Local reactivity of ultrathin platinum overlayers and surface alloys on a gold surface

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The geometric and electronic structure, the stability, and CO adsorption properties of pseudomorphic Pt overlayers and PtAu surface alloys on a Au(111) substrate have been addressed on the basis of first-principles calculations. We have found that two-monolayer thick surface alloys are more stable than one-monolayer thick alloys. The CO binding energies at the top sites of two-monolayer thick surface alloys increase gradually with the Pt concentration, while the energies are almost independent of the concentration for one-monolayer thick surface alloys. This difference is caused by the lower symmetry of the two-monolayer thick surface alloys, which makes the effect of neighboring atoms in the first layer more important.

Keywords: Density functional calculations; chemisorption; bimetallic surfaces; thin film structures; platinum; gold; carbon monoxide

I. INTRODUCTION

The PtAu bimetallic system has recently attracted attention as a promising candidate material for electrocatalytic methanol-oxidation reactors [1–3]. The deposition of Pt on the Au(111) surface is also of fundamental interest because it remarkably modifies the chemical reactivity, as temperature programmed desorption of CO molecules revealed that Pt atoms deposited on Au(111) considerably increase the CO binding energy to values even larger than that for pure Pt(111) with the maximum at approximately 1.3-monolayer (ML) coverage of Pt [4]. As the coverage rises to values above 1.3 ML, the binding energy decreases, although it remains still larger than on the pure Pt(111) surface. Random PtAu surface alloys are observed using scanning tunneling microscopy at low Pt coverages, while additionally deposited Pt atoms lead to ultrathin overlayer islands [4]. It has been known that the lattice expansion of the overlayer due to the lattice mismatch [4, 5] and its ultrathin thickness [6, 7] cause a localization of the d electrons of the Pt atoms resulting in an upward-shift of the d band. Still, further details of the relationship between the atomic composition and the adsorption energy have not been sufficiently clarified yet. In addition, although the bimetallic Pt/Au(111) overlayer system is known to be metastable with respect to annealing-induced diffusion of Pt into the Au bulk, the detailed relationship between the structural stability and the surface atomic composition is an open issue.

Recently, we have analyzed the CO adsorption on the Pt/Au system on the basis of density functional theory (DFT) [8, 9], in particular for pseudomorphic Pt overlayers and 1-ML thick surface alloys on a Au(111) substrate [10]. We have shown that the CO interaction with Pt/Au(111) overlayer systems is stronger than with pure Pt(111), in agreement with previous theoretical studies [11], also for the related Pd/Au(111) system [12, 13]. Furthermore, in the case of the adsorption at the top site of the overlayer system, the binding energy for the 2-ML thick Pt overlayer is larger than that for the 1-ML thick one by 0.38 eV, while there is no such remarkable difference in the case of the adsorption at the fcc hollow site. These findings are due to a remarkable second-layer effect for the top-site adsorption which is much larger than the one for the fcc hollow site. It essentially comes from the highly-directional chemical bonding between C and Pt atoms in the direction perpendicular to the surface, where bonding orbitals have significant overlap with the second-layer atoms [10]. In the case of monolayer PtAu surface alloys on a Au(111) substrate, the CO binding energy is almost independent of the surface-alloy composition for the top-site adsorption. In contrast, the experimental observation for the submonolayer regime has found an gradual increase in the binding energy with rising the Pt concentration [4]. The reason for this discrepancy have remained unclear so far.

Here, we report our extended theoretical investigation of the CO adsorption on Au(111)-supported PtAu bimetallic systems. Adsorption properties of 2-ML thick PtAu surface alloys that have not been considered in our previous study [10] are compared with those of pseudomorphic Pt/Au(111) overlayers and 1-ML thick surface alloys from first principles. We have examined the structural stability of these surface alloys and found that 2-ML thick surface alloys are more stable than 1-ML thick alloys. Furthermore, the change in the adsorption energy for the top-site adsorption on 2-ML thick surface alloys are qualitatively different from that on 1-ML thick surface alloys. We have clarified that the gradual increase in the binding energy for 2-ML thick surface alloys with increasing the Pt concentration in the submonolayer regime that is consistent with the experiment [4] comes from the interaction between the CO molecular orbitals and d electrons of Pt spreading in the direction parallel to the surface, resulting in a contribution of neighboring atoms in the first layer to the chemical bonding with the CO molecule which is absent in the 1-ML thick surface alloy.

