



Surface alloying of immiscible metals induced by surface state shift

X.K. Shu, P. Jiang, J.G. Che *

Department of Physics, Fudan University, Shanghai 200433, People's Republic of China

Received 24 April 2003; accepted for publication 27 August 2003

Abstract

By using first principles calculations, it is found that the noble metal atoms Ag, Au and Cu would like to occupy the vacancy sites of the W(001) or Mo(001) surface to form the substitutional surface alloys, despite the fact that they do not like to form alloy in the bulk. The electronic local function (ELF) for these substitutional surface alloys shows that there is no obvious chemical bonding between the noble metals and W or Mo. The analysis of electronic structures lets us conclude that the surface alloying of immiscible metals may originate from the surface state shift of W (or Mo) induced by changes of the electronic environment of surface W (or Mo) when surface W (or Mo) atoms are alternatively replaced by Ag (Au or Cu).

© 2003 Elsevier B.V. All rights reserved.

Keywords: Density functional calculations; Surface energy; Surface structure, morphology, roughness, and topography; Silver; Gold; Copper; Tungsten; Molybdenum

1. Introduction

Surface alloying has been a subject of extensive interest in recent years because of its applications in many fields such as corrosion, catalysis, and surface hardening. One of the notable aspects in this field is the surface alloys form from elements which do not mix in the bulk. For example, Cu and W are immiscible and do not alloy in the bulk, but when Cu is deposited on W(001) surface, Cu will alternatively substitute surface W to form a single layer surface alloy [1–3]. It is well recognized that whether elements can form substitutional al-

loys in the bulk depends on three factors: atomic size, chemical bonding, and coordination number. However, the mechanism of substitutional surface alloying is not always clearly understood [4,5]. Therefore, it is interesting to show whether substitutional surface alloys of immiscible metals are formed due to one or more of these factors or from any other mechanism. The driving forces of the surface alloying are most noticeable, because surface alloying is believed very important for many surface processes.

It has been reported that noble metals (Cu, Au, Ag) form surface alloys on W(001) and Mo(001) surfaces, although they do not alloy with bulk W or Mo [1,3,6–14]. The formation mechanism of these surface alloys is believed similar. Singh and Krakauer performed ab initio calculations on Cu/

* Corresponding author. Tel.: +86-21-65643427; fax: +86-21-65644261.

E-mail address: jgche@fudan.ac.cn (J.G. Che).

W(001) substitutional surface alloy, i.e., W(001) with W atoms replaced alternatively by Cu atoms [2]. They concluded that no strong bonding between Cu and W atoms exists while the alloy is formed because of the near-instability of ideal W(001) surface against the formation of W(001) $c(2 \times 2)$ surface vacancy.

In order to reveal the driving forces for the formation of the substitutional surface alloy of the noble metals such as Ag, Cu and Au on W(001) or Mo(001), for which no bulk alloy exists, the interaction between adsorbates and substrate must be understood. It has been well established that the difference of the electronegativity between the adsorbate and substrate may induce charge transfer from one to another, leading to a change of surface morphology and other surface properties. A typical example is the surface reconstruction of Ag(110) induced by alkali adsorption [15]. Fu and Ho considered the change of the surface energy as a function of surface charging and showed the charge transfer could possibly result in the reconstruction [16]. It is noticed that noble metals are more electronegative than W on the Pauling scale, therefore, electrons might be depleted from the W(001) surface if adsorption of noble metal atoms on it occurs. Therefore, it is interesting to know if charge transfer is the primary driving force for the formation of substitutional surface alloy i.e., whether the physical effect such as surface charging or the chemical bonding results in the surface alloying.

In order to show the effect of the charge transfer on the substitutional surface alloys of noble metals on W or Mo(001), the physical factors are exclusively considered here without any chemical interactions. It has been shown that an external electric field can induce surface charging due to electrostatic screening, resulting in charge transfer on surfaces. Therefore, the clean W(001) surface under an external electric field is considered in the present work. In this case surface charge transfer does not depend on any of the local chemistry since no adsorbates and therefore no any possible chemical bonding exists. This will be helpful to reveal the real mechanism of the surface alloy on such kind of metal surfaces and to have a better understanding of the underlying physics of such intriguing surface phenomena.

