Au–K co-deposition on MgO(2L)/Ag(001): A first principles study

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ABSTRACT

The Au and K co-deposition on MgO(2L)/Ag(001) is studied by first principles calculations. By comparing the formation energies, several stable Au–K surface structures with different Au–K ratios are found. The Coulomb attractions between Au and K atoms play an essential role in the stabilities of these structures. The addition of K atoms in the Au/MgO(2L)/Ag(001) system modifies the electronic properties of Au significantly. The charge transfer from K atoms to Au atoms is the dominant one, which leads to the significant increase of Au charges, while the charge transfer from the substrate to Au atoms is suppressed. In the stable structures, the charges of Au atoms are different, which may show different Au reactivities.

1. introduction

The structural and electronic properties of Au deposited on metal–oxide surfaces attract many interests because of its unexpected reactivity. Small Au clusters deposited on the MgO surfaces exhibit high activities in the reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$ [1,2]. Further experiments show that the oxygen-vacancies on the MgO surfaces play an essential role in the unexpected reactivity of Au [3]. A widely accepted reason is that the electron transfer occurs between defects and Au clusters. The Au anion makes the bondings of molecules adsorbed on it easier to break and thus promotes the reaction [4,5].

Au atoms deposited on the surfaces of defect free MgO bulk are neutral and inactive. However, if Au clusters are deposited on ultra thin MgO films growing on particular substrates like Mo(001) and Ag(001), the electronic structures of Au clusters are dramatically changed. Since the thickness of MgO films is less than 1 nm, it is possible that the charge transfer occurs between Mo (or Ag) and Au by tunneling [6]. Thus Au atoms are charged [6–8]. The charged Au atoms can result in various phenomena [9]. One is the change of morphologies. On the bulk MgO surface, Au atoms form pyramid like clusters because of Au–Au attractions [10]. While on the MgO thin films, the attractions between the substrate and charged Au atoms are strong, therefore the Au clusters become two-dimensional geometry [11,12].

The charge of Au deposited on the MgO films is affected by various conditions. It is possible to modify the charge values by changing the substrate, the Au–Au distance or the thickness of the MgO films [13]. Previous studies show that K atoms deposited on the MgO film surfaces are positively charged. So we expect that the strong Coulomb attraction between Au anion and K cation will modify the charge and morphologies of Au. In this paper, we have studied the stable structures and their electronic properties of Au on MgO(2L)/Ag(001) surfaces with K atoms co-deposited. We find that the Coulomb attractions between Au and K atoms lead to several stable structures with various Au–K ratios. The electronic structures of Au are also affected by K atoms significantly. In Section 2 we will describe the model and method used in our calculations. In Section 3 we will discuss the results of electronic properties and the stable structures. A conclusion will be given in Section 4.

2. Method

The calculations have been performed using Vienna ab initio simulation program (VASP) [14,15]. In all the calculations, we use the exchange correlation functional with the generalized gradient approximation of PW-91 [16]. The energy cut-off of plane wave basis is 520 eV. To analyze the charge transfer, we use the grid based Bader analysis [17] to calculate the charge around each atoms.

Since the lattice mismatch of MgO and Ag is small (less than 3%), the lattice constants of the MgO films and the Ag substrate are the same as that of the Ag bulk. We consider the substrate as a four layer Ag film. The two bottom layers are kept fixed. This substrate reproduces the bulk band structures well [7]. A two layer MgO film is placed on the Ag surface. Except the two bottom Ag layers, all other atoms are fully relaxed until the atomic forces are less than 0.01 eV/Å. We consider various Au–K structures with

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different primitive cell sizes. For the (1×1) cell, which contains four Ag atoms, two Mg atoms and two O atoms each, the k-mesh is $(10 \times 10 \times 1)$. For the (2×2), (3×3) and (4×4) cells, the corresponding k-mesh are $(5 \times 5 \times 1)$, $(3 \times 3 \times 1)$ and $(1 \times 1 \times 1)$, respectively. In all cases, the vacuum thickness is 15 Å.

To compare the stabilities of different structures, we calculate the adsorbing energy E_b^{AuK}, which is defined as

$$E_b^{AuK} = -(E - E_{MgO/Ag} - n_{Au}E_{Au} - n_K E_K)/(n_{Au} + n_K), \qquad (1)$$

where E is the total energy of a given structure, $E_{MgO/Ag}$ is the energy of the clean MgO(2L)/Ag slab, n_i ($i =$ (Au, K)) is the number of the i atoms per cell and E_i is the energy of a single i atom. For a given ratio of n_{Au}/n_K, the formation energy of the Au–K surface alloy can be written as

$$\Delta E = -E_b^{AuK} + (1 - x)E_b^{Au} + xE_b^{K}, \qquad (2)$$

where $x = n_K/(n_K + n_{Au})$. $E_b^{Au(K)}$ is the adsorbing energy of the most stable pure Au(K)/MgO/Ag structure and calculated with $n_{K(Au)} = 0$.

3. Results and discussion

Firstly, the situations of Au atoms with different patterns adsorbed on MgO/Ag are considered. Previous work shows that the (3×3) pattern with Au atoms adsorbed on top of Mg have lower energy than that on top of O [7]. Our calculations show that it is also true for other patterns. Fig. 1 shows that the adsorbing energy E_b^{Au}, the charge Q_{Au} of Au and the Au–Mg vertical distance z_{Au-Mg} as functions of the nearest Au–Au neighboring distance. All the Au atoms are placed on top of Mg atoms. In all patterns, the Au atoms are negatively charged. The charge value increases with the increase of the Au–Au distance. As a result, the Mg cations right below the Au atoms are attracted by Au atoms and displaced to the positions a little higher than the MgO plane. The increase of Au charge leads to the increase of Au–Mg interaction and the reduction of z_{Au-Mg}. For the Au (3×3) pattern, the Au–Mg distance is 2.57 Å, which agrees with the previous work [7]. Fig. 1c shows that the charge of Au atoms is significantly modified by the Au–Au distance. The Au (1×1) pattern has a much larger adsorbing energy than other patterns, which means that other patterns are unstable.

