Structures and Stabilities of Gold Oxide Films on Gold Surfaces in O₂ Atmosphere

Keju Sun^{1,2*}, Masanori Kohyama², Shingo Tanaka² and Seiji Takeda¹

1) The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka,
Ibaraki, Osaka 567-0047, Japan

2) Research Institute for Ubiquitous Energy Devices, National Institute of Advanced
Industrial Science and Technology (AIST), 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan

*Corresponding author. Tel.: +81-72-751-9732; fax: +81-72-751-9714

Email: keju.sun@aist.go.jp

Abstract

The structures and stabilities of gold oxide films on gold surfaces in O₂ atmosphere are investigated by a combination of thermodynamics and density functional theory (DFT) calculations. It is predicted that the stability of a gold oxide film on a gold surface depends on the formation energy of an isolated gold oxide film, the lattice mismatch, and the oxygen coverage. These predictions are subsequently confirmed by DFT calculations and thermodynamic analysis. The calculation results also display the dual chain structure is stable on most gold surfaces at low oxygen chemical potential except on a Au(111) surface, on which the graphene-like 12 MR structure is more stable. While at the high oxygen chemical potential, the connected dual chain structure is the most stable structure because of the highest oxygen coverage and the lowest formation energy. The phase transformation point from the dual chain structure to the connected dual chain structure on a gold surface depends on the lattice mismatch between the connected dual chain and a gold surface.

Keywords:

Stabilities; Gold oxide film; Density functional theory calculations; Thermodynamic analysis

1. Introduction

Gold was considered as chemically inert for a very long time, for it is hard to be oxidized to Au_2O_3 [1,2,3]. However, a gold oxide film stable under 500 K [4] can easily be produced on a gold surface, via adsorption of atomic oxygen [4,5], chemical oxidation [6,7], or photochemical oxidation with O_3 [8,9]. In past decades, numerous studies have been devoted to explore the nature of gold oxide films, since it is believed to be related to the unique oxidation catalysis of gold catalysts [10,11]. Despite the huge number of experimental and theoretical works, the structure of gold oxide films is still poorly understood. It even remains controversial whether the structure of atomic oxygen adsorption on gold is ordered or not, unlike sulfur or chlorine adsorption on Au(111), which induces a reconstruction to an ordered $\sqrt{3}\times\sqrt{3}$ R30° pattern by low-energy electron diffraction (LEED) [12,13]. Some reports show that no ordered overlayer structure of atomic oxygen adsorption on Au(111) or Au(100) was observed by LEED [4,7,8], while others show that the ordered structure can be formed by the same method or scanning tunneling microscopy (STM) [14,15].

Recently, Uchiyama et al studied a real Au/CeO₂ catalyst in O₂ atmosphere by in situ environmental transmission electron microscopy (ETEM) [16]. They found the gold surface is not steady with oxygen adsorption but fluctuates between Au(111), Au(100) and Au(110) facets with time under the spatial resolution available on the environmental transmission electron microscope. The surface fluctuation makes it challenging to identify the structure of gold oxide films only by experimental methods. Theoretically, Shi and Stampfl investigated the structure and stability of atomic oxygen adsorption and surface oxide formation on Au(111) [17], Au(100) and Au(110) surfaces [18], and found a surface-oxide-like configuration, an added-atom (5x2)-O configuration, and a missing row (2x1)-2O configuration as the most stable structure on Au(111),

Au(100) and Au(110) surfaces, respectively. They suggested the Au(110) facets should be more stable at the higher oxygen chemical potentials. It should be noted that the oxygen saturated coverage in Shi and Stampfl's models with 0.3 ML on Au(111) and 0.1 ML on Au(100) is significantly lower than that in experimental conditions with about 0.8~1.2 ML [4,7,8,19]. So far as we know, the oxygen adsorption structures on gold surface are ambiguous at higher coverage.

Aiming to provide insights into the adsorption of oxygen on gold surfaces especially for the high oxygen coverage structures, we investigate the structures of surface gold oxide films on gold surfaces by the combination of thermodynamics and density functional theory (DFT) calculations [18,20]. In this work, we first propose several possible stable structures of gold oxide films based on the stable linear O-Au-O structure in our previous work [21]. Then stability of these gold oxide films on flat Au(111), Au(100), Au(110) surfaces and stepped Au(221) and Au(211) surfaces are calculated by DFT calculations, and the corresponding surface energies as a function of oxygen chemical potential are plotted in the phase diagram based on the thermodynamical method. Finally, the reason of fluctuation of gold surfaces in O₂ atmosphere is discussed from the view of thermodynamics and dynamics of gold oxide films on gold surfaces.

