Effects of O defects on adsorption of small Ag clusters on a MgO(001) surface*

Deng Yong-He(邓永和)

College of Science, Hunan Institute of Engineering, Xiangtan 411104, *China*

(Received 15 April 2009; revised manuscript received 18 May 2009)

The interaction of Ag atoms with a defective MgO(001) surface is systematically studied based on density functional theory. The Ag clusters are deposited on neutral and charged oxygen vacancies of the MgO(001) surface. The structures of Ag clusters take the shape of simple models of two- or three-dimensional (2D and 3D) metal particles deposited on the MgO surface. When the nucleation of the metal clusters occurs in the F_s (missing neutral O) centre, the interaction with the substrate is considerably stronger than that in the F_s^+ (missing O^-) centre. The results show that the adsorption of Ag atoms on the MgO surface with oxygen vacancy is stronger than on a clear MgO surface, thereby attracting more Ag atoms to cluster together, and forming atomic islands.

Keywords: MgO(001) surface, density functional theory calculations, O defects, Ag clusters
PACC: 7320A, 7115M

1. Introduction

Metal clusters on oxide surfaces are extremely important for technological applications, especially in the field of magnetic nanostructures, catalysis, photonics, and microelectronics.[1−4] At the first stage of the metal atom clustering and metal film growth, the metal atoms are deposited on the oxide substrates with the adsorption of isolated atoms on both regular surface sites and surface defects. In the last few years, new methods of deposition and growth of nanoclusters and small particles under ultrahigh vacuum (UHV) conditions on well-defined faces of crystalline oxides and thin films have been developed.[5,6] It is also possible to study the reactivity of these supported clusters as a function of their size. This research shows that the properties of the deposited nanoclusters determine not only the cluster size, but also the oxide substrate and, in particular, the presence of point and extended defects where the cluster is stabilized.[7] Therefore, it is essential to the identification of the structure and property of the sites where metal particles are bound on the surface of oxide single crystals or thin film. It is evident that the presence of point defects or morphological irregularities on the surface plays an important role in determining the properties of the deposited particles. In particular, the F_s centres have been characterized experimentally.[8−11]

Some models have been developed to investigate the deposition of metal atoms and clusters on regular sites and vacancies of oxide surfaces, such as ZnO(001) and MgO(001). Different terms for defects have been used: F_s (missing neutral O), F_s^+ (missing O^-), F_s^{2+} (missing O^{2-}), V_s (missing neutral Mg), V_s^- (missing Mg^+), and V_s^{2-} (missing Mg^{2+}).[12] Most of the recent computational studies are focused on the metal adsorption on regular surface sites, but few of them are concentrated on F_s centres. Some theoretical studies were devoted to the geometrical structure and electronic characterization of the metal-support interface[5,12] and the effect of these defect sites on the chemical reactivity of adsorbed metal atoms was also studied.[13,14] Different computational approaches have been taken in the study of the metal-support interface. For example, Matveev and Rosch *et al.*[5] studied the electronic properties of deposited transition metals on oxygen vacancies and regular sites of the MgO(001) surface, analysing the changes of the dipolar moment and electronic occupation parameters. They found a displacement of the electron density from the vacancy to the adsorbed metal atom: when the defect site had two electrons, for the F_s^{2+} centre, the shift was larger for Ni; while when it had one electron, for the F_s^+ centre, the shift was larger for Ag and Cu.

Nevertheless, further work is still needed to gain a further understanding of the role of the F_s site for Ag atoms deposition on a MgO substrate, i.e. how the adsorbed metal atoms aggregate and how the structural configurations of this system vary with cluster

*Project supported by the Scientific Research Fund of Hunan Provincial Education Department, China (Grant No. 09B021).
© 2010 Chinese Physical Society and IOP Publishing Ltd

size. In the present paper, the adsorption of small Ag clusters on a MgO(001) surface with O vacancy is systematically studied. The system is modelled as periodic slabs, and the total energy is calculated to determine the stable geometries of the adsorbed clusters. Finally, the bond nature between the Ag adatom and the oxide substrate is investigated in terms of electronic properties.