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Our results indicate that the consideration of 2-ML thick surface alloys is indispensable to analyze the reactivity of Pt/Au(111) surfaces.

II. FIRST-PRINCIPLES CALCULATIONS

First-principles total-energy calculations were performed on the basis of DFT [8, 9] within the generalized gradient approximation [14]. The core electrons have been treated by the projector augmented wave method [15] as implemented in the VASP code [16–18]. Electronic wave functions were expanded using plane-wave basis sets with a cutoff energy of 420 eV. The Pt/Au(111) bimetallic surfaces were modeled by periodic slabs consisting of six monolayers with vacuum separations of a thickness corresponding to approximately five Au monolayers. The atomic structure is fully optimized except for the three bottom layers of the slabs that are kept fixed at their corresponding bulk positions. The sampling for the continuous spectrum of electronic states is made using 15×15×1 and 8×8×1 Monkhorst-Pack **k**-points [19] for the 1×1 and $\sqrt{3}\times\sqrt{3}$ surface unit cells, respectively.

The adsorption energy of the CO molecule has been calculated by the following formula:

$$E_{\mathrm{ads}} = E_{\mathrm{surf+CO}} - (E_{\mathrm{surf}} + E_{\mathrm{CO}}) \quad (1)$$

Here, $E_{\mathrm{surf+CO}}$ is the total energy of the bimetallic Pt/Au(111) system with the CO adsorbate, while E_{surf} and E_{CO} are the energies of the corresponding clean bimetallic system and the free CO molecule, respectively. It should be noted that the adsorption energy becomes negative for stable adsorption. With the term "binding energy" we will refer to the adsorption energy with the opposite sign. In the present calculation, we considered a 0.33-ML coverage of CO molecules by using a $\sqrt{3}\times\sqrt{3}$ surface unit cell.

Although experiments find the top site as the most favorable adsorption site for the CO molecule on the Pt(111) surface, first-principles calculations predict the fcc hollow site to be most stable [20]. There is strong evidence [21] that this discrepancy comes from the fact that first-principles calculations within the generalized gradient approximation [14] considerably underestimate the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [22]. Calculations with an underestimated HOMO-LUMO gap of the CO molecule overestimate the interaction of the LUMO ($2\pi^*$) of the CO molecule with the Pt(111) surface, in particular at the threefold hollow sites resulting in the wrong site preference [21]. The present study focuses on chemical trends as a function of the bimetallic atomic configuration which should be reliably reproduced by first-principles calculations regardless of the correct site preference.

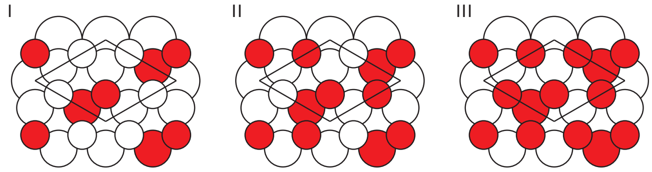

FIG. 1: Model structures for 2-ML thick PtAu surface alloys with the $\sqrt{3}\times\sqrt{3}$ periodicity indicated by rhombi. I: $\mathrm{Pt_{0.33}Au_{0.67}/Pt_{0.33}Au_{0.67}/Au(111)}$ surface including 0.67-ML Pt atoms; II: $\mathrm{Pt_{0.67}Au_{0.33}/Pt_{0.33}Au_{0.67}/Au(111)}$ surface including 1-ML Pt atoms; III: $\mathrm{Pt/Pt_{0.33}Au_{0.67}/Au(111)}$ surface including 1.33-ML Pt atoms. Only the topmost three layers are shown; the smaller the circles, the closer to the surface the corresponding atoms are.

