**Ab Initio Thermodynamics of Surface Oxide Structures under Controlled Growth Conditions**

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**ABSTRACT:** Having a robust and predictive ab initio thermodynamic model to examine and describe the interplay of the oxygen gas and evaporated metal atoms on another metal substrate may prove to be very helpful in understanding the surface phase diagrams of these oxygen/metal systems. In this work, we examine the O/Cu/Au(111) system and provide a refined atomistic thermodynamic model which takes different definitions of the chemical potential of the less abundant metal, Cu into account. We argue that the latter highly depends on the various surface structures (overlayers and alloys) that forms on the metal substrate under growth conditions. We demonstrate that our improved thermodynamic model rationalizes new experimentally observed oxide structures and may pave a systematic way to predict new surface structures of reduced stoichiometries, which would otherwise be missed by the common practice of taking only the bulk limits.

**INTRODUCTION**

Ultrathin oxide films grown on metal substrates show remarkably different structural properties from those of bulk oxides in the monolayers and the submonolayer regime, depending on the growth conditions. The ultrathin oxides on metal supports exhibit distinct physical and chemical properties, which can increase the performance of nanoscale devices, as well as representing an alternative model to study heterogeneous catalysis. The development of experimental spectroscopic and scanning probe techniques has led to vast improvements in the characterization of the films at the atomic scale. In line with the progress of nanoscale measurements, theory also has successfully provided insights to complement the experimental observations via atomistic modeling coupled with advanced thermodynamic approaches, namely ab initio atomistic thermodynamics (aiAT). These approaches make it possible to predict accurate local atomic structures and the thermodynamic stability of thin film oxides on metal and oxide surfaces as a function of temperature and pressure of reactive molecules species, by combining general concepts in thermodynamics with total energy calculations based on density-functional theory (DFT).

These thin oxide layers are commonly prepared by two different methods: Either depositing metal atoms in an O2 atmosphere or evaporating metal atoms in ultrahigh vacuum (UHV) followed by an oxidation step. In these processes, the interfacial coupling between the thin oxide layer and the relevant metal supports has been commonly exploited to obtain the required morphologies and stoichiometries of the ultrathin film oxides, which are highly linked to their physical and chemical properties. Interestingly, it has been reported that the amount of evaporated reactive metal source significantly influences the morphology and the stoichiometry of the grown oxide layer, but to date a quantitative description of these correlations is still lacking.

Nanostructures of Cu2O/Au have caught a lot of interest due to their extraordinary performance in photocatalytic and photochemical applications, due to the fact that they display photoluminescence properties that differ significantly from that of Cu2O bulk. Via X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) experiments at 400 and 700 K, various Cu thin film oxides were observed and characterized. Low energy thin film oxides were modeled using DFT, displaying simulated STM images in good agreement with experiments. DFT calculations conventionally consider the chemical reservoir of Cu originated from its bulk phase. In our study, the deposited Cu atoms may first form only a few monolayers on the Au surface, deviating from our conventional assumption of using bulk Cu as the chemical reservoir. According to the experiments, the deposited copper indeed forms a few monolayers of metallic Cu on Au surface.

In this step, the film thickness was initially adjusted to about 10 to 15 ML and it then decreased to about 5 ML upon annealing at 700 K. In the case of the CeO2/Cu(111) system, it was revealed that the final surface structure highly depends on the initial deposition conditions of cerium. Likewise in the Cu/Au(111) system, nanocomposites such as overlayers or surface alloys can form depending the deposition conditions of Cu. However, it is still an open question which chemical potential...
values do nanocomposites have and how they affect the energetic stability in the thin film oxides.

Here, we use a refined a2AT approach to search for the most favorable atomic configurations adopted by Cu–O thin oxides on Au(111). We assume that Cu atoms deposited on Au(111) act as a reservoir of Cu for the formation of the surface thin oxides. Our results show that different definitions of the Cu chemical potential can have a dramatic effect on the stability of metal supported oxides. We therefore investigate the dependence of the Cu chemical potential on the Cu coverage as well as on the atomic structure of the Cu/Au system. Furthermore, we propose the ideal amount of Cu to deposit for obtaining a specific oxodic structure.

