A Theoretical Study of O/Ti Co-Adsorption on Ag(100)*

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I. INTRODUCTION

In recent years, the titanium oxides have attracted much attention because of their technological importance. In particular, the physical and chemical properties of Ti dioxide (TiO$_2$) have been extensively studied both experimentally and theoretically because of its practical applications to a catalytic support, photocatalysts, gas-sensor and so on [1]. Ti monoxide (TiO) is also of particular interest because of its unusual physical properties such as extreme hardness, a high melting point and a metallic conductivity [2]. These physical properties are essentially related to the electronic structure in the crystal. Recently the x-ray photoelectron spectroscopy (XPS) and x-ray emission spectroscopy (XES) studies have been made to elucidate the electronic structures of monoclinic- and cubic-TiO powders [3]. However, very few experimental investigations have been performed on the electronic structure of the well-defined TiO crystal. This is primarily because it is difficult to synthesize the single crystal of TiO under an atmospheric pressure. Recently it has been revealed that a TiO single crystal film can be grown on some crystal surfaces such as MgO(100) [4, 5], TiC(100) [6–8], and Ag(100) [9, 10]. It is considered that the TiO(100) film can be grown epitaxially on these solid surfaces because the lattices of the film and the substrates are well matched; the lattice constant of TiO is 4.18 Å [11], which is close to those of MgO (4.21 Å [4]), TiC (4.33 Å [12]) and Ag (4.09 Å [13]).

Recently, Kaneko et al. have found that ordered TiO and TiO$_2$ films can be formed selectively on Ag(100) [10]; the ordered TiO(100) film is formed by Ti deposition in O$_2$ atmosphere at 5.0×10$^{-9}$–1.0×10$^{-8}$ Torr followed by annealing at 600 °C, while the ordered TiO$_2$–(5×1) film is formed by Ti deposition in O$_2$ atmosphere at 10$^{-7}$–10$^{-5}$ Torr followed by annealing at 600 °C. In the case of the TiO$_2$/Ag(100) systems, the chemical state of the film can be clearly identified by XPS measurements, because the core levels of Ti and O can be observed without the interference of Ag core levels. This is contrary to the cases of the TiO/MgO(100) and TiO/TiC(100) systems where either Ti or O core levels are interfered with the substrate Ag core levels. This is contrary to the cases of the TiO/MgO(100) and TiO/TiC(100) systems where either Ti or O core levels are interfered with the substrate Ag core levels. Thus, the TiO film on Ag(100) is considered to be the most well-defined TiO single-crystal film among those obtained thus far. Recently angle-resolved photoelectron spectroscopy (ARPES) measurements with synchrotron radiation have been performed for the TiO/Ag(100) system, and the two-dimensional band structure of the film was determined [10].

As described above, the data on the atomic and electronic structures of the TiO films have been accumulated to some extent, however, detailed information on the growth mechanism of TiO on Ag(100) has not been obtained yet. In order to establish the procedure of the TiO

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film formation, it is important to elucidate the growth mechanism of the TiO film on Ag(100) in an atomic scale. A theoretical simulation should be useful to elucidate the growth mechanism microscopically, however, the theoretical simulation for the growth of a TiO film is not an easy task because it is difficult to construct the proper model systems which include co-adsorbed O/Ti components. The adsorption and dissociation of O$_2$ on Ag have been theoretically investigated on cesium deposited and undeposited Ag(111) cluster surfaces [14]. The study showed that O$_2$ molecules readily dissociate on Cs-deposited surfaces [14] while those do not react with the clean surface. Similar results have been obtained by the molecular beam study in which it is shown that the O$_2$ molecule scarcely adsorbs on Ag(100) because the interaction between the O$_2$ molecule and Ag(100) is weak [15]. Therefore, the formation of the TiO film on Ag(100) is considered to be initiated by the Ti adsorption. In this paper, we will show the results of the theoretical simulation using the density functional theory (DFT) for the reaction mechanism of O$_2$ with Ti-precovered Ag(100) surfaces.

II. COMPUTATIONAL DETAILS

All electronic structure calculations were carried out with Gaussian03 program package [16], and optimized structures were produced by the XCRYSDEN graphical package [17]. The spin-unrestricted B97-2 hybrid exchange-correlation functional devised by Wilson et al. [18] was adopted. The LanL2DZ effective core potential devised by Hay and Wadt [19–21] was used for Ag and Ti atoms, while the D95V(d) standard basis set devised by Dunning and Huzinaga [22] was employed for O atoms in all calculations. The calculated O–O bond length in a free molecule was 1.210 Å, well agreed with experimental value of 1.208 Å [23].