III. STABILITY OF DEPOSITED Pt ATOMS

First, we have analyzed the structural stability of PtAu bimetallic systems supported on a Au(111) substrate. In addition to pseudomorphic Pt overlayers, we have considered PtAu surface alloys on Au(111). In Fig. 1, we illustrate the models for the 2-ML thick PtAu surface alloys that we have used in our study. In all three cases considered, the composition of the second layer is $\mathrm{Pt_{0.33}Au_{0.67}}$. The total amount of Pt is 0.67 ML for the $\mathrm{Pt_{0.33}Au_{0.67}/Pt_{0.33}Au_{0.67}/Au(111)}$ surface (structure I), 1 ML for the $\mathrm{Pt_{0.67}Au_{0.33}/Pt_{0.33}Au_{0.67}/Au(111)}$ surface (structure II), and 1.33 ML for the $\mathrm{Pt/Pt_{0.33}Au_{0.67}/Au(111)}$ surface (structure III). Though random surface alloys have been observed in experiments, the present model structures of ordered PtAu surface alloys should be useful to examine the nature of the local chemical bonding on the atomic scale. Moreover, 2-ML thick surface alloys are more realistic than 1-ML thick alloys in the sense that they have higher entropies. In the present study, we have not considered 3-ML thick surface alloys, because the effect of the third layer is rather implicit [10].

In Fig. 2, we have plotted the surface alloy formation enthalpy ΔH calculated according to [23]

$$\Delta H = E_{\mathrm{Pt}_x\mathrm{Au}_{(1-x)}/\mathrm{Au(111)}} - \left[E_{\mathrm{Au(111)}} + x\left(E^{\mathrm{coh}}_{\mathrm{Pt}} - E^{\mathrm{coh}}_{\mathrm{Au}}\right)\right]. \quad (2)$$

Here, $E_{\mathrm{Pt}_x\mathrm{Au}_{(1-x)}/\mathrm{Au(111)}}$ is the total energy of the $\mathrm{Pt}_x\mathrm{Au}_{(1-x)}$/Au(111) electrode, $E_{\mathrm{Au(111)}}$ is the one of the Au(111) electrode without Pt, and $E^{\mathrm{coh}}_{\mathrm{X}}$ is the cohesive energy of element X. This formation enthalpy is the energy difference between the PtAu/Au(111) system and a Au(111) electrode with the corresponding number of Pt and Au atoms exchanged from a bulk reservoir. It should be noted that ΔH is the difference in the corresponding Gibbs free energy at zero temperature where the cohesive energy $E^{\mathrm{coh}}_{\mathrm{X}}$ is equivalent to the chemical potential of the atoms in the bulk. Figure 2 clearly shows that 2-ML thick surface alloys (structures I and II) have lower formation enthalpies, and thus are more stable than 1-ML thick alloys, probably due to the better strain relief in the 2-ML thick surface alloys.

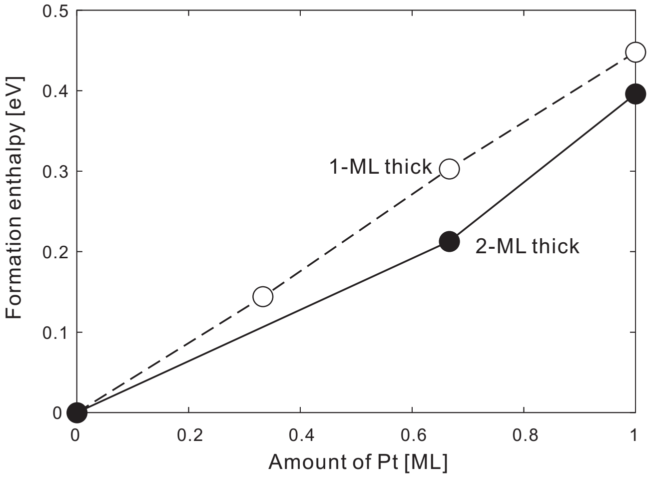

FIG. 2: Surface alloy formation enthalpy ΔH calculated as the difference in the total energy between a Pt/Au(111) electrode and a Au(111) electrode with corresponding number of Pt and Au atoms exchanged from a bulk reservoir (see eq. (2)).