2. Computation details

The present work is based on density functional theory in the generalized gradient approximation (GGA) (using the PW-91 exchange-correlation functional). The method was implemented in the Vienna *Ab initio* Simulation Package (VASP) program, in which a plane-wave basis set with a kinetic energy cutoff at 420 eV and ultrasoft pseudopotentials for the electron-ion interaction were used, 4×4×1 and 8×8×8 k point meshes of the Monkhorst–Pack (MP) algorithm were used to sample the super cell which consisted of (2×2) surface MgO units and 1×1×1 MgO bulk respectively, and spin-polarized effects were included. The convergence tests with respect to these parameters showed that the error bar for the total energy was less than 1 meV/atom (≈0.1 kJ/mol).[13,15] Ionic relaxation and electronic energy minimization were performed by using the conjugate gradient (CG) algorithm. For the calculation for the density of states (DOS), the tetrahedron method with Bloch corrections was used as implemented in VASP.

Firstly, the structural properties of the pure MgO (001) surface were investigated. The calculated lattice constant of MgO was 4.24 Å (1 Å=0.1 nm) and it was in good agreement with the experimental value of 4.21 Å[14] and other theoretical values[16,17] where a 2 × 2 super cell was used to represent the MgO surface. Calculations of oxide slabs with 3 up to 8 layers confirmed that a three-layer oxide slab was thick enough for our study. In the present calculations, each slab consisted of four MgO(001) layers, adsorbed Ag atoms were adsorbed on one side of the slab, and the vacuum gap was approximately 15 Å (7 Mg-O distance intervals). The positions of atoms in the two topmost MgO layers and those of all the adsorbed Ag atoms were fully optimized until the sum of the Hellmann–Feynman forces on all unconstrained atoms converged to less than 0.02 eV/Å.

In the present work, two types of interaction energies, namely, the adsorption energy $E_{\rm ads}$ and the adhesion energy $E_{\rm adh}$ were calculated. The calculations are carried out in steps (2) and (3) below. The formation of the metal/oxide interface (see expression (3)) can be considered to be composed of two consecutive steps (1) and (2), and it is calculated according to the chemical equations[18] as follows:

$$\begin{aligned}
&{\rm Ag(g)} \rightarrow {\rm Ag(cluster)},\\
&E_{\rm IB} = [n \times E_{\rm Ag(g)} - E_{\rm Ag(cluster)}]/n, \qquad (1)\\
&{\rm Ag(cluster)} + {\rm MgO(slab)} \rightarrow {\rm Ag/MgO(slab)},\\
&E_{\rm adh} = [E_{\rm Ag(cluster)} + E_{\rm MgO(slab)}\\
&\qquad - E_{\rm Ag/MgO(slab)})]/n, \qquad (2)\\
&{\rm Ag(g)} + {\rm MgO(slab)} \rightarrow {\rm Ag/MgO(slab)},\\
&E_{\rm ads} = (E_{\rm adh} + E_{\rm IB}), \qquad (3)
\end{aligned}$$

where the $E_{\rm Ag}$, $E_{\rm MgO}$, $E_{\rm Ag(cluster)}$ and $E_{\rm Ag/MgO(slab)}$ represent the total energy of an isolated Ag atom, a defective MgO slab with O vacancy, an adsorbed Ag cluster and the whole adsorbate-substrate system respectively.