The convergence of self-consistent-field (SCF) iteration including many heavy atoms is generally difficult to be achieved, and we succeeded in the convergence of the SCF iteration by the use of the pseudo-fractional occupation number (pFON) [24] or the quadratically convergent-SCF (QCSCF) [25]. The former includes the adjustment of orbital occupations on the basis of pseudo-Fermi–Dirac distribution, while the latter includes the calculations in the SCF iteration using both the linear search and the Newton–Raphson approach. Although the QCSCF approach usually leads to excellent convergence, it consumes enormous CPU time compared with the pFON approach. Therefore, the pFON approach was performed for all systems at first, and the QCSCF approach was adopted only when the system was so complicated that the SCF iteration was not converged by the pFON approach. These approaches were adopted properly in this work, and the calculations using the above approaches give nearly the same adsorption energies and geometric parameters. The methodology adopted for each optimized structure was inscribed in tables given below.

We chose the Ag(100) bare model cluster which has fourteen silver atoms and consists of three-layers in this study. There are 9, 4 and 1 Ag atoms in the top, middle and bottom layer, respectively. The model cluster surface was depicted in Fig. 1.

The nuclear coordinates of all Ag atoms were set to be consistent with the experimental lattice constant (4.09 Å) [13] and were fixed during all calculations because the low energy electron diffraction (LEED) study showed that the (1×1) atomic arrangement of the Ag(100) substrate was almost intact after TiO$_x$ film formation [10]. We therefore determined optimized structures on a potential energy surface by means of the diagonalization of the partial-Hessian matrix with respect to the only adsorbed species [26].

The adsorption energy ($E_{ad}$) was estimated using the following standard supermolecular technique:

$$E_{ad} = E_C - (E_S + E_A)$$

where, $E_C$, $E_S$ and $E_A$ stand for total energies of a complex, an isolated substrate and an isolated adsorbate, respectively. Each of them includes the free energy correction at 298.15 K and the zero-point energy [27]. We also estimated the basis-set superposition error (BSSE) using the Boys–Bernardi’s counterpoise approach [28] in order to eliminate physically and chemically unreal interaction between the substrate–adsorbate.

The formation of titanium oxides on Ag(100)-Ag$_{14}(9/4/1)$ cluster surface is assumed to proceed via the following steps: (1) Simultaneous adsorption of nTi ($n = 1 ~ 4$) on Ag(100)-Ag$_{14}$ cluster surface and (2) the adsorption of single O$_2$ molecule on each nTi/Ag$_{14}$ system.

III. RESULTS AND DISCUSSION

A. nTi/Ag(100)

We first show the results about adsorption of nTi ($n = 1$-4) on the Ag(100) cluster surface. The optimized structures were shown in Fig. 2, and adsorption energies and main structural parameters were summarized in Table I.

The most stable adsorption site of the single Ti atom is a four-fold hollow site. The counterpoise (CP)-corrected adsorption energy of the single Ti atom on this site was –0.62 eV. The absolute value of $E_{ad}$ was abruptly increased when the number of adsorbed Ti atoms was increased to two, and was roughly proportional to the number of deposited Ti atoms at $n \geq 2$ although the adjacent Ag–Ti distance was around 2.7 Å in all coverages. We found that the four-fold hollow site is a stable site for Ti adsorption in every case, however, a Ti–Ti coupled structure which
FIG. 2: The optimized structures which adsorbed \( n \) Ti atoms \((n = 1 \sim 4)\) on Ag\((100)\)-Ag\(_{14}\) cluster surface. Ti atom is colored by light-blue in the figure.