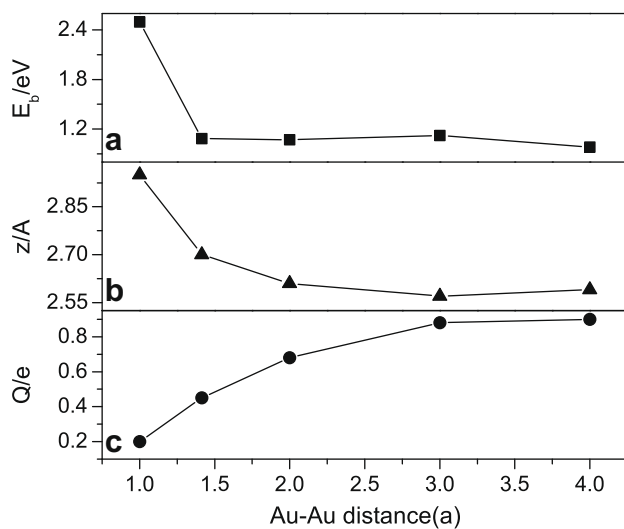Secondly, we consider the adsorb of K atoms on MgO/Ag. Our calculations show that K atoms are more likely to be adsorbed on top of O atoms, which is consistent with the previous results [7]. The strong repulsion between K cations leads to high energy of the K (1×1) pattern and makes it unstable. The adsorbing energy of K does not increase monotonously with the K–K distance. Our calculations show that the K (2×2) pattern is the most stable structure. The corresponding E_b^K is 0.61 eV. Compared to E_b^{Au} of 2.50 eV, the binding of K atoms on the MgO(2L)/Ag substrate is rather weak. K atoms adsorbed on the MgO(2L)/Ag is positively charged. For the K (2×2) pattern, The charge of K atoms is about 0.4e. This raises the probability that when Au and K are co-deposited on MgO(2L)/Ag, various structures would be stable because of the Coulomb attraction between Au and K atoms.

To find the stable structures of Au–K surface alloys, we have calculated the adsorbing energies of the Au–K surface alloy structures shown in Fig. 2. The first row of Fig. 2 is the structures with $n_{Au} : n_K = 1 : 1$. In order to make the Coulomb attractions between Au and K atoms the largest, the atoms are arranged alternatively like the CsCl structure. In Fig. 2a, the nearest Au–Au neighboring distance d_{Au-Au} is $\sqrt{2}$ times of the nearest O–O neighboring distance. Since all Au and K atoms are adsorbed on top of the O atoms, we denote this structure as AuK $c\left(\sqrt{2} \times \sqrt{2}\right)_O$. For the same reason, the structures in Fig. 2b and c are denoted as AuK $c(2 \times 2)_O$ and AuK $c(3 \times 3)$, respectively. For the first two structures, the corresponding structures with all atoms adsorbed on top of the Mg atoms are also considered. The AuK $c(1 \times 1)_O$ structure is excluded because the strong repulsions between K atoms make it unstable. The other structures in Fig. 2 are those with other Au–K ratios. The structures in the second row of Fig. 2 are the patterns with various combinations of K atoms on the O atoms and Au atoms on the Mg atoms. Since the Au $(1 \times 1)_{Mg}$ pattern is much more stable than the other Au patterns, all Au patterns in these structures are taken as (1×1). On the hand, the K patterns in Fig. 2d–f are $\left(\sqrt{2} \times \sqrt{2}\right)$, (2×2) and (3×3), respectively.
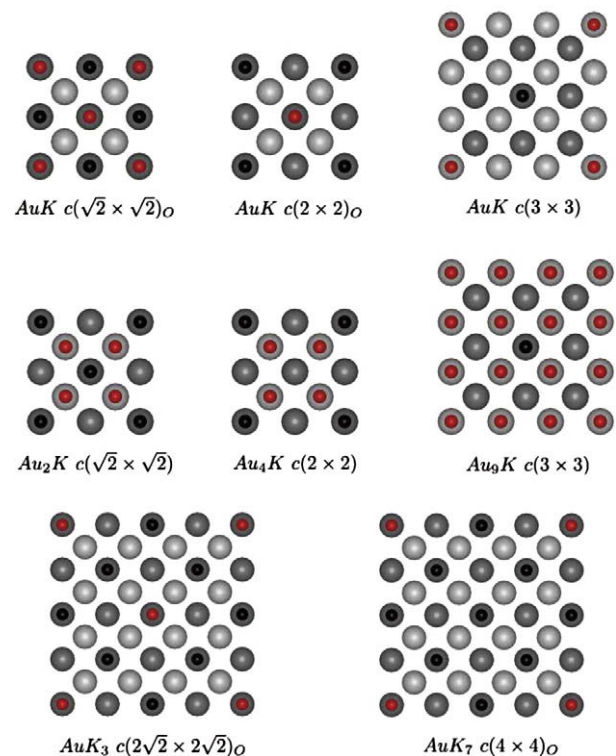

Fig. 2. The schematic structures. The dark gray balls and light gray balls denote O atoms and Mg atoms of the substrate, respectively. The small light balls and dark balls denote Au atoms and K atoms respectively.

Fig. 1. (a) Adsorption energy, (b) Au–Mg distance and (c) Au charge of different Au patterns adsorbed on top of Mg atoms. The x axis is the Au–Au nearest neighboring distance in the unit of lattice constant a.