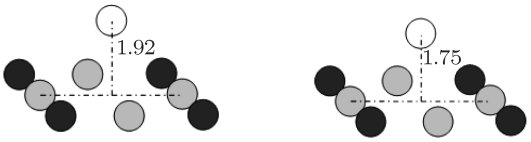
These definitions of $E_{\rm ads}$ and $E_{\rm adh}$ follow the usual convention in the literature, but step (1) above is also highlighted, since the energy contribution becomes particularly interesting when adsorption energies in different ranges are compared. $E_{\rm IB}$ is the internal binding energy when an Ag cluster is produced from the isolated metal atoms and $E_{\rm adh}$ describes the strength of the adsorbate-substrate interaction. For $E_{\rm ads}$, it represents the relative stability of the whole adsorbate-substrate system. To make comparison easy, all of these energy terms are normalized by the number of adatoms, i.e. the number given in units of per adatom.

3. Results and discussion

3.1. Adsorption of a single Ag atom

The adsorption of a single Ag atom on a defective MgO(001) surface with a neutral ($F_{\rm s}$) and charged O vacancy ($F_{\rm s}^{+}$) was considered, the initial position of the Ag atom was directly situated above the O vacancy as shown in Fig. 1.

From the calculation results, the values of adsorption energy $E_{\rm ads}$ for a single Ag atom absorbed at $F_{\rm s}$ and $F_{\rm s}^{+}$ site are 1.71 eV/atom and 2.59 eV/atom, respectively. At the $F_{\rm s}$ site, the distance from the Ag atom to the MgO(001) surface is 1.92 Å, for the $F_{\rm s}^{+}$ site, it is 1.75 Å. The adsorption energy and distance from the Ag atom to the MgO surface are in good agreement with those of other *ab initio*

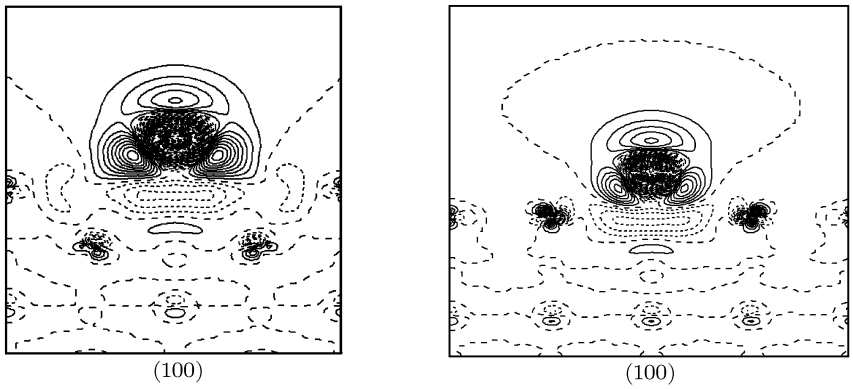


(a) Ag-F_s (b) Ag-F_s^+

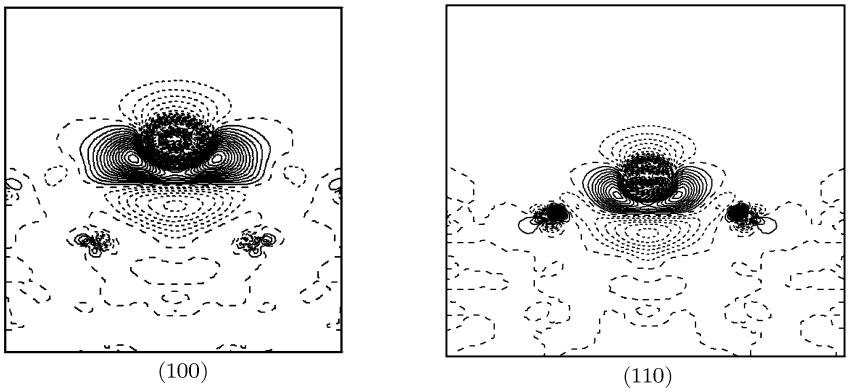
Fig. 1. Geometry properties of a single Ag atom adsorbed on (a) F_s, (b) F_s^+ site on a defective MgO(001) surface. (black ball: O atom, grey ball: Mg atom, white ball: Ag atom).

calculations.[19] From the data of an Ag atom adsorbed at regular MgO(001) in our previous work[20] (0.49 eV/atom for Ag adsorbed at the O atom of a MgO surface), it could be found that the existence of O vacancy has greatly enhanced the interaction between single Ag atoms and the MgO substrate.