TABLE I: The adsorption energy \( (E_{ad}: \text{eV}) \) and main structural parameters \((d_{Ag-Ti}, d_{Ti-Ti}: \text{\AA})\) in titanium adsorption on Ag\((100)\)-Ag\(_{14}\) cluster surface. The methodology in self-consistent field (SCF) iteration for each optimized structure is also inscribed.

| Structure | \( E_{ad} \) | \( d_{Ag-Ti} \) | \( d_{Ti-Ti} \) | SCF       |
|-----------|-------------|----------------|----------------|-----------|
| T1        | -0.62       | 2.729          |                | QCSCF     |
| T2a       | -1.59       | 2.731          | 3.926          | pFON      |
| T2b       | -3.68       | 2.737          | 2.035          | pFON      |
| T3        | -5.65       | 2.702          | 2.019, 2.800, 2.952 | QCSCF   |
| T4        | -7.57       | 2.710          | 2.548, 3.603   | pFON      |

\( ^a \) BSSE is already subtracted. Then, the system is divided into Ag\((100)\) and titanium fragments. The counterpoise approach is performed by a single-point calculation at the level of the UB97-2/LanL2DZ.

\( ^b \) Adjacent distance.

includes the Ti atoms in the four-fold hollow site and that in the bridge site is also stable in some cases. The formation of Ti–Ti bond is found to play an important role in stabilizing the system because \( E_{ad} \) in T2b was about twice as large as that of T2a. It is noted that the unit cell of the adsorbed Ti layer shown in T4 was smaller than that of Ag\((100)\) cluster surface by about 12 %. It was found that no bonding orbital was formed between the Ag–Ti interface in every case, and the Ti–Ti coupling seems to be more stronger than the Ag–Ti coupling. The lack of the bonding orbital between Ti and Ag is clearly shown in a charge density plot, and an example for T4 is described in Fig. 3. Figure 3 shows that the electron density of the valence electrons in Ti was delocalized in the titanium film, while it was sparse between the Ag–Ti interface, clearly indicating that the bonding orbitals are not formed in the interface. The similar charge density map was obtained for \( n \leq 3 \) (not shown here).

B. \( O_2 \) adsorption on Ti-precovered Ag\((100)\)

We studied the adsorption of a single \( O_2 \) molecule on the \( n \)Ti-precovered Ag\((100)\), which is thought to be an initial reaction path in the formation of TiO\(_x\)-film structures. First, we discuss the adsorption structure of \( O_2 \) on one Ti-precovered Ag\((100)(T1)\). The optimized structures of \( O_2/Ti/Ag\(_{14}\) system were shown in Fig. 4. The adsorption energies and main structural parameters were summarized in Table II.

We found two kinds of possible structures which arise

TABLE II: The adsorption energy \( (E_{ad}: \text{eV}) \) and adjacent structural parameters \((d_{Ag-Ti}, d_{Ag-O}: \text{\AA})\) at the interface in \( O_2/Ti/Ag\(_{14}\) system. The methodology in SCF iteration for each optimized structure is also inscribed.

| Structure | \( E_{ad} \) | \( d_{Ag-Ti} \) | \( d_{Ag-O} \) | SCF       |
|-----------|-------------|----------------|----------------|-----------|
| la        | -7.45       | 2.887          | 2.357          | pFON      |
| lb        | -3.90       | 2.769          | 2.230          | pFON      |
| lc        | -3.90       | 2.794          | 3.421          | pFON      |
| ld        | -2.08       | 2.774          | 2.813          | pFON      |
| le        | -2.01       | 2.792          | 3.403          | pFON      |

\( ^a \) The system is divided into three fragments of Ag\(_{14}\), TiO and O in 1b during the counterpoise calculation.
form dissociative O$_2$ adsorption; one formed a TiO$_2$ unit including an Ag–O bond (1a), and the other formed a TiO unit as well as the chemisorption of O atoms on the fourfold hollow site of Ag(100) (1b). In addition, we found three kinds of molecular adsorption structures (1c–1e). The adsorption energies of the dissociatively adsorbed systems are generally larger than those of the molecularly adsorbed systems. However, the CP-corrected $E_{\text{ad}}$ of 1b was nearly identical to that of 1c. It directly indicates that (1a) is essential for stabilizing the system.

The calculations for O$_2$ adsorption were also performed on both 2Ti-precovered surfaces discussed in section A (T2a and T2b).

