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Oxygenation mediating the valence density-of-states and work function of Ti(0001) skin

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Abstract

Consistency between density function theory calculations and photoelectron spectroscopy observations confirmed predictions based on the framework of bond-band-barrier (3B) correlation notation [Sun, *Prog Mater Sci* 48, 521-685 (2003)] that an oxygen adsorbate interacts with Ti(0001) skin atoms to form a tetrahedron with creation of four valence density-of-state features: O-Ti bonding electron pairs, O nonbonding lone pairs, Ti electronic holes, and Ti antibonding dipoles. Formation of the dipoles lowers the work function of the Ti(0001) skin and electron-hole generation turns the metallic Ti(0001) into the semiconductive O-Ti(0001). Findings confirm the universality of the 3B correlation in understanding the dynamics of oxygen chemisorption and the associated valence electrons involved in the process of oxidation.

Keywords: Ti(0001); Oxidation; TiO₂; DFT; UPS

ABSTRACT	1
1. INTRODUCTION	3
2. PRINCIPLE: BOND-BAND-BARRIER (3B) CORRELATION.....	5
3. DFT CALCULATIONS	7
4. RESULTS AND DISCUSSION	8
<i>4.1 Adsorption sites and O-Ti bond lengths.....</i>	<i>8</i>
<i>4.2 Valence density of states</i>	<i>12</i>
<i>4.3 Band gap creation and work function modulation</i>	<i>14</i>
5. CONCLUSION.....	14

1. Introduction

Bond formation and relaxation and the associated energetics, densification localization, polarization of electrons mediate the performance of a substance subjecting to stimulus such as undercoordination, hetero-coordination, and chemisorption [1]. Oxidation of a metal skin is related to the performance of materials in applications to microelectronics (metal-oxide-semiconductor field effect transistor gate device and sensors) [2, 3], photoelectronics (photocataluminescence, conductance and field emission) [4, 5], magneto-electronics (giant magnetoresistance and superconductivity) [6], photocatalysis [7], etc. Therefore, comprehension of the electronic structure upon bond formation in terms of density-of-states (DOS) has attracted much attention from an atomistic to a macroscopic point of view both experimentally and theoretically [8-12]. A recent bond-band-barrier (3B) correlation notation [1] suggests that oxygen adsorption creates four additional DOS features to the valence band and above of the host upon oxidation, i.e., the O-M bonding electron pairs, oxygen nonbonding lone pairs, metal electronic holes, and metal antibonding dipoles, which dominate the performance of an oxide compound. The 3B correlation mechanism has been affirmed from atomic valences, bond geometrical, valence-DOS and bond strength as well as bond forming kinetics of oxidized metal surfaces [1].

Owing to its nontoxicity, low cost, favorable band edge positions, and tunable work function, TiO_2 has been recognized as one of the most promising photocatalysts for applications in various fields [13, 14]. The TiO_2 has triggered broad interest and intensive studies of the inherent mechanism of TiO_2 photocatalyst. However, the detailed mechanism from the perspective of bond formation and relaxation and the associated charge localization and polarization remains poorly understood.

The adsorption of atomic or molecular species on metal surfaces is currently attracting a significant amount of attention. Especially the mechanism of workfunction changes induced by adsorbates has been controversial. There are two mechanisms has been recognized widely, though their universality remains to be proved. Using cluster calculations to represent the metallic substrate, Bagus et al. [15] related the work-function decrease for I - Cu(111) to the polarization in the metal substrate induced by the presence of the anionic adsorbate. On the other hand, based on periodic density-functional theory (DFT) calculations, Michaelides [16] et al.

explained the N-induced work-function change on W(100) by a reduction in the surface overspill electron density into the vacuum. Moreover, in the calculation of oxide films formed on Al(111) surface, Baran et al. [17] confirmed limiting thickness of oxide films originates from a diminishing oxygen adsorption energy beyond a certain oxide film thickness. The O-Ti(0001) system has been extensively studied by experimental investigation and first-principles calculations [18-24]. Through a study using low-energy electron diffraction (LEED) and auger electron spectroscopy (AES) of the oxidation of Ti(0001) at room temperature, Shih et al.[19]found that at low oxygen coverage a $p(2\times 2)$ superstructure presents. This superstructure gradually converts to a (1×1) pattern with increasing oxygen exposure. The work function of the clean Ti(0001) skin is in the range of 4.45-4.60 eV. Oxidation evolves the work function with a initially tiny decrease, then increases until the Ti(0001) surface becomes saturated with oxygen coverage [25]. However, upon a 523 K flash anneal, the increased workfunction at higher exposures abruptly recover to 5.15 eV associated with the well-ordered $p(2\times 2)$ LEED pattern.