## METHODOLOGY

All calculations are performed using Kohn–Sham DFT and the generalized gradient approximation (GGA) to the exchange-correlation functional due to Perdew, Burke, and Ernzerhof (PBE), as implemented in the Vienna ab initio simulation package (VASP). The Kohn–Sham orbitals are expanded in a planewave basis set with a kinetic energy cutoff of up to 500 eV and the electron–ion interactions are described using the projector augmented wave (PAW) method. All atomic calculations have been performed with spin polarization. For the surface structures, we have also tested and found that they all possess a nonmagnetic ground-state solution. Ultrathin films of O/Cu on Au(111) and bimetallic system of Cu on Au(111) are modeled using asymmetric periodic supercell models. In addition, referring to eq 1, to obtain a more accurate description of \( E_{\text{O}_2} \), the experimental binding energy of an O\(_2\) molecule (5.22 eV) is used to correct for the large known error in the PBE binding energy of O\(_2\). As estimated in our earlier work, the vibrational contributions to the Gibbs free energy of adsorption in O/Cu systems are found to be negligible and is thus not included in this work. In addition, via the Stirling’s approximation, we have estimated the contribution of configurational entropy to our calculated Gibbs free energies of adsorption, and have found it to be less than 25 meV/\( \text{Å}^2 \) for \( T < 700 \text{ K} \). In order to estimate this, the inclusion of configurational entropy will not change the conclusions drawn here, and thus neglected in this work.

## RESULTS AND DISCUSSION

When a metal (Cu) source is deposited on different metal surface (Au surface) in contact with an oxygen atmosphere, the gas phase acts as a reservoir of oxygen, interchanging oxygen atoms with the metal surface. The Gibbs free energy of adsorption can be defined by

\[
\Delta G(T, p) = \frac{1}{A} \left( G_{\text{O}/\text{Cu}/\text{Au}} - G_{\text{Au}(111)} \right) - N_{\text{Au}} \mu_{\text{Au}} \nonumber \\
- \Delta N_{\text{Cu}} \mu_{\text{Cu}} - N_{\text{O}} \mu_{\text{O}} \tag{1}
\]

where \( G_{\text{O}/\text{Cu}/\text{Au}} \) and \( G_{\text{Au}(111)} \) are the Gibbs free energies of the O/Cu/Au system and pristine Au(111), respectively. \( A \) is the surface area of unit cell and, \( \mu_{\text{Au}}, \mu_{\text{O}}, \) and \( \mu_{\text{Cu}} \) are the chemical potentials of the Au, O and Cu atoms, accordingly. \( \Delta N_{\text{Au}} \) and \( \Delta N_{\text{Cu}} \) are the change of the number of species to involve in forming oxide layer and substrate. \( N_{\text{O}} \) is the number of adsorbed O atoms. When \( \Delta N_{\text{Au}} \) is zero, the Gibbs free energy can be interpreted as a function of \( \mu_{\text{Cu}} \) and \( \mu_{\text{O}} \).

The chemical reservoir of Cu, i.e. the source of Cu atoms forming the ultrathin oxide layer, has been conventionally chosen to be Cu bulk phase. In this assumption, it is regarded that the amount of evaporated Cu atoms is enough to reach equilibrium condition to the bulk phase (\( \mu_{\text{Cu}} \approx E_{\text{Cu}}^{\text{bulk}} \)). However, under the experimental conditions where the amount of atomic source of Cu is minute compared to that of Au and controlled as a certain amount to prepare the oxide layer in the monolayer regime, the reservoir of Cu cannot be simply assumed as the bulk Cu (\( \mu_{\text{Cu}} \neq E_{\text{Cu}}^{\text{bulk}} \)).

When a minute amount of Cu is deposited in an O\(_2\) ambience, the evaporated Cu atoms can react with substrate and locally form nanocomposite alloys, Cu\(_x\)Au\(_{1-x}\)/Au(111) (where \( x \ll y \)). Experiments monitoring the formation of thin Cu oxide layers after Cu evaporation on Au(111) have detected the appearance of few monolayers of Cu on Au(111) as well as Au\(_x\)Cu\(_y\) alloys prior to the formation of the oxide.

In modeling these systems, we therefore need to consider that the sources of Cu atoms forming the oxide are these nanocomposite structures (overlayers and alloys) formed on Au(111). Since the chemical potential of Cu atoms in these structures will be different depending on their structure and composition, we need to investigate the impact this has on the thermodynamic stability of the surface oxides. Our approach implicitly assumes that the amount of Cu deposited on the Au substrate is very large compared to the amount of Cu that ends up forming the thin oxide layers, so that the chemical potential of Cu is determined by structure adopted by Au/Cu system after the deposition of Cu. In particular, in previous theoretical and experimental studies, various nanocomposite (Cu\(_x\)Au\(_y\)) structures have been reported as thermodynamic products under different conditions, showing structural diversities from overlayer to heterostructures.