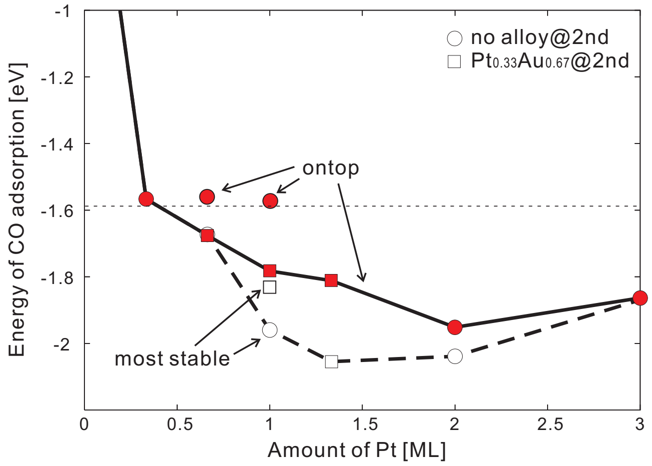

FIG. 3: CO adsorption energies on PtAu surface alloys and pseudomorphic Pt overlayers on Au(111) with and without a surface alloy in the second layer (boxes and circles, respectively). The horizontal line indicates the CO adsorption energy at the top site of the pure Pt(111) surface. Filled symbols denote the CO adsorption energies at the top sites whereas open symbols indicate the adsorption energies at the most stable sites. These are the Pt top site for $Pt_{0.33}Au_{0.67}$ and $Pt_{0.33}Au_{0.67}/Pt_{0.33}Au_{0.67}$ (structure I), the fcc hollow site for the pseudomorphic overlayers (1, 2, and 3 ML) and $Pt/Pt_{0.33}Au_{0.67}$ (structure III), and the Pt-Pt bridge site for $Pt_{0.67}Au_{0.33}$ and $Pt_{0.67}Au_{0.33}/Pt_{0.33}Au_{0.67}$ (structure II).

It is obvious from Fig. 2 that the surface alloy formation energies are positive for the Pt/Au(111) system which means that it costs free energy to form these surface alloys, and, thus, they are thermodynamically *not* stable. However, it should be noted that experimentally the surface alloys are not necessarily in thermodynamic equilibrium because of kinetic hindering caused by the presence of diffusion barriers. In fact, PtAu surface alloys have indeed been observed in experiments [4] provided that the annealing temperatures are not too high.

IV. ADSORPTION OF CO

Next, we have analyzed the CO adsorption on ultrathin PtAu films deposited on a Au(111) substrate. Figure 3 shows the calculated CO adsorption energies on pseudomorphic Pt overlayers and PtAu surface alloys. The energies have been obtained, performing full structure relaxation as described above, for the adsorption of the CO molecule at the top site, the fcc hollow site, the hcp hollow site, and the bridge site in order to identify the most stable adsorption site. The calculated most stable adsorption sites are the Pt top site for the $Pt_{0.33}Au_{0.67}$/Au(111) surface alloy and the 2-ML thick surface alloy I, the fcc hollow site for the pseudomorphic overlayers with thicknesses of 1, 2, and 3 ML and the 2-ML thick surface alloy III, and the Pt-Pt bridge site for the $Pt_{0.67}Au_{0.33}$/Au(111) surface alloy and the 2-ML thick surface alloy II. For the CO adsorption at the most stable sites, the 2-ML thick alloy I for 0.67 ML has almost the same binding energy as the $Pt_{0.67}Au_{0.33}$/Au(111) surface alloy, while the 1-ML thick pseudomorphic overlayer exhibits stronger CO binding than the 2-ML thick surface alloy II at 1-ML Pt.

Recall the wrong site preference for the pure Pt(111) surface as mentioned above [20] leading to an overestimation of the binding energy at the fcc hollow site by at least 0.14 eV with respect to the top site. The dashed horizontal line in Fig. 3 indicates the CO adsorption energy at the top site of pure Pt(111) (without Au). As far as the surface alloys with Pt atoms in the second layer are concerned, the CO binding at the top sites is in fact stronger than for the pure Pt(111) surface. As will be demonstrated below, this is caused by localization effects coming from the ultrathin thickness of the PtAu system and additionally from strain effects due to the lateral lattice expansion by 5% because of the larger lattice constant of the Au(111) substrate.