The optimized structures of these systems are shown in Fig. 5, in which the 2a, 2b and 2c structures arise from the O$_2$ adsorption on T2a and the 2d structure arises from the O$_2$ adsorption on T2b. The results of energetic and structural analyses were summarized in Table III. In Table III, we showed not only the usual relative adsorption energy on either T2a or T2b (out of parentheses) but also the total energy difference relative to the whole O$_2$/2Ti/Ag$_{14}$ systems (in parentheses) because the value of $E_u$ term in Eq. (1) was apparently dependent on the models. Both dissociative and molecular adsorption were found to be possible on the T2a surface. The former produced a (TiO)$_2$ unit including a Ti–Ti bond (2a) or a TiO-chain unit along the [001] direction (2b). The latter produced molecularly chemisorbed O$_2$ whose molecular axis was parallel to the surface (2c).

In the 2c structure, O$_2$ sits on one of Ti atoms. On the other hand, only a dissociative adsorption structure involving a TiO-chain along the [011] direction has been found on the T2b surface (2d). The adsorption energies of the 2a, 2b, and 2c structures were calculated to be about −11.1, −10.1 and −4.1 eV, respectively, while that of the 2d structure was estimated to be −8.4 eV. The relative energies of the 2a, 2b, 2c, 2d structures were 0.0, 1.0, 7.0, and 0.5 eV, respectively. These results suggest that the structure formed through the dissociation of O$_2$ was more stable also on the 2Ti-precovered surfaces.

Our calculations also revealed the detailed structures in the O$_2$/3Ti/Ag$_{14}$ system which arise from O$_2$ adsorption on the T3 structure (Fig. 2). The optimized structures and energetic/structural information were described in Fig. 6 and Table IV, respectively. On the 3Ti/Ag$_{14}$ system, any stable structures including molecularly adsorbed O$_2$ were not found.

We found five kinds of stable structures whose adsorption energies are converged within the small energy range of 1 eV. The most stable structure (3a) has a Ti–O–Ti bond along the [001] direction and that along the direction slightly tilted from the [011] direction. The one of the

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### Table III: The adsorption energy ($E_{\text{ad}}$: eV) and adjacent structural parameters ($d_{\text{Ag–Ti}}, d_{\text{Ag–O}}$: Å) at the interface in O$_2$ adsorption on both T2a and T2b surfaces. The methodology in SCF iteration for each optimized structure is also included.

| Structure | $E_{\text{ad}}$ | $d_{\text{Ag–Ti}}$ | $d_{\text{Ag–O}}$ | Method |
|-----------|----------------|-----------------|-----------------|--------|
| 2a        | −11.10 (0.00)  | 2.743           | 3.165           | pFON   |
| 2b        | −10.13 (0.97)  | 2.654           | 2.691           | pFON   |
| 2c        | −4.11 (6.99)   | 2.655           | 3.851           | QCSCF  |
| 2d        | −8.36 (0.49)   | 2.828           | 2.558           | pFON   |

*The values out of parentheses are the relative adsorption energies normalized on each surface, while energies in parenthesis indicate the relative energies normalized by lowest energy in two types of O$_2$/2Ti/Ag$_{14}$ systems.

### Table IV: The estimated adsorption energy ($E_{\text{ad}}$: eV) and adjacent structural parameters ($d_{\text{Ag–Ti}}, d_{\text{Ag–O}}$: Å) at the interface in O$_2$/3Ti/Ag$_{14}$ system. The methodology in SCF iteration for each optimized structure is also included.

| Structure | $E_{\text{ad}}$ | $d_{\text{Ag–Ti}}$ | $d_{\text{Ag–O}}$ | Method |
|-----------|----------------|-----------------|-----------------|--------|
| 3a        | −10.13         | 2.681           | 3.178           | pFON   |
| 3b        | −9.92          | 2.804           | 2.903           | QCSCF  |
| 3c        | −9.82          | 2.743           | 3.250           | QCSCF  |
| 3d        | −9.63          | 2.658           | 3.032           | pFON   |
| 3e        | −9.21          | 2.715           | 2.809           | pFON   |
analyses showed that bonding orbitals were formed only when the number of precovered Ti atoms. Our theoretical simulations showed that the formation of Ti–O–Ti or O-induced Ti–Ti bonds play an important role in stabilization of the O$_2$/nTi/Ag$_{14}$ systems. There is an alternative possible growth process of Ti oxide film, which is initiated by Ti adsorption on O$_2$-precovered surface. However, our simulations showed that this process is hard to proceed, because no stable adsorption structure was formed for O$_2$/Ag(100). It is consistent with the results of the molecular beam study, which showed that the interaction between Ag(100) and O$_2$ is weak [15]. However, the formation of several types of O-induced missing-row reconstructions and silver-oxides have been theoretically suggested when a dissociated O atom was adsorbed on Ag(100) surface [29–31]. Therefore, we will search a possibility for the growth mechanism triggered by the formation of Ti/O/Ag(100) systems in the future. Similarly, it is important to discuss a simultaneous adsorption of Ti and O$_2$ because Ti was deposited on the surface in O$_2$ atmosphere in the experiment. However, it is difficult to control the reaction mechanism such a complicated system at this point, and we will perform an ab initio molecular dynamics simulation in near future.