2. Methods

Periodic DFT calculations using Vienna Ab Initio Simulation Package (VASP)[22] were performed to examine the structure and stability of gold oxide films on gold surfaces. The exchange-correlation energy and potential are described by generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) [23]. Plane waves are used to expand wave functions with a cutoff of 400 eV for projector augmented wave (PAW) potentials.[24,25]

The cutoff of 400 eV is a reasonable compromise between the calculation accuracy and calculation speed based on the testing results (See supporting information in Figure 1S). The criteria for the convergence in the structural determination is the residual force less than 0.02 eV $\text{\AA}^{-1}$. The calculated lattice constant for bulk Au was 4.17 $\text{\AA}$, which is in reasonable agreement with the experimental value of 4.08 $\text{\AA}$ and the previous theoretical value of 4.18 $\text{\AA}$. [26] All surfaces including Au(111), Au(100), Au(110), Au(221) and Au(211) surfaces with oxygen adsorption are modeled by a seven-layer slab except for the structures of Au surfaces covered by the graphene-like 12 MR structures. For latter, the structures are modeled by a five-layer slab due to their large super cells. The adsorbed oxygen species on gold surfaces are placed on both sides and the vacuum thickness is 15 $\text{\AA}$. Spin polarizations are considered and all the atoms in the slab are relaxed during all the calculations, and the high spin species is only found for the isolated AuO_4 structure with five unpaired electrons. The transition state of gold atom diffusion on a Au(111) surface is searched by force reversed method [27].

It was reported that the low Miller indexed Au(111), Au(100) and Au(110) surfaces are reconstructed to Au(111)-(23 $\times\sqrt{3}$), Au(100)-(1 $\times$ 5) and Au(110)-(1 $\times$ 2) surfaces in most cases [28]. However, in this work the simple unreconstructed surfaces instead of the reconstructed surfaces are calculated due to the following reasons: (1) The structures of unreconstructed surfaces are more simple than those of the reconstructed surfaces, therefore they are generally adopted in the theoretical studies [29]. (2) The recent TEM experimental results showed that the structures of Au(100) and Au(111) surfaces on gold cluster are unreconstructed in the vacuum [30], which indicates that the unreconstructed surfaces are stable especially on the gold nanoparticles.

To overcome the underestimation of weak cohesive energy of gold originated from d^{10} - d^{10} interaction [31,32], the method of DFT with D3 correction [33] is used for all atoms in the

systems. The calculated surface energies of clean Au(111) surface, Au(100) and Au(110) surface without D3 correction are 46.4, 54.0 and 58.8 meV/Å², respectively, which are in good agreement with the previous calculation results by DFT method of 46.2, 53.1 and 56.2 meV/Å², correspondingly.[29] However, the calculated surface energies are significantly underestimated compared to the experimental value of 93.6 meV/Å². [34] With D3 correction, the calculated surface energies are 89.6, 96.9 and 98.2 meV/Å², respectively, which agree well with the experimental results.

The surface free energy of a gold surface with oxygen adsorption (O/Au system) is a measure to judge the stability. In this work, the surface free energy of an O/Au system is defined as

$$\gamma(T, p) = (G_{O/Au}^{slab} - N_{Au}\mu_{Au} - N_O\mu_O) / A \quad (1)$$

where $G_{O/Au}^{slab}$ is the Gibbs free energy of the O/Au system under consideration. N_{Au} and N_O are the numbers of Au and O atoms in the O/Au system. μ_{Au} and μ_O are the chemical potentials of Au and O atoms and A is the surface area of the O/Au system. $\mu_{Au} = E_{Au}^{bulk}$ and $G_{O/Au}^{slab} = E_{O/Au}^{slab}$ are adopted since the contribution from pV term of solids in Gibbs free energy can be neglected for the pressure lower than 100 atm [17]. μ_O is normally defined as [20]

$$\mu_O(T, p) = \frac{1}{2} [E_{O_2} + \Delta\mu_{O_2}(T, p^0) + k_B T \ln(\frac{p_{O_2}}{p^0})] = \frac{1}{2} [E_{O_2} + \Delta\mu_{O_2}(T, p)] \quad (2)$$

where E_{O_2} is the total energy of the O₂ molecule, $\Delta\mu_{O_2}(T, p^0)$ and $\Delta\mu_{O_2}(T, p)$ include the contribution from translations, rotations, vibrations of the O₂ molecule at the pressure of p^0 (1 atm) and p , respectively, which can be calculated by thermodynamics formulas or obtained from experimental thermodynamic tables. The DFT calculation with GGA exchange correlation functional overestimates the binding energy of O₂ molecule in triplet state, which will induce an overestimation of all the surface energy of the surfaces with oxygen adsorption. Therefore, the

argument of the oxygen chemical potential ($\Delta\mu_{\text{O}}=\Delta\mu_{\text{O}_2}(T,p)/2$) is used instead of two arguments of the temperature (T) and the pressure (p) in order to simplify the discussion. It should be noted that low $\Delta\mu_{\text{O}}$ corresponds to high temperature and low O_2 pressure.