In this spirit, we examine and consider various Cu–Au bimetallic structures in this work. In a schematic view, we propose the various chemical origins of Cu from different Au\(_x\)Cu\(_y\)/Au(111) nanocomposite systems to form thin oxide layers in Figure 1. Specifically, we present a scheme displaying various Au\(_x\)Cu\(_y\)/Au(111) nanocomposite systems that can act as a potential source of Cu atoms for the oxide layer.

The thin oxide formation reactions could be examined and approximated as a two-step process, i.e. the initial formation of these mildly doped bimetallic alloy surfaces (cf. eq 2), and then...
the oxidation of these surfaces (cf. eq 3). First, the evaporated 
Cu atoms lead to the formation of Cu–Au nanocomposites:
\[ x\text{Cu}^{\text{atom}} + y\text{Au}^{\text{bulk}} + \text{Au}(111) \rightarrow \text{Cu}_{x}\text{Au}_{y}/\text{Au}(111) \]  
(2)

This Cu–Au nanocomposite system acts as the thermodynamic
reservoir which provides Cu atoms to form the Cu oxide layer
on Au as shown in eq 3:
\[ \text{Cu}_{x}\text{Au}_{y}/\text{Au}(111) + O_2(g) \rightarrow O/\text{Cu}_{x}\text{Au}_{y}/\text{Au}(111) \]  
(3)

where \( x \ll y \). The Gibbs free energy of \( \text{Cu}_{x}\text{Au}_{y}/\text{Au}(111) \) system can be written as
\[ G_{\text{Cu}_{x}\text{Au}_{y}} = N_x\mu_{\text{Cu}} + N_y\mu_{\text{Au}} \]  
(4)

where \( N_x \) and \( N_y \) are the number of atoms of Cu and Au in the
\( \text{Cu}_{x}\text{Au}_{y} \), nanocomposite, respectively. Assuming thermodynamic
equilibrium between the \( \text{Cu}_{x}\text{Au}_{y} \) nanoalloy and the underlying
\( \text{Au}(111) \) surface, the chemical potential of \( \text{Au}, \mu_{\text{Au}} \) can be taken
equal to the chemical potential of bulk Au, \( E_{\text{Au}^{\text{bulk}}} \). We now define
that the change of Cu chemical potential with respect to the
atom energy of Cu, \( \Delta\mu_{\text{Cu}} = \mu_{\text{Cu}} - E_{\text{Cu}^{\text{atom}}} \). Then eq 4 can be reformulated as
\[ \Delta\mu_{\text{Cu}} = \frac{1}{N_x} \left( G_{\text{Cu}_{x}\text{Au}_{y}} - N_x\mu_{\text{Cu}} - N_yE_{\text{Cu}^{\text{atom}}} \right) \]  
(5)

We computed \( \Delta\mu_{\text{Cu}} \) for the various Cu–Au nanocomposite
systems as shown in Figure 2a (and listed in Table S1 of the
Supporting Information). In here, \( \mu_{\text{Au}} \) is taken as \( E_{\text{Au}^{\text{bulk}}} \), since
Au(111) is close to the infinite amount. We have tested various
nanocomposite models on Au(111), controlling the surface
coverage of Cu (\( \Theta_{\text{Cu}} \)) on Au(111) substrate (see Figure 2a).
The computed values of \( \Delta\mu_{\text{Cu}} \) have similar tendencies for
various structural models. First, \( \Delta\mu_{\text{Cu}} \) values saturate to that of
bulk Cu when \( \Theta_{\text{Cu}} \) is larger than about 1.00 ML. Second, if \( \Theta_{\text{Cu}} \)
is less than 1.00 ML, \( \Delta\mu_{\text{Cu}} \) values become positive, compared to
that of bulk Cu. Later, we discuss more about the impact of
these values of \( \Delta\mu_{\text{Cu}} \) on the stability of the thin oxide films.

