet multiplicity as were shown in Figure 2, respectively.

3. Results and Discussion

Modified surface structures, where the benzoic acid derivatives of Y-C₆H₄-COOH (Y: H, F, Cl, CCl₃ and CF₃)

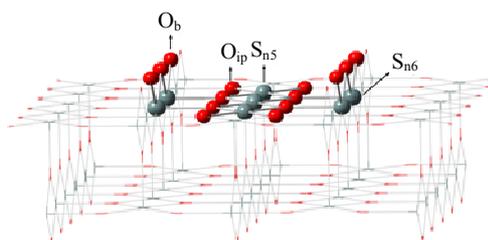


Figure 1. Structure of the Sn₇O₁₄ cluster model embedded in a point charge potential. Sn₅; 5-fold tin, Sn₆; 6-fold tin, O_b; bridging oxygen, O_{ip}; in-plane oxygen atoms.

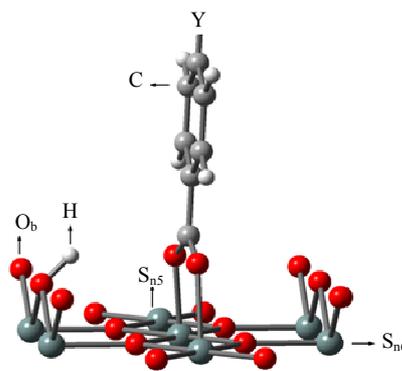


Figure 2. The binding structure of Y-C₆H₄-COOH after optimization. PCs are not shown for simplicity.

bind to the SnO₂ surface, were investigated using DFT calculation. As the fragments of the cleavage of benzoic acid derivatives of H and Y-C₆H₄-COO were modeled to bind to the bridging oxygen (O_b) and the 5-fold tin (Sn₅) atoms, the bound structures were first optimized to check the adequacy of its binding structure. In the optimization, surface atoms of the Sn₇O₁₄ cluster were fixed in the calculation. After the successful optimization of the binding structures of Y-C₆H₄-COO on Sn₇O₁₄-H cluster, it was found that the plane of benzene ring was oriented close to normal to the SnO₂(110) surface. By using the optimized bound structure, dipole moments perpendicular to the surface of SnO₂(110), μ_{\perp} , were evaluated. The obtained values were shown in **Table 1**. To investigate the relationship between μ_{\perp} and $\mu_{\perp,mono}$ shown in Equation (4), we calculated the values of the dipole moment of the modified monolayer component normal to SnO₂(110) surface, $\mu_{\perp,mono}$. According to the model of Zehner *et al.* [20], $\mu_{\perp,mono}$ corresponds to the dipole moment of Y-C₆H₄-COO radicals. This component of the dipole moment of Y-C₆H₄-COO radicals (Y: H, F, Cl, CF₃, CCl₃) was calculated and the dipole moments along to the normal to the surface were shown in **Table 1** as $\mu_{\perp,mono}$. The relation between the dipole moment of μ_{\perp} and $\mu_{\perp,mono}$ is shown in **Figure 3**. It shows that there is a good linear relationship between these two dipole moments. The square of the correlation coefficient is 0.998. The value of the slope is 1.102 and the intercept is -22.1 D. As the slope value is close to 1, we can estimate from Equation (4) that the value of k is almost similar to k_{mono} . On the other hand, the intercept value of -22.1 D corresponds to $(k/k_{Sn-OOC}) \mu_{Sn-OOC}$ term in equation 4. If we assume the values of k and k_{Sn-OOC} are also equal, the dipole moment for the Sn-OOC bonds, μ_{Sn-OOC} , can be estimated. The evaluated value of μ_{Sn-OOC} is -22.1 D.

It shows that the contribution of the binding group -COO to the surface dipole moment is constant in the series of Y-C₆H₄-COO molecules, even though the terminal groups of Y in the Y-C₆H₄-COO molecules are different. Carrara *et al.* [30] investigated the surface adsorption of carboxylic acid derivatives on both alumin-

ium and indium-tin oxide surfaces and reported that the contribution of the binding group of -COO to the surface permanent dipole is relevant and +0.7 D and -2.2 D respectively in each series. Zehner *et al.* obtained the value of 2.3 - 3.8 D for some series of thiols on Au surface [20]. Compared to their values, the evaluated value of -22.1 D seems a little large. However, two Sn-OOC bonds are involved in the linkage in this model. By using the partial charges of Sn and oxygen of the carboxyl group, which were evaluated in this model, Sn-O average dipole moment was roughly estimated 12.11 D by using two Sn-O bonds for all five terminal groups (Y: H, F, Cl, CF₃, CCl₃). As two Sn-OOC bonds are involved in the linkage at the surface, the estimation of the dipole moment for the Sn-OOC bonds, μ_{Sn-OOC} , value seems to be reasonable.

By using Equation (3), work function change can be estimated. As the value of the surface molecular density N can not be found in the literature, the value of $1.3 \times 10^{14} \text{ cm}^{-2}$, which was measured for nitrobenzoic acid by Langmuir isotherms, [31] was used as a rough estimation value for our cluster Sn₇O₁₄ model. k_{mono} and k_{Sn-OOC} were chosen as benzoic acid dielectric constant equals to 2.5 [31]. The obtained work function changes are shown

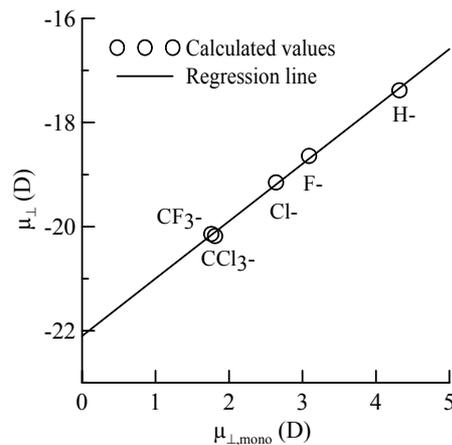


Figure 3. Relationship between the calculated dipole moments of μ_{\perp} and $\mu_{\perp,mono}$.

Table 1. Calculated dipole moments normal to the SnO₂(110) surface.

Terminal group Y:	Dipole moment, (Debye)				Work function change, (eV)
	μ_{\perp}	$\mu_{\perp,mono}$	μ_{Sn-OOC}	Dipole moment of the Sn ₇ O ₁₄ cluster in PCs, μ_{SnO_2}	
H	-17.38	4.32			5.176
F	-18.64	3.09			4.935
Cl	-19.15	2.64	-22.1	12.54	4.847
CF ₃	-20.14	1.76			4.674
CCl ₃	-20.18	1.81			4.684

in **Table 1**. Calculated values of work function change are large compared to the experimentally observed work function changes obtained by Nüesch *et al.* [30,31] and Appleyard *et al.* [32] on ITO and Aluminium surfaces graftification. Further calculation works on different series of metal oxide surfaces and the experimental work on the work function change and the molecular density of chemisorbed SAM should be desired.

4. Conclusion

Density functional calculation on the modified surface of SnO₂(110) with benzoic acid derivatives was performed to obtain the information of the surface dipole moment and the work function changed using the cluster model. The result shows the linear relationship between the surface dipole moment μ_{\perp} and the dipole moment of binding molecule $\mu_{\perp,mono}$. From this relation, dipole moment of the linkage of the Sn and OOC bonds at the surface was evaluated and the average value of -22.1 D was obtained.

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