3. Preliminary and general analysis

The possible configurations of adsorbed oxygen on a gold surface are so numerous that it is hard to investigate all the possibilities. A preliminary screening is necessary based on some basic rules or principles before DFT calculations. According to our previous study [21,35], the π bond plays a key role in the interaction between Au and O and the adsorbed atomic oxygen on gold thermodynamically prefers to form the linear O-Au-O structure. Likewise, it should be energetically favorable to form the crossed AuO_4 structure consisting of two linear O-Au-O structures with strengthened Au-O π bonding. Therefore, we believe that the surface gold oxide films should be composed of the linear O-Au-O structure (Figure 1a) and/or the crossed AuO_4 structure (Figure 1b), since the linear O-Au-O structure could strengthen the Au-O interaction compared to those without linear O-Au-O structure [36]. Since the π bonding is dominant for Au-O interaction, a large flat structure with delocalized π bonding in a wide range is expected. Furthermore, the fundamental to form a delocalized conjugated π bond is the coplanar configuration of atoms, so the surface gold oxide film with one atomic layer is expected, which agrees well with the experimental results that only the surface top layer is oxidized [16] and the saturated oxygen coverage is about 1ML [19,37,38].

It was proven that the gold oxide with four-coordinated oxygen via sp^3 hybridization is unstable compared to that with two-coordinated and three-coordinated oxygen by Shi and Stampfl [39]. Our DFT calculations also indicate that the four-coordinated oxygen is not as

stable as three-coordinated and two-coordinated oxygen in O/Au systems. This can be well understood since the contribution of π bonding plays a key role in O/Au systems [21]. The three-coordinated or two-coordinated oxygen with sp^2 hybridization could form Au-O π bonding via the non-hybridized p orbital of oxygen and some d orbitals of gold, while the four-coordinated oxygen with sp^3 hybridization could not form Au-O π bonding because all the orbitals of oxygen form σ bonds. Therefore, the coordination number of oxygen in an O/Au system could be two or three. In addition, the single coordinated oxygen is not considered as stable as two or three coordinated oxygen, since it will break the bond network in a gold oxide film and therefore destroy the delocalized conjugated π bond.

According to our previous study, [21] the total binding energy increases with the coordination number, and thus it is easily predicted that the surface gold oxide with the highest coordination number for gold and oxygen will be the most stable structure. As we discussed above, the highest coordination numbers for gold and oxygen are four and three, so the most stable surface gold oxide should be composed of four-coordinated Au and three-coordinated O, and the basic structure for gold is the crossed AuO_4 . It can be seen that the structure of bulk Au_2O_3 also obeys this rule [39,40], where local configurations can be regarded as the crossed AuO_4 structure and the maximum coordination number for oxygen is three.

Compared to an isolated gold film, the stability of the gold oxide film on a gold surface is more complicated, where the adhesion energy between the gold oxide film and a gold surface is also important. It is commonly believed that the adhesion energy is related to the lattice mismatch [41] between the gold oxide film and gold surface. The lattice constant includes two factors: the lattice side length (u and v), and the angle (α) between the sides. It is very convenient to judge the matching degree of angle. For example, the angle for the hexagonal structure with

60° or 120° is not equal to that of 90° in a tetragonal structure, leading to a mismatch with each other from the angle. Certainly, the hexagonal structure also can be regarded as the tetragonal structure after the lattice constant multiplied by $\sqrt{3}$. There are several different methods to calculate the lattice mismatch degree (δ) between the film and surface, and in this work it is defined as [42],

$$\delta = \frac{|L_{Film} - L_{surface}|}{L_{surface}} \times 100\% \quad (3)$$

where L_{Film} is the lattice constant of a gold oxide film on a gold surface and $L_{surface}$ is the lattice constant of the gold surface. We predict that the oxide film on a gold surface with less lattice mismatch will be more stable.

The intrinsic stability of a gold oxide film on a gold surface depends on the stability of the isolated gold oxide film and the lattice mismatch. At O₂ atmosphere, the stability is also depends on the oxygen chemical potential in the thermodynamics. From equations (1) and (2), it is concluded that the surface energy (γ) has linear relationship with $-\Delta\mu_O(N_O/A)$. Thus the surface with lower oxygen coverage (N_O/A) is more stable for lower oxygen chemical potential $\Delta\mu_O$ (more negative), while the surface with higher oxygen coverage is more stable for high oxygen chemical potential. In this work, the surface coverage of oxygen in monolayer (ML) is defined as the numbers of oxygen atoms in each unit cell. Theoretically, there are three factors, the formation energy of an isolated gold oxide film, the lattice mismatch and the oxygen coverage, affecting the stability of gold oxide films on gold surfaces at given O₂ atmosphere, and so DFT calculations with thermodynamics are necessary to find out the most stable structure.