The plots of charge densities are shown in Fig. 2. It can be clearly seen that the F_s sites and the F_s^+ sites all exhibit a metallic character which could be oxidized by losing electrons. It also can be seen that the electron rearrangement for Ag adsorbed at the F_s^+ site is stronger than that at the F_s site. This difference is attributed mainly to electrostatic stabilization at the F_s site. The species at the F_s site shows a consequence of significant accumulation of electron density on the adsorbed Ag atom. Covalent interaction between the absorbed Ag atom and the F_s site may counteract this electrostatic stabilization and even change the trend. The analysis and the discussion show that the F_s^+ site takes on a more energetically favourable property than the F_s site.



(a)



(b)

Fig. 2. Differences of charge densities (the total density minus a superposition of the densities for the isolated Ag atom and MgO slabs) for the cases: (a) a single Ag atom on the F_s site and (b) a single Ag atom on the F_s^+ site. The solid contour lines denote electron excess, dot lines represent electron loss. The contour lines are drawn with an increase factor of 0.005 e·Å^{-3}.

3.2. Adsorption of Ag_n (n=4, 5, 6) clusters

In order to investigate the role of O vacancy for the Ag atom's aggregation and nucleation, three kinds of Ag clusters, i.e. a two-dimensional (2D) one-layer Ag_4 cluster without a direct Ag-F_s (F_s^+) bond, a three-

dimensional (3D) Ag_5 cluster in an upside-down square pyramid configuration with an Ag atom directly bonded to an F_s (F_s^+) site, and an octahedral configuration for an Ag_6 cluster, and they are shown in Fig. 3. For the three structures, compared with the property of an isolated Ag atom adsorbed at F_s site, we can easily make a comparison to analyse the roles of the F_s and F_s^+ sites for aggregation and nucleation of Ag atoms.

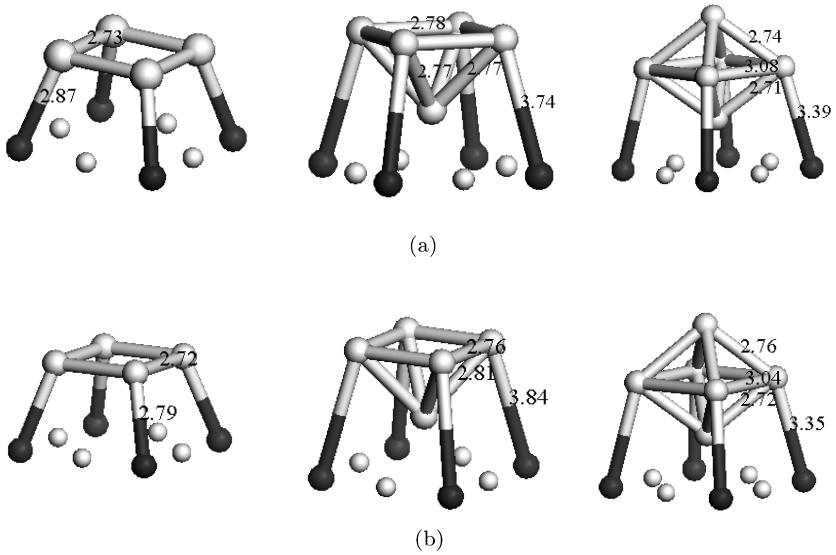


Fig. 3. Optimized structures of Ag_n (n=4, 5, 6) on the F_s site (a) and the F_s^+ site (b). Selected distances are in Å (black spheres: O, small grey spheres: Mg, big grey spheres: Ag).