Having established how the value of the chemical potential of
Cu changes depending on the structures formed by the Cu/Au
system upon evaporation of Cu on Au(111), we can now
explore the stability of the thin oxide structures formed once
the system is exposed to an oxygen atmosphere. In the case of
oxygen, the chemical potential of oxygen is defined with respect
to the half of the total energy of the \( \text{O}_2 \) molecule, i.e.
\[ \Delta\mu_{\text{O}} = \mu_{\text{O}} - \frac{1}{2}E_{\text{O}_2} \]. Notably, the thin oxide layer is not only in
equilibrium with the \( \text{O}_2 \) gas phase, but also in equilibrium with the
underlying specific Cu–Au nanocomposite on Au(111). Here,
we can write the surface free energy of adsorption as
\[ \Delta G(\Delta\mu_{\text{Cu}}, \Delta\mu_{\text{O}}) = \frac{1}{A} \left[ G_{\text{O}/\text{Cu}/\text{Au}} - G_{\text{Au}(111)} \right. \right.
\[ \left. - N_x(\Delta\mu_{\text{Cu}} + E_{\text{Cu}^{\text{atom}}}) \right. \right.
\[ \left. - N_y(\Delta\mu_{\text{O}} + \frac{1}{2}E_{\text{O}_2}) \right] \]  
(6)

where \( \Delta\mu_{\text{Cu}} = \frac{1}{N_x}(G_{\text{Cu}_{x}\text{Au}_{y}} - N_xE_{\text{Cu}^{\text{atom}}} - N_yE_{\text{Cu}^{\text{atom}}} \). Via eq 6, we plot a 2D surface phase diagram as a continuous function as
shown Figure 3, illustrating accessible surface compositions in
Figure 3. The surface structures we investigate in this work have
been proposed in our previous publication,16 matching with
experiment.18 Here, we briefly outline their structural character-

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Illustrations of various Cu–Au nanocomposites on Au(111) are shown in part a, where the Cu and Au atoms are depicted as blue and gray circles accordingly. The corresponding changes in the Cu chemical potential (\( \Delta\mu_{\text{Cu}} \)) are plotted in part b, with respect to the Cu surface coverage (\( \Theta_{\text{Cu}} \)).

![Figure 3](https://example.com/figure3.png)

**Figure 3.** PBE-calculated surface phase diagram for thin Cu surface oxide layers on Au(111): The change in the Gibbs free energy of adsorption as a function of both the change in the chemical potentials of oxygen (\( \Delta\mu_{\text{O}} \)) and copper (\( \Delta\mu_{\text{Cu}} \)). The top- and side-views of surface atomic structures, \( p_2 \), \( p_2 + \text{Cu}_p \), \( p_2s \), \( p_2s + \text{Cu}_p \), and \( p_2s + \text{Cu}_p - \text{O}_x \) on Au(111) are shown. The Au, Cu, and O atoms are depicted as white, blue, and red circles, respectively. \( \Delta\mu_{\text{O}} = 0 \) corresponds to \( \mu_{\text{O}} = \frac{1}{2}E_{\text{O}_2} \), as determined from the experimentally
corrected DFT binding energy of the O(2) molecule.15,27 The pressure scales for 400 and 700 K are included at the bottom of the figure. To calculate the \( \Delta G \) in Figure 4, \( \Delta\mu_{\text{Cu}} \) is defined as (a) bulk Cu, (b) \( \Theta_{\text{Cu}} = 2.63 \text{ ML} \), and (c) \( \Theta_{\text{Cu}} = 0.33 \text{ ML} \) (as indicated by the labeled horizontal dotted lines).
istics: The p2 surface structures have a distorted p(1 × 1) Cu2O(O(111))-like trilayer on p(2 × 2) Au(111). p2 + Cu improves this p2 motif by adding extra Cu adatoms at the fcc-hollow site on Au(111) in the center of the Cu–O hexagonal network. These p2-family structures have been proposed as the thermodynamic product in previous experimental reports. Next, the p2s structure adds an extra row/strip of Cu atoms in p2 by artificially breaking the surface symmetry, and p2s + CuF adds additional Cu adatoms at the center of Cu–O hexagonal network. As a result, p2s + CuF – O1 structure is formed by extracting the nearest O atom from the Cu adatoms line (Cu2) from p2s + CuF. For a more detailed atomic analysis of Cu oxide layer on Au(111), we refer the reader to our previous publication.

When Δμ_{CuO} is set to the bulk Cu value (marked in Figure 3c), p2s structures is the most stable over a range of Δμ_{O}. As Δμ_{CuO} (above ~3.52 eV) becomes more positive, the stable surfaces contain an increasing amount of Cu atoms, transitioning from p2s to p2s + CuF and p2s + CuF – O1 via the adsorption of Cu atoms at the center of the Cu–O hexagonal ring.

As discussed earlier, we can link the specific Δμ_{CuO} values with corresponding Cu–Au nanocomposites, which is directly connected to the Θ_{CuO} as shown in Figure 2. For further analysis of the relationship between Δμ_{CuO} and the stability of oxide layer, we choose two representative conditions for the surface underneath the thin oxide layers, namely Cu monolayers (Θ_{Cu} = 2.63 ML, Δμ_{Cu} = −3.12 eV) and Cu overlayers (Θ_{Cu} = 0.33 ML, Δμ_{Cu} = −0.53 eV) (marked using horizontal dotted lines in Figure 3 in parts b and c), and plot ΔG for various Cu oxide structures on Au(111) (see Figure 4) comparing with that when Δμ_{CuO} assumes the bulk value.