4. Results and discussion

4.1 The stability of the isolated gold oxide films

As mentioned above, the gold oxide films should be composed of the linear O-Au-O structure and/or the cross AuO_4 structure, and the coordination numbers are two or four for gold and two or three for oxygen. Therefore, we build four models of surface gold oxide based on the coordination number, as shown in Figure 1c-f. The coordination numbers of gold and oxygen are all two in Figure 1c (single chain), four and two in Figure 1d (dual chain), two and three in Figure 1e (graphene-like 12 MR), respectively. It should be noted that the structure with four-coordinated gold and three-coordinated oxygen will break the symmetry of the crossed AuO_4 structure, and then decrease the stability. Therefore, two kinds of gold atoms with the coordination numbers of four and two are found in Figure 1f (connected dual chain). Figure 1 also shows the formation energy (E_{form}), as defined in the following,

$$E_{\text{form}} = \frac{E_{\text{O/Au}} - N_{\text{Au}} E_{\text{Au}}^{\text{bulk}} - \frac{N_{\text{O}}}{2} E_{\text{O}_2}}{N_{\text{O}}} \quad (4)$$

where $E_{\text{O/Au}}$, $E_{\text{Au}}^{\text{bulk}}$, and E_{O_2} are the total energies of the O/Au system, a bulk gold atom, and an O_2 molecule, respectively. It is found that the formation energy decreased with the increase of the coordination number of gold or oxygen and the formation energy is the lowest for the connected dual chain. These results confirm our previous prediction that the surface gold oxide with the highest coordination number for gold and oxygen will be the most stable isolated structure.

4.2 The stability of gold oxide films on Au(111) surface

Having studied the stability of isolated surface gold oxide films, we then investigate the stability of gold oxide films on Au surfaces. The close-packed Au(111) surface is first investigated. Figure 2a and 2b show the structures of single chain and dual chain on the Au(111) surface. Since the surface energy is related to the oxygen coverage, the structures of single chain and dual chain with the coverage of $1/2$ ML, $1/3$ ML and $1/4$ ML are calculated, where the coverage is set by changing the distance between the chains arrayed along the $\langle 011 \rangle$ direction on the surface. Note that the density of the dual chains is always half of that of the single chains for the same coverage, due to the double density of oxygen atoms per chain (see Figure 2a and Figure 2b for the coverage of $1/2$ ML). In Figure 2c, the dual chain (D) structure on Au(111) is always more stable than the single chain (S) structure for each coverage. The reason can be assigned to the lower formation energy (per oxygen atom) of the isolated dual chain structure, 0.67 eV, in contrast to 1.24 eV for the single chain structure (Figure 1d and 1c).). Since the sizes of the periodicity in the two kinds of chains are very similar, the lattice mismatch between the chain and all gold surfaces is similar for the single chain and dual chain. The influence of the oxygen chemical potential can also be ignored if the oxygen coverage is the same. As a result, the relative stability of isolated single chain and dual chain structures should be dominant, and the dual chain structure should be more stable than the single chain structure on all gold surfaces, thus only the dual chain structure is discussed thereafter.

The stability of graphene-like 12 MR structures on Au(111) is also examined as shown in Figure 3a-d. Since both of the symmetry of the graphene-like 12 MR structure and the Au(111) surface are hexagonal, two structures with high symmetry can be formed for graphene-like 12 MR adsorption on the Au(111) surface. In one structure, the Au-O bond in graphene-like 12 MR

is parallel to the Au-Au bond in the Au(111) surface (Figure 3d), as denoted by eclipsed conformer. In the other one, the graphene-like 12 MR film is rotated by 30° degree (Figure 3a) compared to the eclipsed conformer, and it is called staggered conformer. As denoted in Figure 3a,d, proper two-dimensional supercells are naturally selected. Nine rings of graphene-like 12 MR and 49 Au atoms constitute one coincidence supercell for the staggered conformer, and three rings and 16 Au atoms constitute that for the eclipsed conformer. There is no substantial deformation in the gold oxide layer to attain such coincidence.

It is well known that the staggered conformer of ethane molecule has higher stability than the eclipsed conformer due to the strong repulsion between two groups of CH₃ σ bonds for the eclipsed conformer (Figure 4). Likewise, the graphene-like 12 MR on Au(111) with the staggered conformer should be more stable than those with the eclipsed conformer (Figure 4). The lattice mismatch degree for the staggered conformer is 133 %, which is almost equal to that for the eclipsed conformer by 131 %. Therefore the influence of lattice mismatch can be ignored when their relative stabilities are studied. In addition, the influence of oxygen chemical potential can also be ignored since the oxygen coverage of the staggered conformer with 0.367 ML is almost same as the eclipsed conformer with 0.375 ML. As we can see in Figure 3e, the staggered conformer is more stable than the eclipsed conformer. The energy difference between the staggered and eclipsed conformers is about 0.32 eV for each unit of graphene-like 12 MR, which may make only the staggered conformer to be observed. Since the repulsion between two groups with σ bonds is general, this behavior could be used to explain the stability of similar structures, such as graphene on transition metals. It was reported that only the staggered structures were observed in the experiments.[43,44]

The work of Shi and Stampfl showed that the structure of graphene-like 12 MR with some oxygen vacancies (Figure 3c) is more stable. [17] We thus investigate the stability of the graphene-like 12 MR with oxygen vacancies on the Au(111) surface. For the eclipsed conformer, the graphene-like 12 MR with oxygen vacancies (Figure 3c) is really more stable than that without oxygen vacancies (Figure 3d), which agrees well with Shi and Stampfl's results. However, for the staggered conformer, the graphene-like 12 MR without oxygen vacancies is more stable. The role of oxygen vacancies in stabilizing the eclipsed conformer of graphene-like 12 MR may be reducing the repulsive interactions between parallel Au-O σ and Au-Au σ bonds in the gold oxide film and the Au(111) surface, respectively. No matter the presence of oxygen vacancies or not, the staggered conformers are always more stable than the eclipsed conformer, and the stability of the staggered conformers can be assigned to the weaker repulsion between Au-Au σ bond and O-Au σ bond similar to ethane molecule.