After structure optimization, the calculated energy properties are listed in Table 1. The first property of interest is the adsorption energy of the Ag cluster on the MgO surface. From the results, it could be found that the Ag cluster at the F_s site possesses a more energetically stable property than at the F_s^+ site and the result is contrary to the result of isolated Ag atom adsorption at O vacancy. For the Ag_4 cluster, it is 1.52 eV/atom and 1.47 eV/atom for the F_s and F_s^+ centres, respectively. For the internal-binding energy in the Ag_4 cluster, it has only a little difference: 0.98 eV/atom for the F_s site and 0.99 eV/atom for F_s^+, so the values of adhesion energy E_{adh} could be easily calculated, i.e. 0.54 eV/atom and 0.48 eV/atom for the F_s and F_s^+ sites respectively.

Table 1. Calculated energy properties of Ag_n (n = 4, 5, 6) clusters on MgO(001) surface with O vacancy, in units of eV/atom.

ads structure	$E_{ads}(F_s)$	$E_{ads}(F_s^+)$	$E_{adh}(F_s)$	$E_{adh}(F_s^+)$	$E_{IB}(F_s)$	$E_{IB}(F_s^+)$
Ag_4	1.52	1.47	0.54	0.48	0.98	0.99
Ag_5	1.73	1.60	0.59	0.45	1.14	1.15
Ag_6	1.85	1.75	0.60	0.51	1.25	1.24

For the Ag_5 cluster, it could be found that with the increase of cluster size, the values of adsorption energy of the Ag cluster increase to 1.73 eV/atom for the F_s site and 1.60 eV/atom for the F_s^+ site, and the values of internal-binding energy in the Ag cluster also increase i.e. 1.14 eV/atom for the F_s site and 1.15 eV/atom for F_s^+: they are very similar. But the interaction energy between the Ag cluster and MgO substrate-adhesion is in contrast to the above, when there is an Ag atom directly bonded to an F_s^+ site; the adhesion energy decreases from 0.48 eV/atom to 0.45 eV/atom. Another comparison can also be made to investigate the role of the F_s^+ site. For the Ag_5 cluster, the whole adhesion energy is 0.45 eV×5 = 2.25 eV, and the previous calculation showed that the interaction between an isolated Ag atom and the MgO substrate was 2.59 eV. This strange result showed that in real conditions, the Ag atoms around the F_s^+ site had a lower tendency to form a cluster; this is because the spin coupling (for-

mation of a direct Ag–Ag bond) leads to a net stabilization which is not very affected by the strength of the Ag–substrate bond. On an F_s^+ site the formation of a strong covalent bond between the Ag atom and the F_s^+ site results in a low tendency of the surface complex to add an additional Ag atom. In this respect, a paramagnetic defect (F_s^+) on the MgO surface is not a good aggregation and nucleation centre for an Ag atom. For the F_s site, the total adhesion energy is 0.60 eV×5 = 3.0 eV; it is bigger than the 1.71 eV for the isolated Ag atom, showing that the whole interaction between the Ag cluster and the MgO substrate increases with the increase of cluster size, which means that the F_s site has a good tendency for Ag atoms to aggregate and nucleate.

These results lead to a conclusion, i.e. the discussion of Ag_6 clusters is only helpful for the F_s site, when an additional Ag atom is added to the top of the Ag_5 cluster at the F_s site. The adsorption energy E_{ads} increases to 1.85 eV/atom, the internal binding energy for the Ag cluster is 1.25 eV/atom, and the adhesion energy is 0.60 eV/atom. These figures mean that the increasing of the size of the Ag cluster makes both the interaction between the cluster and the surface and the internal interaction in the Ag cluster stronger. It can be ascribed to the interaction of the cluster atoms with the defect as well as other surface oxygen atoms and therefore increasing the adsorption energy. For the F_s^+ site, the adsorption energy E_{ads}, adhesion energy E_{adh} and the Ag cluster internal binding energy E_{IB} are 1.75 eV, 1.24 eV, 0.51 eV, respectively; compared with an isolated Ag atom at the F_s^+ site, the total adhesion energy does not increase too much.