This sequence of workfunction evolution was attributed to the presence of two distinct binding states of oxygen on the Ti(0001) surface: one is the “ α state” with a lower workfunction, and the other the “ β state” with a higher workfunction [20]. Liu et al.[18]proposed the monolayer and multilayer adsorption models to explain oxygen adsorption on Ti surface. They suggested that the location of the adsorbed oxygen mediates the workfunction of the Ti(0001) surface. If the oxygen atoms are located above the surface, formation of the surface dipoles tends to raise the work function, whereas if the oxygen atoms are located just below the outermost atomic layer, the dipole points in the opposite direction and reduces the work function. Moreover, Ultraviolet photoelectron spectra (UPS) measurements revealed an additional peak to the valence DOS of the clean Ti(0001) surface upon adsorption. With increasing exposure to oxygen, the new peak was broadened and the centre of the new peak also shifted to higher binding energy [21, 22].

When exposed to air, semiconductor TiO_2 layers cover the metallic titanium surface [26-28]. Under high temperature and very low oxygen pressure, substoichiometric phases of TiO , Ti_2O_3 , and other titanium oxides could form on the surface. Question

remains open on the role of oxygen in opening the band gap and modulating the work function despite intensive studies in the regard.

In the present work, we report density functional theory (DFT) observations that confirm the presence of predicted DOS features of holes and nonbonding lone pair DOS near the valence band edge of oxygen adsorption on the Ti(0001) surface. The polarization of the conduction electrons by the nonbonding states lowers the work function of the Ti(000) skin upon oxygen adsorption. The generation of the electronic holes turns the conductor into semiconductor.

2. Principle: bond-band-barrier (3B) correlation

The 3B correlation notation [1] indicates that the sp^3 -orbital hybridization is necessary for O, N, and C interacting with atoms in the solid phase to form quasi-tetrahedron like H_2O , NH_3 , and CH_4 , which determines the crystallography, morphology, band structure, and the chemical physical properties of the chemisorbed skins. The original idea of the model is to extend the H_2O molecular structure to a solid skin with chemisorbed oxygen by replacing the H atom with a host atom of an arbitrary element B that should be less electronegative than O.

Upon interacting with atoms B in a solid phase, oxygen atom captures two electrons from B atoms and the 2s and 2p levels of oxygen are fully occupied with eight electrons that will hybridize the sp orbit to form four directional orbits. Therefore, two of the four hybridized orbits are occupied by shared electron pairs. The remaining two are occupied by the lone electron pairs of oxygen, which entitles an oxide quasi-tetrahedron of C_{2v} group symmetry. Therefore, one oxygen atom can never catch more than one-electron from a specific host atom because of the directionally hybridized orbits.

This oxidation defines four features to the valence band of the chemisorbed system in the following electronic dynamics, as illustrated in Figure 1a:

- (i) Oxygen catches electrons from its neighboring B atoms to O-B bond and fill its $2s^2p^4$ orbits, which produces energy states slightly lower than the 2p-level

- of the oxygen;
- (ii) The O-B bond formation also creates electron holes leave behind the B^+ ion, which evaluates electron below the E_F .
 - (iii) The sp^3 -orbit hybridization takes place, which creates the nonbonding lone pair states just below the Fermi level (E_F).
 - (iv) The lone pair polarizes its neighboring atoms to form the pinned dipoles (B^{dipole}) that fill the antibonding orbits.
 - (v) Overdosing oxygen in chemisorption, H-like bond network forms at the skin, which annihilates the skin dipoles and raises the work function.

Electron-hole production turns the metal conductor into the compound semiconductor or even an insulator. The polarized states lower the work function. The localized lone pairs and dipoles neither follow the regular dispersion relation nor occupy the allowed energy states in the valence band and below as defined by Hamiltonian. However, they add impurity states near E_F . Upon being overdosed with oxygen, the atomic ratio O:B is rising, some of the surface B atoms has to interact with oxygen neighbors through both ionic bond and lone pairs. The overdosed oxygen gets electrons from the dipoles that are polarized into antibonding states, and the B^{dipole} becomes $B^{+/dipole}$. H-like bonding differs from the classical hydrogen bond simply in that, the $B^{+/dipole}$ replaces the $H^{+/dipole}$ in the hydrogen bond ($O^{-2}-H^{+/dipole}:O^{-2}$), the '-' and ':' represent the bonding pair and the nonbonding lone pair, respectively. The arrow from the antibonding states above E_F to the deeper bonding sub-band represents the process of H-like bond formation (Figure 1(a)).