We then turn to the stability of the connected dual chain structure on the Au(111) surface. Two typical structures of the connected dual chain adsorption are examined. In the first structure, the two-coordinated gold (Au(2)) is located much lower than the four-coordinated gold (Au(4)) so as to attain higher oxygen coverage as shown in Figure 5a. In this structure, the angle of O-Au(2)-O is far less than 180° . In the second structure of $3/4$ ML, the Au(2) atoms are located almost in the same plane with Au(4), and the angle of O-Au(2)-O is close to 180° as shown in Figure 5b. In the connected dual chain structure, the angle of O-Au(2)-O, the lattice constant along the chain, the lattice mismatch degree and the oxygen coverage have mutual correlation as shown in Figure 5c. It is found that the surface energies of the connected dual chain structures are similar if the coverage is close to each other, since they have the similar formation energy and similar lattice mismatch degree. Around some coverage, there are several similar connected

dual chain configurations, which make it possible to transform from one configuration to another. In our results, the flat connected dual chain structure with the coverage of $3/4$ ML is the most stable in a wider range of oxygen chemical potential, while it will transform to that with higher oxygen coverage (for instant, $7/9$ ML) for higher oxygen chemical potential, since the structure with high oxygen coverage is more stable for high oxygen chemical potential.

We examined the relative stability among the single chain, dual chain, graphene-like 12 MR and connected dual chain structures on the Au(111) surface as a function of the oxygen chemical potential. Except for the single chain structure which is always more unstable than the dual chain structure, the surface energies of other three structures are shown in Figure 6, where each line of the three structures reveals several segments with different slopes, corresponding to the most stable configuration with a difference coverage value for each region of the oxygen chemical potential, via the examination of various coverage configurations. In Figure 6, it is found that the graphene-like 12 MR structure is the most stable at lower oxygen chemical potential, whereas at higher oxygen chemical potential, the connected dual chain structure is the most stable, due to its higher oxygen coverage. Since the formation energy of the isolated graphene-like 12 MR, 1.21 eV, is higher than those of dual chain structure and connected dual chain structures, 0.67 eV and 0.45 eV, respectively, the stability of graphene-like 12 MR on the Au(111) surface can be assigned to the high adhesive energy due to its hexagonal symmetry similar to the Au(111) surface.

4.3 The stability of gold oxide films on Au(100), Au(110), Au(221) and Au(211) surfaces

Similarly to the gold-oxide films on Au(111) surface, we examined the stability of the films on Au(100) surface for the dual chain, connected dual chain and graphene-like 12 MR structures as shown in Figure 7. In Figure 7d, it is found that the dual chain structure is always more stable

than the graphene-like 12 MR structure on the Au(100) surface. The graphene-like 12 MR structure is unstable on the Au(100) surface compared to that on the Au(111) surface, which can be ascribed to the larger lattice mismatch. The graphene-like 12 MR has hexagonal symmetry similar to the Au(111) surface, which is quite different from the Au(100) surface with square symmetry.

When the oxygen chemical potential is low, the dual chain structure is more stable, and the connected dual chain structure becomes more stable at higher oxygen chemical potential. In Figures 7a and 7b, we can see that the dual chain structure and connected dual chain structure have similar configurations, and the lattice mismatch should be the same. The relative stability depending on the oxygen chemical potential can be explained by the oxygen coverage. The dual chain structure with lower oxygen coverage is more stable at the low oxygen chemical potential, while the connected dual chain structure with higher oxygen coverage is more stable at the high oxygen chemical potential. On the Au(100) surface, the phase transformation point from the dual chain structure to the connected dual chain structure is -0.21 eV, which is lower than the point of the formation of Au_2O_3 (-0.14 eV).

Similar gold-oxide film adsorption was examined on the Au(110) surface for dual chain, connected dual chain and graphene-like 12 MR structures as shown in Figure 8. The graphene-like 12 MR structure is also unstable on Au(110), since the symmetry of the Au(110) surface is tetragonal, differently from that of the graphene-like 12 MR structure. The dual chain structure is the most stable in a very wide range of the oxygen chemical potential, which agrees well with Shi and Stampfl's result [18]. This can be explained by the lattice mismatch with the Au(110) surface. In Figures 8a and 8b, the lattice mismatch degrees are zero and 50 % for the dual chain

and connected dual chain structures, respectively. Thus the phase transformation point from the dual chain structure to the connected dual chain structure is much higher (higher than -0.14 eV).