Figure 4 shows the charge density redistribution, i.e. the change in electron density when an Ag cluster is adsorbed on the F_s (F_s^+) site with an Ag_5 cluster on it. In all of these figures, the charge redistribution was essentially localized within the first layer of MgO, electrons were depleted out of both the surface oxygen vacancy and the Ag adatom and 'spilt over' to the interstitial region. Complex polarization features were formed upon metal deposition. It can also be found that when there was no Ag atom directly bonded to an F_s (F_s^+) site for the Ag_4 cluster, the charge density redistribution between the Ag cluster and the F_s site was somewhat stronger than between the Ag cluster and the F_s^+ site, which was consistent with the adhesion energy result.

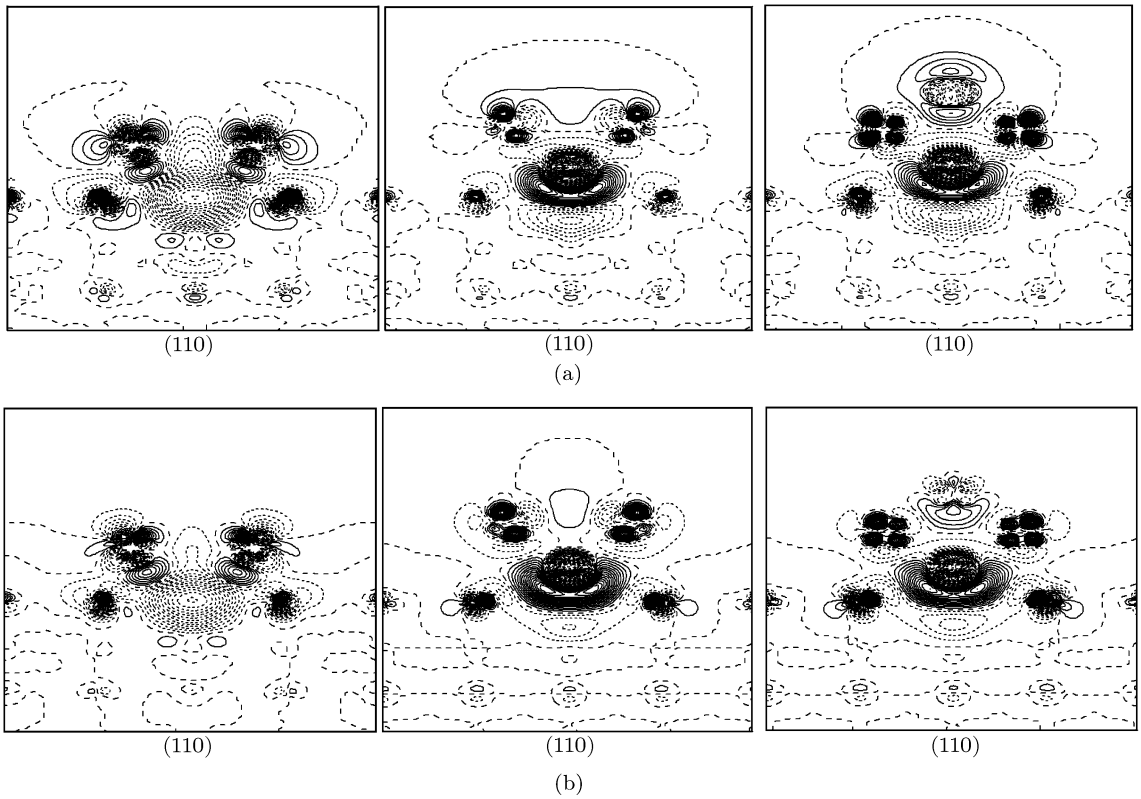


Fig. 4. Differences of charge densities (the total density minus a superposition of the densities for the Ag cluster and MgO slabs) for the cases: Ag_n (n = 4, 5, 6, from left to right) on the F_s site (a) and Ag_n (n = 4, 5, 6, from left to right) on the F_s^+ site (b). The solid contour lines denote electron excess, dot lines represent electron loss. The contour lines are drawn with an increase factor of 0.005 e·Å^{-3}.