FIG. 7: The optimized structures for the O$_2$ adsorption on the 4Ti-precovered Ag(100)–Ag$_{14}$ cluster surface.

TABLE V: The calculated adsorption energy ($E_{ad}$: eV) and adjacent structural parameters ($d_{Ag_Ti}$, $d_{Ag_O}$: Å) at the interface in O$_2$/4Ti/Ag$_{14}$ system. The methodology in SCF iteration for each optimized structure is also inscribed.

| Structure | $E_{ad}$ | $d_{Ag_Ti}$ | $d_{Ag_O}$ | Method |
|-----------|---------|-------------|-------------|---------|
| 4a        | -10.54  | 2.719       | 3.293       | pFON    |
| 4b        | -10.37  | 2.812       | 3.432       | QCSCF   |
| 4c        | -10.12  | 2.618       | 3.258       | pFON    |

adsorbed O atoms was found to be sit on the three-fold hollow site of the three Ti atoms in 3b, 3d and 3e. We also found a symmetric Ti–O–Ti chain structure along the [001] axis in 3c.

The optimized structures of the O$_2$/4Ti/Ag$_{14}$ system were shown in Fig. 7, and their energetic and structural information were summarized in Table V. All the optimized structures were formed through the dissociative adsorption on the 4Ti-precovered surface. The released O atoms adsorbed either at the three-fold hollow site or at the bridge site. The 4b and 4c structures are considered to be important because each of them included a locally symmetric chain structure along the [011] or [001] direction, respectively, and the formation of these structures can be viewed as the initial steps of an epitaxial growth of titanium oxide films. All the $E_{ad}$s were close to that of 3a and were included within the energy range of −10.10–−10.55 eV.

The results described above show that the energy of the stabilization induced by O$_2$ adsorption was generally increased with increasing the number of precovered Ti atoms. However, the adjacent Ag–Ti distances were almost invariant after O$_2$ adsorption irrespective of the number of precovered Ti atoms at $n = 1–4$. Furthermore, the adjacent Ag–O distances were increased with increasing the number of precovered Ti atoms. Our theoretical analyses showed that bonding orbitals were formed only in Ti–O–Ti and Ti–Ti units, and that the interactions between Ag and Ti and those between Ag and O were weak. These results clearly indicate that the formations of Ti–O–Ti or O-induced Ti–Ti bonds play an important role in stabilization of the O$_2$/nTi/Ag$_{14}$ systems.

IV. CONCLUSION

We presented here the results of density functional theory calculations with respect to the successive adsorption of titanium atom and oxygen molecule on the Ag(100) cluster surface in order to investigate the detailed atomic arrangement of titanium oxides on Ag(100).

The SCF iteration was efficiently converged by means of the QCSCF approach or the pFON approach.

The formation of Ti–Ti bond appeared to stabilize nTi/Ag(100) systems, and the analyses of the charge density distribution explicitly revealed that no bonding orbital was found at the Ag–Ti interface after the deposition of nTi ($n = 1–4$).

The adsorption energy of O$_2$ on the nTi-precovered surfaces was larger than that on the bare-Ag(100) surface. It is similar to the case of Cs-precovered Ag(111) surface [14]. O$_2$ was dissociated more easily as the number of Ti atoms increased. The dissociated O atoms mainly incorporated between Ti atoms forming TiO-chains or TiO-cyclic units, which can be viewed as the initial steps in the growth of a TiO film. The adsorption energy of O$_2$ on nTi/Ag(100) was increased as the number of precovered Ti atoms increased. Our theoretical simulations showed that the formation of a Ti–O–Ti and an O-induced Ti–Ti unit mainly contribute to the stabilization of the O$_2$/nTi/Ag(100) system.

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