From the above results, the graphene-like 12 MR structure with hexagonal symmetry seems to be stable only on the Au(111) surface with similar hexagonal symmetry. Thus for the stepped Au(221) and Au(211) surfaces with tetragonal symmetry, only the dual chain and connected dual chain structures were examined. It is easily found that the dual chain structure matches well with the Au(221) surface in Figure 9a, while the lattice mismatch degree of the connected dual chain on the Au(221) surface is as high as 33% (Figure 9b). As shown in Figure 9c, the phase transformation point from the dual chain structure to the connected dual chain structure is higher than -0.14 eV. On the Au(211) surface, the connected dual chain structure is reconstructed to a partly connected dual chain structure as shown in Figure 10b, due to high lattice mismatch. After reconstruction, the partly connected dual chain structure matches well with the Au(211) surface, and thus the phase transformation point from the dual chain structure to the connected dual chain structure (-0.18 eV) is lower than -0.14 eV.

On the comparison of the stability of the gold oxide films among various Au surfaces examined, it is found that the dual chain structure is always stable at the low oxygen chemical potential except for the Au(111) surface, due to the high match with the surfaces. For the connected dual chain structure, it only matches well with the Au(100) and Au(211) surfaces, and so the phase transformation point from the dual chain structure to the connected dual chain structure is lower than -0.14 eV on these gold surfaces. On the other hand, the phase transformation point is higher than -0.14 eV on the Au(110) and Au(221) surfaces, due to the large lattice mismatches for these surfaces. In this way, it can be said that the relative stability of gold oxide films on gold surfaces is strongly dependent on the lattice mismatch degree.

According to our calculations, Au_2O_3 is the stable crystal phase, when the oxygen chemical potential is higher than -0.14 eV. However, so far as we know, there is no report that Au_2O_3 was prepared by the method of gold direct oxidation. The oxidation of gold to Au_2O_3 may be hindered by the dynamic reason if the oxygen chemical potential is not high enough. Therefore the gold film is still possibly stable for the oxygen potential higher than -0.14 eV. For the situation with very high oxygen chemical potential (>0.1 eV, for instance), the connected dual chain structure is stable, since its oxygen coverage is highest in all the structures studied. Since the lattice constants of gold oxide films are different from the Au surfaces, we expect that the difference could be observed by high resolution transmission electron microscopy (HRTEM) directly in O_2 atmosphere.

4.4 The discussion on the fluctuation of gold surfaces in O_2 atmosphere

We are now in a position to address the observed surface fluctuation of Au clusters in O_2 atmosphere. Table 1 shows the surface energies of clean gold surfaces, and those of oxidized gold surfaces at $\Delta\mu_{\text{O}} = -0.14$ eV obtained as gold-oxide film adsorption in the present examination. It is found that all the gold surface energies are decreased from γ_1 to γ_2 . According to Wulff construction [45], the distance from the center of a crystal to the surface is dependent on the surface energy. Therefore the variation of the surface area due to the O_2 atmosphere is relative to the variation of the corresponding surface energy (Δ). From Table 1, the variation of the Au(111) surface energy is the smallest, and the Au(111) surface energy becomes relatively higher in the O_2 atmosphere, implying that the area of the Au(111) surface should be dramatically decreased. The variation of the Au(110) surface energy is the largest, leading to the lowest value in the O_2 atmosphere, which indicates the increase of the Au(110) surface area. The results agree well with Shi and Stampfl's calculation results [18] and Uchiyama's experimental results that the Au(110)

surfaces appear in O₂ atmosphere [16]. Since the variation of the surface energy is dependent on the oxygen chemical potential, the shape of gold clusters and the structure of gold oxide films should change thermodynamically according to the oxygen chemical potential change.

To investigate the surface fluctuation of Au clusters from the viewpoint of dynamics, we calculated the gold-atom adsorption and diffusion on the Au(111) surface. It is found that the adsorption energies of a gold atom on the Au(111) surface are -2.29, -2.91, and -2.86 eV on the top, fcc and hcp sites, respectively, indicating that the interaction between a gold atom and a gold surface is strong, due to the strong Au-Au metallic bond. Our calculation results on the Au(111) surface show that the diffusion barrier from the hcp site to the fcc site is 0.08 eV and that from fcc to hcp is 0.13 eV. Although the adsorption of a gold atom on a gold surface is very strong (> 2 eV), the diffusion barrier is only 0.08~0.13 eV. The low diffusion barrier originates from the Au-Au metallic bond characters such as relative softness and isotropic nature, typical of noble metals, different from transition metals or ionic or covalent materials. The barrier is so low that the diffusion of gold atoms on gold surfaces very easily occurs, which should support the formation of gold oxide films according to the O₂ atmosphere. As a result, the surface fluctuation of Au clusters should easily occur in O₂ atmosphere from the viewpoint of dynamics.