Figure 1 Schematic illustration of the electronic dynamics at oxidation (a) and the associated four valence DOS features (b). Arrows in (a) indicate that O catches electrons in the conduction band (CB) from two B neighbors and creates nonbonding lone pairs. The lone pairs polarize the conduction electrons of another two neighbors into dipoles. Over dosed O will catch the dipole to continue the bonding processes. The arrow from the antibonding sub-band to the bond states corresponds to the process of H-like bond ($\text{O}^{-2}\text{-B}^{+/\text{dipole}}\text{:O}^{-2}$) formation [1].

3. DFT calculations

In order to verify the 3B predictions we conducted the spin-polarized DFT calculation using the CASTEP code [29] with ultrasoft pseudopotentials, and a kinetic energy cutoff of 400 eV. The exchange correlation function was formulated using the generalized gradient approximation (GGA) with the Perdew–Wang parameterization (known as GGA - PW91)[30]. Integrations in Brillouin zone were performed using special k-points generated with a $15 \times 15 \times 15$ mesh parameters grid for Ti primitive cell and $6 \times 6 \times 1$ for both the surface and interlayers of the Ti(0001). The structural optimization was performed until the energy change per atom was less than 5×10^{-7} eV, the forces on atoms were less than 0.01 eV/Å, all the stress components were less than 0.02 GPa, and maximum displacement of 5.0×10^{-4} Å. To estimate the accuracy of the calculations, we studied the lattice constant of Ti bulk and interlayer relaxation of clean Ti (0001) surface. With the simulation setup described above, the computed values of the lattice parameters a and c/a of Ti bulk are 2.935 Å and 1.581, respectively, slightly smaller than in experimental 2.949 Å, 1.586 as usually observed with GGA[31]. Meanwhile, when relaxing the (0001) slab, the outer most layer spacing contracts by about 3%, the second layer spacing contracts by about 2%, and the third contracts by about 1%, the relaxation trend is consistent with experimental measurements [32] and the bond order-length-strength (BOLS) notation expectation[33]. The calculated workfunction of clean surface is 4.44 eV that is consistent with experimental value (4.45 - 4.60eV)[22] and previous DFT calculations (4.45 eV)[34].

4. Results and discussion

4.1 Adsorption sites and O-Ti bond lengths

With respect to observations [18, 20, 35, 36], we assumed that oxygen adsorbs to the Ti (0001) skin in a mixture of monolayer and multilayer configuration. According to LEED and AES measurements [20], an initial p(2×2) pattern can rationalize the subsequent DFT calculations. We took a 8-Ti-layer structure with a 15 Å thick vacuum slab insertion to model the clean Ti(0001) surface, the bottom two layers were fixed at their bulk truncated structure.

Figure 2 shows the possible chemisorption sites. A series of repeated optimization results in the average adsorption energy of oxygen atoms and workfunction for possible adsorption sites, as summarized in Table 1.

The following formulates the adsorption energy:

$$E_{ads} = \frac{1}{N} \left(E_{clean} + \frac{N}{2} E_{O_2} - E_{O/Ti(0001)} \right);$$

where N is the number of oxygen atoms in the unit cell, $E_{O/Ti(0001)}$, E_{clean} and E_{O_2} represent the total energies per unit cell of the oxygen-adsorbed Ti slab, the clean Ti slab, and the O_2 molecule, respectively.

Figure 2 The (a) octahedral and (b) tetrahedral insertion sites at the Ti(0001) interatomic layers. The symbol Oct (i, j) denotes oxygen atoms at the octahedral sites

between the i th and $i+1$ th layer, and Tet ($i, :aj(\text{or } bi)$) means the oxygen atom at the tetrahedral site located directly below the i th layer.

Table 1 Average adsorption energy per O atom at various adsorption sites of Ti(0001) skin and the derived workfunction. The workfunction of the clean surface is 4.44 eV.

Adsorption concentration (ML)	Adsorption site	Adsorption Energy (eV)	Work function (eV)
0.25ML	FCC	5.98	4.39
	HCP	5.72	4.38
	Oct(1,2)	5.20	4.50
	Tet (1,2)	4.12	4.45
	Oct(2,3)	5.78	4.44
	Tet (2,3)	4.26	4.45
0.50ML	FCC	5.83	4.51
	FCC+ Oct(1,2)	-	-
	FCC+Oct(2,3)	5.91	4.38
	HCP+Tet(2,3)	5.01	4.37
0.75ML	FCC	5.65	4.52
	FCC+Oct(2,3)	5.80	4.50
	FCC+Oct(2,3)+Oct(4,5)	5.86	4.36
1.00ML	FCC	5.39	4.77
	FCC+Oct(2,3)	5.79	4.53
	FCC+Oct(2,3) +Oct(4,5) +Oct(6,7)	5.86	4.36

Results in Table 1 indicate the following.