In Fig. 3, the maximum CO binding energy is found at a Pt concentration of 1.33 ML at the fcc hollow site of the 2-ML thick surface alloy. This is in very good agreement with the experimental results [4]. At the top site, the binding energy has its maximum for 2 ML of Pt. At this site, the CO molecular orbitals directly interact with second-layer Pt atoms, because the chemical bonding between CO and the Pt overlayer is highly directional in the direction perpendicular to the surface [10]. Thus, the chemical bonding is strongest for the case of the 2-ML thick overlayer having only Pt atoms in the second layer. In contrast, the effect of the second layer is rather implicit in the case of the adsorption at the fcc hollow site, because the adsorption-induced rearrangement of the electron density occurs almost only within the first layer [10]. In this case, the effect of the localization of the Pt d electrons as illustrated by the upward-shift of the d-band center [10] plays a more important role. This makes the 2-ML thick surface alloy III more reactive than the 2-ML thick Pt overlayer. Thus, the present results indicate that the strongest adsorption can be attributed to a subtle balance between localization effects of Pt d electrons due to a decrease in the number of Pt atoms and an increase in the CO-Pt interaction with the number of Pt atoms in the second layer.

The most significant feature of the top-site adsorption seen in Fig. 3 is that the lowest adsorption energy in the considered cases of 2-ML thick surface alloys decreases gradually as the amount of Pt increases. This behavior agrees much better with the experiment [4] than the case of 1-ML thick surface alloys where the CO adsorption energy is almost independent of the composition. In the latter case, the bonding orbitals that are highly directional in the direction perpendicular to the surface are hardly affected by the surrounding topmost-layer atoms regardless of whether neighboring atoms in the first layer are Pt or Au [10]

In order to clarify the origin of the gradual increase in the binding energy for the top-site CO adsorption for the 2-ML thick surface alloys, we have analyzed the local density of states as shown in Fig. 4 for the case of the 2-ML thick surface alloy III. The sharp peaks in Fig. 4 (a) at -10.0 eV and -7.5 eV correspond to σ states, while the peak at -6.7 eV comes from a π state. For $-6 < E < -1$ eV, there is a significant amount of the density of states at the O atom, while there is very little at the C atom. This state comes from hybridization between the 1π orbital and the $2\pi^*$ orbital that is the LUMO of the free CO molecule. Since this state has very small amplitude at the C atom, it hardly contributes to chemical bonding between the CO molecule and the Pt atom [24]. On the other hand, the interaction between the HOMO (5σ) and Pt electrons results in a significant stabilization of the σ electrons having a lower energy than the π electrons, which involves remarkable electron transfer from the C atom to the O atom. From the viewpoint of molecular orbital theory, it can also be interpreted as a strong hybridization between 4σ and 5σ orbitals [25].

As Fig. 4 demonstrates remarkably, the σ states at -10.0 eV and -7.5 eV interact weakly but still significantly with the d_{zx} and d_{yz} orbitals of Pt, while the π state at -6.7 eV couples partially with the d_{z^2} orbital in the case of the top-site CO adsorption for the 2-ML thick surface alloy III. It should be noted that, for the 1-ML thick Pt/Au(111) system and the pure Pt(111) surface, the 4σ and 5σ orbitals of the ontop-site CO form chemical bonds almost entirely with the Pt d_{z^2} orbital, while the 1π and $2\pi^*$ orbitals interact with the d_{zx} and d_{yz} orbitals because of symmetry constraints. These couplings in the case of the 2-ML thick surface alloy are due to their lower symmetry where the second-layer Pt atoms breaks the three-fold symmetry at the top-site (see Fig. 1). In fact, the CO molecular axis is tilted by approximately 9° from the direction perpendicular to the surface because of the interaction with the second-layer Pt atom. Since the d_{zx} and d_{yz} orbitals couple with the CO σ orbitals, neighboring atoms in the first layer play a larger role compared to the case of the 1-ML thick surface alloys that lacks such couplings due to the higher symmetry. Therefore, in the case of the 2-ML thick surface alloys, because of the strong CO-Pt interaction the binding energy of the CO molecule at the top site increases gradually with the number of the Pt atoms in the first layer, which agrees well with the experiment in the Pt submonolayer regime [4]. This behavior is not observed at the top sites of the 1-ML thick surface alloys; hence, the analysis of PtAu surface alloys on Au(111) considering only 1-ML thick surface alloys can be misleading. It is therefore indispensable to examine 2-ML thick surface alloys in the case of the bimetallic Pt/Au(111) system.