5. Conclusions

The stability of gold oxide films on various gold surfaces in O₂ atmosphere is investigated. Based on the preliminary and general analysis, it is predicted that the O/Au system with the crossed AuO₄ composed of three-coordinated oxygen and four-coordinated gold atoms is the most stable structure for an isolated gold oxide film. While for gold oxide films on gold surfaces in O₂ atmosphere, the formation energy of the isolated gold oxide film, the lattice mismatch and

the oxygen coverage affect the stability. The structure with less lattice mismatch should be more stable, and the structure with higher oxygen coverage should be more stable at high oxygen chemical potential. By thermodynamic analysis based on DFT calculations, it is found that the graphene-like 12 MR structure is stable only on the Au(111) surface at low oxygen chemical potential, due to the symmetry match between the film and the surface. On all the other gold surfaces, the dual chain structure is the most stable at the low oxygen chemical potential, and the connected dual chain structure becomes more stable at the high oxygen chemical potential due to its higher oxygen coverage. The transformation point from the dual chain structure to the connected dual chain structure depends on the lattice mismatch between the connected dual chain structure and the gold surface. The surface fluctuation of Au clusters in O₂ atmosphere can be assigned to the variation of the surface energies due to the generation of gold oxide films, according to the oxygen chemical potential change in thermodynamics, which should be assisted by low diffusion barriers for gold atoms on gold surfaces in dynamics.

Acknowledgments

This study was supported by Grant-in-Aid for Specially Promoted Research Grant No. 19001005 from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). A part of this study was supported by the Management Expenses Grants for National Universities Corporations from MEXT, and by Japan Science and Technology Agency (JST), Core Research for Evolutional Science and Technology (CREST).

Figure 1. The proposed structures of isolated O/Au systems based on the coordination numbers of gold and oxygen. The gold balls denote the gold atoms and the red ones are oxygen atoms, and the dashed lines display the unit cell. (similarly hereinafter).

Figure 2. The structures of single chain (a) and dual chain (b) on the Au(111) surface and corresponding surface energies for these structures as a function of the oxygen chemical potential (c). In the figures a and b, the top parts show the top view and the bottom parts display the side view. To clarify, only the atoms in the top two layers are shown in the top view (similarly hereinafter). The labels “1/2 ML”, “1/3 ML” and “1/4 ML” denote the oxygen coverage in the corresponding structures.

Figure 3. Top view of four different structures of graphene-like 12 MR on the Au(111) surface (a-d) and corresponding surface energies for these structures as a function of the oxygen chemical potential (e). To clarify, the atoms in the top layer are marked as small balls and the atoms in the second layer are marked as large balls. The surface energy of a clean Au(111) surface is also shown as reference.

Figure 4. The top view of local configurations of graphene-like 12 MR on the Au(111) surface and ethane molecules with eclipsed conformer and staggered conformer. The deep color balls show the atoms in the top layer and the light color balls denote the atoms in the second layer.

Figure 5. Two typical structures of connected dual chain on the Au(111) surface (a,b) and the surface energies for these two structures and some similar structures at difference coverage as a function of the oxygen chemical potential (c). The surface energy of a clean Au(111) surface is also shown as reference.

Figure 6. The surface energies for the structures of dual chain, connected dual chain and graphene-like 12 MR on the Au(111) surface as a function of the oxygen chemical potential. The surface energy of a clean Au(111) surface is also shown as reference. Segments in each line with different slopes represent the most stable structure with different oxygen coverage for each structure in each range of the oxygen chemical potential.

Figure 7. Three different structures of dual chain (a), connected dual chain (b) and graphene-like 12 MR (c) on the Au(100) surface and corresponding surface energies as a function of the oxygen chemical potential (d). The surface energy of a clean Au(100) surface is also shown as reference.

Figure 8. Three different structures of dual chain (a), connected dual chain (b) and graphene-like 12 MR (c) on the Au(110) surface and corresponding surface energies for these structures as a function of the oxygen chemical potential (d). The surface energy of a clean Au(110) surface is also shown as reference.

Figure 9. Two structures of dual chain (a), connected dual chain (b) on the Au(221) surface and corresponding surface energies for these structures as a function of the oxygen chemical potential (c). The surface energy of a clean Au(221) surface is also shown as reference.

Figure 10. Two structures of dual chain (a) and connected dual chain (b) on the Au(211) surface and corresponding surface energies for these structures as a function of the oxygen chemical potential (c). The surface energy of a clean Au(211) surface is also shown as reference.

Table 1. The surface energies ($\text{meV}/\text{\AA}^2$) of a clean surface (γ_1) and an oxidized surface at $\Delta\mu_0 = -0.14$ eV (γ_2) and the variation of the surface energy (Δ) from γ_1 to γ_2 .

	γ_1 (clean)	γ_2 (oxidized)	$\Delta=(1-\gamma_2/\gamma_1)$
Au(111)	89.6	78.5	12.4 %
Au(100)	96.9	72.0	25.7 %
Au(110)	98.2	67.9	30.9 %
Au(221)	95.1	75.7	20.4 %
Au(211)	97.1	79.1	18.5 %