Firstly, for the monolayer adsorption model, the FCC site is energetically more favorable than the hexagonal close-packed (HCP) sites and the interlayer sites from the first, second and third layers. After relaxation, the Top and the Bridge sites are energetically unfavorable for oxygen.

Secondly, with oxygen concentration increasing, oxygen trends to diffuse into the subsurface or into the bulk in the multilayer adsorption scheme. However, there are strong repulsive interactions between two adsorption oxygen atoms when they occupy the adjacent interstitial sites. In this case, the most energetically stable sites are FCC + Oct(2,3), FCC + Oct(2,3) + Oct(4,5), and FCC + Oct(2,3) + Oct(4,5) + Oct(6,7), at 1/2, 3/4, and 1 ML coverage, respectively (see Figure 4).

Thirdly, the workfunction changes with the adsorption site on the Ti(0001) skin, as shown in Figure 3. In the monolayer adsorption model, oxygen adatoms are restricted to the most stable FCC sites, which lowers the workfunction slightly for low oxygen coverage. The workfunction recovers gradually with the increase of oxygen coverage, being consistent with experimental results [22]. However, in the multilayer adsorption model, oxygen atoms occupy the energetically most favorable sites, which lowers the workfunction slightly as the oxygen coverage increases.

Figure 3 Workfunction of the most stable systems in both the monolayer and multilayer adsorption models. Inset is the trend of measurements [22]. The fact that workfunction drops abruptly upon a flash anneal according measurement Indicates oxygen penetrates into the subsurface following the multilayer adsorption model.

Figure 4 The energetically stable adsorption sites of O-Ti(0001) skin at (a) 1/4; (b) 1/2; (c) 3/4; and (d) 1.00 ML oxygen coverage.

Table 2 lists the O-Ti bond length of the O-Ti(0001) skin. In the monolayer adsorption model, the O-Ti average bond length decreases with oxygen coverage. In the multilayer adsorption model, there exist two distinct bonding types with different bond lengths. One occupies the FCC sites, another occupies the octahedral interstitial sites. The shorter O-Ti bond length in the monolayer model follows the bond order-length-strength (BOLS) correlation mechanism indicating that bond between undercoordinated atoms is shorter and stronger [1].

Table 2 O-Ti bond length for oxygen adsorbed on various sites in the Ti(0001) skin.

Adsorption models	Adsorption		Oxygen		Average bond lengths (Å)
	concentration (ML)	Adsorption sites	atoms site	O-Ti Bond lengths (Å)	
Monolayer adsorption	0.25	FCC	FCC	1.933(2)/1.932(1)	1.933
	0.50	FCC	FCC	1.924(3)/ 1.925(1)/ 1.915(1)/1.917(1)	1.922
	0.75	FCC	FCC	1.941(1)/1.942(1)/1.943(3)/1.944(1)/ 1.859(1)/1.860(2)	1.915
	1.00	FCC	FCC	1.894(1)/1.896(1)/1.897(1)/ 1.904(1)/1.906(3)/1.908(2)/ 1.909(1)/1.911(1)/1.913(1)	1.905
			FCC	1.932(2)/1.930(1)	1.931
Multilayer adsorption	0.50	FCC+Oct(2,3)	Oct(2,3)	2.085(2)/2.087(1)/ 2.092(1)/2.093(1)/2.094(1)	2.089
			FCC	1.931(2) /1.929(1)	1.930
	0.75	FCC+Oct(2,3)+Oct(4,5)	Oct(2,3)	2.090(1)/2.091(2)/2.095(1)/ 2.087(1)/2.088(1)	2.090
			Oct(4,5)	2.087(2)/2.088(1)/2.089(2)/2.090(1)	2.088
			FCC	1.930(2)/ 1.931(1)	1.930
	1.00	FCC+Oct(2,3)+ Oct(4,5) +Oct(6,7)	Oct(2,3)	2.089(3)/2.090(2)/2.091(1)	2.090
			Oct(4,5)	2.090(1)/2.091(2)/ 2.094(1)/2.095(1)/2.096(1)	2.093

4.2 Valence density of states

Figure 5 shows the coverage dependence of the valence DOS for the O-Ti(0001) skin at the most stable adsorption sites and different overages. Compared with the clean Ti(0001) skin (

Figure 6b), oxygen adsorption creates obvious DOS features at +1.6(anti-bonding), ~ -1.5(nonbonding), -2.3 ~ +1.0 (holes) and -5.0 ~ -8.0 eV (bonding), which are consistent surprisingly well with predictions of the 3B premise.