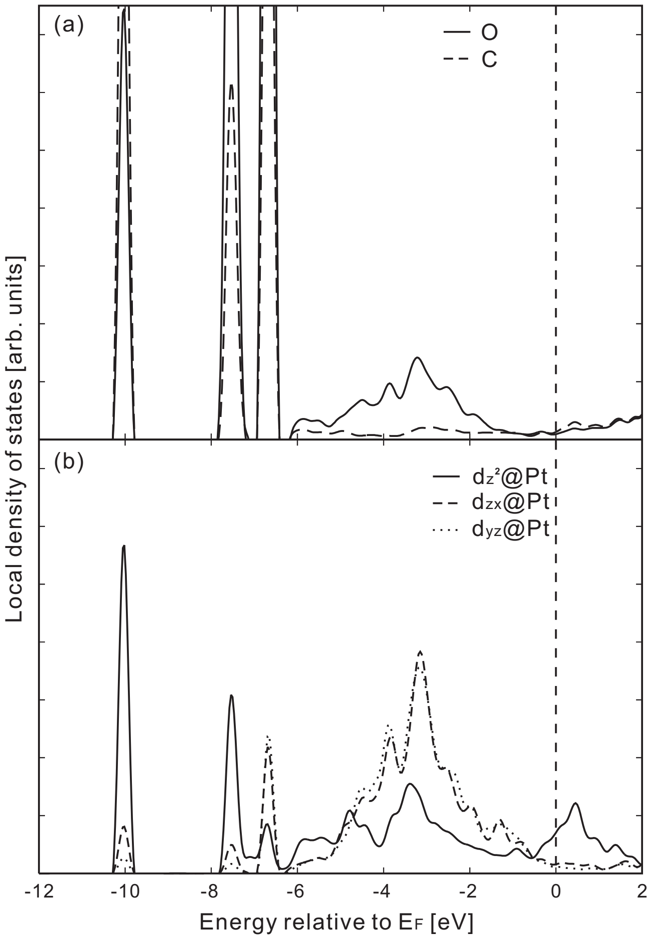

FIG. 4: Local density of states calculated by projection of wave functions onto the atomic orbitals in the case of the CO adsorption at the top site of the 2-ML thick surface alloy III, i.e. the $Pt/Pt_{0.33}Au_{0.67}/Au(111)$ surface, (a) for the C and O atoms and (b) for the three d orbitals (d_{z^2}, d_{zx}, and d_{yz}) of the Pt atom the CO molecule is bound to.

V. CONCLUSIONS

In conclusion, we have investigated pseudomorphic Pt overlayers and PtAu surface alloys on a Au(111) substrate on the basis of DFT. First, the structural stability of this ultrathin PtAu bimetallic system has been examined. Although PtAu surface alloys on Au(111) do not correspond to a thermodynamic equilibrium configuration, they are metastable with 2-ML thick surface alloys being more favorable than 1-ML thick alloys. Next, we have analyzed the adsorption properties of the CO molecule. We obtained the maximum binding energy at the fcc hollow site for a Pt concentration of 1.33 ML, where the strongest adsorption comes from a subtle balance between localization effects of the Pt d electrons and an enhanced CO-Pt interaction. In the case of the top-site adsorption, the adsorption energy for 2-ML thick surface alloys decreases gradually as the amount of Pt increases up to 2 ML which is not seen for 1-ML thick alloys. These findings agree well with the results of CO temperature-programmed desorption experiments. By analyzing the local density of states, we have clarified that the gradual decrease in the adsorption energy at the top sites is caused by the coupling between the CO σ orbitals and the Pt d_{zx} and d_{yz} orbitals due to the lower symmetry of the 2-ML thick surface alloys making contributions of the neighboring first-layer atoms more significant.

Acknowledgments

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