Reference

- [1] R.H. Gerke, M.D. Rourke, J. Am. Chem. Soc. 49 (1927) 1855.
- [2] T.E. Jones, S. Piccinin, C. Stampfl, Mater. Chem. Phys. 141 (2013) 14.
- [3] J. Szlachetko, J. Sa, M. Nachtegaal, U. Hartfelder, J.C. Dousse, J. Hozowska, D.L.A. Fernandes, H.Q. Shi, C. Stampfl, J. Phys. Chem. Lett. 5 (2014) 80.
- [4] K.A. Davis, D.W. Goodman, J. Phys. Chem. B 104 (2000) 8557.
- [5] J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, Surf. Sci. 511 (2002) 65.
- [6] H. Ron, I. Rubinstein, Langmuir 10 (1994) 4566.
- [7] D.H. Parker, B.E. Koel, J. Vac. Sci. Technol., A 8 (1990) 2585.
- [8] N. Saliba, D.H. Parker, B.E. Koel, Surf. Sci. 410 (1998) 270.
- [9] J.A.M. Sondagh, L.G.J. Fokink, Langmuir 8 (1992) 2560.
- [10] N.D.S. Canning, D. Outka, R.J. Madix, Surf. Sci. 141 (1984) 240.
- [11] D.A. Outka, R.J. Madix, Surf. Sci. 179 (1987) 351.
- [12] D.C. Jackson, A. Chaudhuri, T.J. Leretholi, D.P. Woodruff, R.G. Jones, V.R. Dhanak, Surf. Sci. 603 (2009) 807.
- [13] G.N. Kastanas, B.E. Koel, Appl. Surf. Sci. 64 (1993) 235.
- [14] B.K. Min, A.R. Alemozafar, D. Pinnaduwege, X. Deng, C.M. Friend, J. Phys. Chem. B 110 (2006) 19833.
- [15] J. Chevrier, L. Huang, P. Zeppenfeld, G. Comsa, Surf. Sci. 355 (1996) 1.
- [16] T. Uchiyama, H. Yoshida, Y. Kuwauchi, S. Ichikawa, S. Shimada, M. Haruta, S. Takeda, Angew. Chem. Int. Ed. 50 (2011) 10157.
- [17] H. Shi, C. Stampfl, Phys. Rev. B 76 (2007) 075327.

- [18] H.Q. Shi, C. Stampfl, Phys. Rev. B 77 (2008) 094127.
- [19] T. Fukushima, S. Galvagno, G. Parravano, J. Catal. 57 (1979) 177.
- [20] W.X. Li, C. Stampfl, M. Scheffler, Phys. Rev. Lett. 90 (2003) 256102.
- [21] K.J. Sun, M. Kohyama, S. Tanaka, S. Takeda, J. Phys. Chem. A 116 (2012) 9568.
- [22] G. Kresse, J. Hafner, Phys. Rev. B 48 (1993) 13115.
- [23] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [24] P.E. Blochl, Phys. Rev. B 50 (1994) 17953.
- [25] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
- [26] M. Mavrikakis, P. Stoltze, J.K. Norskov, Catal. Lett. 64 (2000) 101.
- [27] K.J. Sun, Y.H. Zhao, H.Y. Su, W.X. Li, Theor. Chem. Acc. 131 (2012) 1118.
- [28] R. Meyer, C. Lemire, S.K. Shaikhutdinov, H. Freund, Gold Bulletin 37 (2004) 72.
- [29] N.E. Singh-Miller, N. Marzari, Phys. Rev. B 80 (2009).
- [30] H. Yoshida, Y. Kuwauchi, J.R. Jinschek, K.J. Sun, S. Tanaka, M. Kohyama, S. Shimada, M. Haruta, S. Takeda, Science 335 (2012) 317.
- [31] P. Pyykko, Angew. Chem. Int. Ed. 43 (2004) 4412.
- [32] A. Ikeda, Y. Nakao, H. Sato, S. Sakaki, J. Phys. Chem. A 111 (2007) 7124.
- [33] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132 (2010) 154104.
- [34] W.R. Tyson, W.A. Miller, Surf. Sci. 62 (1977) 267.
- [35] K.J. Sun, M. Kohyama, S. Tanaka, S. Takeda, J. Phys. Chem. C 118 (2014) 1611.
- [36] K.J. Sun, M. Kohyama, S. Tanaka, S. Takeda, ChemCatChem 5 (2013) 2217.
- [37] J. Kim, E. Samano, B.E. Koel, Surf. Sci. 600 (2006) 4622.
- [38] V.A. Bondzie, S.C. Parker, C.T. Campbell, J. Vac. Sci. Technol., A 17 (1999) 1717.
- [39] H.Q. Shi, R. Asahi, C. Stampfl, Phys. Rev. B 75 (2007) 205125.
- [40] N. Weiher, E.A. Willneff, C. Figulla-Kroschel, M. Jansen, S.L.M. Schroeder, Solid State Commun. 125 (2003) 317.
- [41] B.W. Dodson, Phys. Rev. B 36 (1987) 6288.
- [42] P.Y. Hsiao, Z.H. Tsai, J.H. Huang, G.P. Yu, Phys. Rev. B 79 (2009) 155414.
- [43] S. Marchini, S. Gunther, J. Wintterlin, Phys. Rev. B 76 (2007).
- [44] B. Wang, X.F. Ma, M. Caffio, R. Schaub, W.X. Li, Nano Lett. 11 (2011) 424.
- [45] G. Wulff, Zeitschrift Fur Krystallographie Und Mineralogie 34 (1901) 449.