To establish a physically meaningful upper limit to the range of values of the oxygen chemical potential, we need to consider that the thin oxide film on substrate cannot exist when the values of Δμ_{O} are larger than the bulk oxide’s heat of formation per O atom, due to the bulk oxide being thermodynamically more stable than thin oxide films. Of the possible bulk oxides that can form, the enthalpy of formation per O atom of Cu2O is the most negative, ΔH_{Cu2O} = −1.67 eV. However, here we argue that the upper limit of the oxygen chemical potential may be better described by extending the physically meaningful range for the O chemical potential to the formation of bulk Au oxide. Thus, the oxygen rich limit of adsorption energy can be defined as Δμ_{O—limit} = 1/3 ΔH_{Au2O3}^{f}, where ΔH_{Au2O3}^{f} (−1.77 eV) is the enthalpy of formation of Au2O3. These thermodynamic limits are noted in Figure 4. Notwithstanding the importance of thermodynamic analysis in this work, we stress that kinetic effects may also play a role and could alter the thermodynamically controlled surface phase diagram of O/Cu/Au(111). This has been discussed in a previous study where bulk oxide phases were kinetically hindered, leading to the formation of thin metal oxide layers under oxygen-rich conditions, even up to ambient pressures. Now, to further assess the thermodynamic stability of the thin Cu oxide layers, ΔG is computed when chemical reservoir of Cu is defined as (a) bulk, (b) Θ_{Cu} = 2.63 ML, and (c) Θ_{Cu} = 0.33 ML as shown in Figure 4. In the case where Δμ_{CuO} is set to that of bulk Cu, the pristine Au(111) surface is thermodynamically most stable surface phase for the values of Δμ_{O} less than −2.33 eV. In addition, p2 and p2s surface structures are found to be the most stable across the range of Δμ_{O} from −1.85 to −0.59 eV. After that, bulk Au2O3 may start to form as the thermodynamic product. When Δμ_{CuO} is extracted from Cu monolayers model (Θ_{Cu} = 2.63 ML) on Au(111), both the p2 + CuF – O1 (−2.54 to −2.33 eV) and p2s (−2.33 to −0.59 eV) are found to be stable.
limits. surface oxide structures of reduced stoichiometries, which about 1 ML. This approach of analyzing the thermodynamic structural transition at $\Delta$ forms Cu can indeed be stabilized if the amount of deposited Cu atoms tunability of stoichiometries in these oxide layers. Particularly based on our results, if the deposited amount of evaporated atoms forms Cu–Au nanocomposites below about 1 ML, then the Cu atoms on hexagonal networks can be stabilized, leading reduced stoichiometries of thin Cu$_2$O layers.

■ CONCLUSION

In conclusion, we have refined the atomistic thermodynamic model for describing the interaction of oxygen with a bimetallic system where one metal is significantly minute as compared to the other metal (here, Cu $\ll$ Au). We have argued that deviating from the bulk limit of the deposited metal (i.e., Cu in this study), its chemical potential can take discrete values highly depending on the various surface structures (overlayers and alloys) formed on the metal substrate (i.e., Au(111) in this work). In an attempt to rationalize the experimentally observed O/Cu/Au(111) structures, we have then demonstrated that taking a different definition of the Cu chemical potential dramatically affects the stability of thin Cu surface oxide structures on Au(111). In particular, with respect to the controversy of the existence of the 3-fold Cu adatoms in the center of the hexagonal network, the p2s + CuF oxide structure can indeed be stabilized if the amount of deposited Cu atoms forms Cu–Au nanocomposites below a Cu surface coverage of about 1 ML. This approach of analyzing the thermodynamic surface phase diagram may pave a new way to discover novel surface oxide structures of reduced stoichiometries, which would otherwise be missed by commonly taking only the bulk limits.

■ ASSOCIATED CONTENT

4 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b11445. Computed Cu chemical potential ($\Delta\mu_{Cu}$) values for various models of Cu$_x$Au$_{1-x}$/Au(111) nanocomposite system, Gibbs free energy of adsorption, and $\Delta G$ for various thin film oxides of Cu on Au(111) (PDF)

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Notes
The authors declare no competing financial interest.

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