Oxygen does not simply add its 2s and 2p states to the valence bands of Ti metals but exchanges and polarizes electrons of the Ti atoms. The DOS features between -8.0 and -5.0 eV are derivatives of the Ti-O bonds that are stronger than the original pure Ti-Ti bonds. The stronger interaction lowers the system energy and stabilizes the system. The bonding state consists of two parts which correspond to bonding types: deeper energy states (~ -7.0 eV) and shallower energy states (~ -5.5 eV), the deeper energy states only appear in the multilayer adsorption modes. Bonds between oxygen and Ti atoms underneath the second layer or in the bulk should be stronger than bond between oxygen and Ti atoms at the skin.

The antibond states (+1.6eV) arise from polarization of the Ti d electronics by the lone pairs of oxygen. Furthermore, locally densely entrapped bonding and core electrons of the undercoordinated skin atoms further polarize the dipoles, which explains why metal atoms, like gold on TiO₂ exhibit strong polarization attributes contribute to catalytic ability [37].

Figure 6a shows the differential UPS spectra for Ti(0001) surface with varied oxygen exposures based on the zone-resolved photoelectron spectroscopy (ZPS) technique [38]. The ZPS features below E_F confirms the presence of the mixed hole-nonbonding features as spectral valley near the E_F and the bonding attributes at -8.0 ~ -5.0 eV as a peak.

Figure 5 Oxygen coverage dependence of the valence DOS of Ti at the most stable adsorption sites (0 ML – Clean; 0.25ML - FCC; 0.50ML - FCC + Oct(2,3); 0.75 ML - FCC + Oct(2,3) + Oct(4,5) and 1.00ML - FCC + Oct(2,3) + Oct(4,5) + Oct(6,7)). The dotted line represents the Fermi level as reference at 0 eV.

Figure 6 The (a) measured [22] and (b) calculated ZPS profiles of $n(\text{Ti}+\text{O}) - n(\text{Ti})$, at 0.25, 0.50, 0.75, 1.00 ML with respect to that of clean Ti(0001) surface. Where $n(\text{Ti}+\text{O})$ is the DOS of the adsorbate system Ti(0001)-O, and $n(\text{Ti})$ the clean Ti(0001). Results reveal four DOS features corresponding to antibonding ($\sim +1.6\text{eV}$), nonbonding ($\sim -1.5\text{eV}$), holes ($-2.3 \sim 1\text{eV}$) and bonding (-5.5 eV and -7.0 eV) states, which concur with the 3B prediction and measurement (a).

Figure 7 Oxygen site-resolved valence-DOS of O-Ti(0001) skin at 0.75 ML coverage: (a) FCC, (b) FCC + Oct(2,3), (c) FCC + Oct(2,3) + Oct(4,5). Inset shows that the upward shift of the antibonding states lowers the workfunction when oxygen atoms go deeper into the bulk.

4.3 Band gap creation and work function modulation

The presence of holes (-2.3 ~ 1.0 eV) in

Figure 6(b) creates the band gap, which turns the metal Ti(0001) into TiO₂ semiconductor as we expected. This mechanism may provide reference for band gap modulation of TiO₂ photocatalyst.

Figure 7 shows the site resolved valence-DOS ZPS at 0.75ML oxygen coverage: (a) FCC, (b) FCC + Oct(2,3) and, (c) FCC + Oct(2,3) + Oct(4,5). Results show that the penetration of the oxygen adsorbate into deeper sublayers lowers the workfunction. This finding explains that the observed workfunction reduces at low oxygen coverage and increases steadily to saturation when the coverage increases. The abrupt workfunction drop at 250 °C flash at high exposures is explained as follows. Overdosing oxygen adatoms annihilate the skin dipoles but flash annealing evaporates partially the weakly bonded oxygen to recover the dipoles and the work function.

5. Conclusion

Consistency in the 3B theory expectation, DFT calculations, and UPS measurement clarified the essentiality of tetrahedron formation of O-Ti with four additional DOS features: bonding electron pairs, nonbonding lone pairs, empty holes, and antibonding dipoles. These DOS features determine the physical properties of the chemisorbed Ti(0001) surface. Ti-O bonding states lower the system energy and passivate the

Ti(0001) surface; nonbonding lone pairs and antibonding dipoles modify the work function that changes with adsorption concentration and adsorption sites of oxygen. Creation of electron holes opens the bandgap turning metallic Ti into TiO₂ semiconductor. These findings may provide guidelines for controllable modification of electron structures of TiO₂ photocatalyst.

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