When there was an Ag atom directly bonded to an F_s^+ site, the interaction between the Ag atoms which were directly adsorbed at the F_s^+ site and the other Ag atoms is relatively weaker than that at the F_s^+ site. This result also proves that the F_s^+ site has a low tendency for aggregation and nucleation.

4. Conclusions

In this work, we analyse the evolution of Ag adsorption at O-vacancy sites over a MgO(001) surface by using the systematic density functional theory-generalized gradient approximation (DFT-GGA) method and also describe the features due to Ag–substrate interactions. Though there exist some calculation limitations in the adopted model, a few tentative conclusions can be drawn from the studies.

Due to its metallic character, the F_s vacancy with two valence electrons forms an electropositive hole and can be easily oxidized by losing electrons, and these are indicated in the plot of charge density difference. However, F_s^+ shows a more strong adsorption property for isolated Ag atoms mainly from direct coupling of the unpaired electron of the vacancy with the 5s electron of Ag.

From the investigation of Ag clusters separately at F_s and F_s^+ vacancies with several different Ag clusters, a conclusion can be easily drawn that although there is a strong covalent bond between the surface and the Ag atom, the F_s^+ centres are not good nucleation sites.

References

[1] Campbell C T 1997 *Surf. Sci. Rep.* **27** 1
[2] Tan K E, Finnis M W, Horsfield A P and Sutton A P 1996 *Surf. Sci.* **348** 49
[3] Henry C R 1998 *Surf. Sci. Rep.* **31** 231
[4] Moseler M, Hakkinen H, Landmann U 2002 *Phys. Rev. Lett.* **89** 176103
[5] Matveev A V, Neyman K M, Yudanoy I V and Rosch N 1999 *Surf. Sci.* **426** 123
[6] Valentin C D, Giordano L, Pacchioni G and Rosch N 2003 *Surf. Sci.* **522** 175
[7] Sanchez A, Abbet S, Heiz U, Schneider W D, Hakinnen H, Barnett R N and Landmann U 1999 *J. Phys. Chem.* A **103** 9573
[8] Campbell C T, Parker S C and Starr D E 2002 *Science* **5594** 811
[9] Larsen J H, Ranney J T, Starr D E, Musgrove J E and Campbell C T 2001 *Phys. Rev.* B **63** 195410
[10] Revenant C, Renaud G, Lazzari R and Jupille J 2006 *Phys. Res.* B **246** 112
[11] Valentin C D, Scagnelli A, Pacchioni G, Risse T and Freund H J 2006 *Surf. Sci.* **600** 2434
[12] Lopez N, Paniagua J C and Illas F 2002 *J. Chem. Phys.* **117** 9445
[13] Causa M, Dovesi R, Pisani C and Roetti C 1986 *Surf. Sci.* **175** 551
[14] Zhang W B, Hu Y L, Han K L and Tang B Y 2006 *Phys. Rev.* B **74** 054421
[15] Deng Y H, Wang T F, Zhang W B, Tang B Y, Zeng X Q and Ding W J 2008 *Trans. Nonferrous Met. Soc. China* **18** 416
[16] Giordano L, Baistrocchi M and Pacchioni G 2005 *Phys. Rev.* B **72** 115403
[17] Dong Y F, Wang S J, Mi Y Y, Feng Y P and Huan A C H 2006 *Surf. Sci.* **600** 2154
[18] Ma S Y and Wang S Q 2008 *Chin. Phys.* B **17** 3856
[19] Zhukovskiia Y F, Kotomina E A and Borstel G 2004 *Vacuum* **74** 235
[20] Hu Y L, Zhang W B, Deng Y H and Tang B Y 2008 *Comput. Mater. Sci.* **42** 43