In the present work the detailed mechanism in surface alloying of immiscible metals is studied as following four steps. First, the surface formation energy of Ag on fourfold-hollow site and substitutional site of W(001) surface are calculated by ab initio calculations based on the DFT and norm-conserving pseudopotential method with plane wave basis set to know if these surface alloys favor in energy. The substitutional surface alloy is modeled as that W surface atoms on both sides of a W(001) slab are alternatively replaced by Ag atoms. Second, the electronic localization function (ELF) [17–19] for these systems is calculated to investigate the effect of the chemical bonding. It has been shown that in a many electron system the value of ELF is large (close to one) in the regions where electrons are paired up to form covalent bonds, while it is small in low electron density regions; ELF value is also close to one where the unpaired lone electron is localized on a dangling bond. On the other hand, for a homogeneous electron gas ELF equals 0.5 no matter what electron density is. This means that an ELF close to 0.5 will correspond to a bond of metallic character [20]. Third, in order to reveal the underlying mechanism clearly and to see if only the surface charging can induce surface alloying, chemical factors on the surface alloying should be excluded. In this connection the surface charging is modeled by imposing an external electric field on the W(001) $c(2 \times 2)$ vacancy structure and the charge transfer is compared with that of Ag/W(001). The charge variation of W(001) $c(2 \times 2)$ vacancy structure under an external electric field is calculated by using the method proposed by Che et al. [21]. Finally, the surface density of states (SDOS) of Ag/W(001) substitutional array is shown to explain that the Ag-induced shift of surface states of surface W atom near the Fermi level should be responsible to this kind of surface alloying of immiscible metals.

2. Methods

The first principles calculations are performed within the local density functional formalism [22,23], together with norm-conserving pseudopo-

tentials [24]. The wave functions are expanded by means of a mixed-basis set consisting of plane waves with kinetic energy up to a certain cutoff energy, plus a set of localized numerical functions centered at atomic sites describing the more tightly bound d orbitals [25]. This approach has been successfully applied to the electronic and structural properties of many transition metals [26]. The shape of the numerical orbitals is chosen to optimize the total energy and after this is done, the total energies can converge with a relatively small set of plane waves. In the calculations a plane-wave basis with kinetic energy up to 11.5 Ry is used, which is sufficient to provide a total energy convergence better than 0.01 eV. For the bulk tungsten, this approach gives a lattice constant $a_0 = 3.14 \text{ \AA}$, which agrees well with experimental data of 3.17 \AA.

The surfaces are modeled by the standard slab geometry. Slabs of nine atomic layers (seven of substrate and two adlayers), separated by a vacuum of 18 \AA, are used and repeated periodically along the normal direction of surfaces. The k points are sampled on an 8×8 and 12×12 mesh within the surface Brillouin zone (SBZ) for $c(2 \times 2)$ and $p(1 \times 1)$ unit cell respectively. All atoms in the unit cell are fully relaxed by computing the Hellmann–Feynman forces on the atoms. Relaxation of atomic positions is facilitated by a force matrix, which is initially taken to be a diagonal matrix with force constants estimated from the Debye temperature. The force matrix is then updated during the course of atomic relaxations by using a modified Broyden scheme [27]. The whole procedure is accelerated by a force–corrector scheme [28] and the relaxation terminates when the maximum of the remaining forces is smaller than 0.01 eV/\AA.

Adsorption of Ag atoms on the W(001) surface may lead to two different configurations. One is an overlayer structure that the Ag atoms are on the fourfold-hollow sites above the W(001) surface forming a $c(2 \times 2)$ array, while another is surface alloy that the W atoms of the top layer are replaced alternatively by Ag atoms, forming an ordered $c(2 \times 2)$ substitutional surface alloy. The top view of this two structures is shown in Fig. 1. In order to compare the energetics of the two struc-

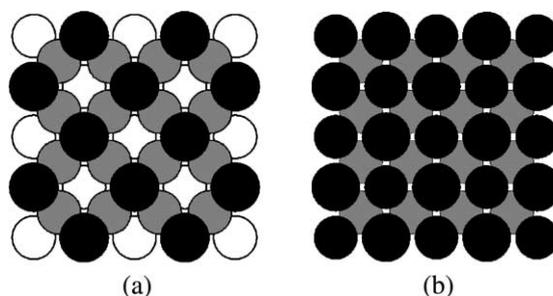


Fig. 1. Top view of Ag atoms forming a $c(2 \times 2)$ array on the fourfold-hollow sites above the W(001) surface (a) and Ag/W(001) $c(2 \times 2)$ substitutional surface alloy (b). Small and large circles represent W and Ag atoms respectively. Atoms in the first, second, and third layers are represented by black, gray, and white circles, respectively.

tures, a surface formation energy per surface atom (E_s) is defined as

$$E_s = \frac{1}{2N} [E_{(\text{Ag/W})\text{slab}} - (E_{(\text{W})\text{substrate}} + n\mu_{\text{Ag}})] + \sigma, \quad (1)$$

where N is the number of atoms per surface unit cell, $E_{(\text{Ag/W})\text{slab}}$ is the total energy per unit cell of the slab with Ag adsorbed on W, $E_{(\text{W})\text{substrate}}$ is the total energy of the clean W substrate, n is the total number of Ag atoms in the surface unit cell, μ_{Ag} is the chemical potential of the Ag atoms, and σ is the surface energy per surface atom of the clean W substrate. The factor of 2 in the denominator accounts for the fact that Ag atoms are located on both sides of the W slab.

The surface formation energy for the two Ag configurations (overlayer and alloy) can be compared directly and the configuration which has lower energy is the energetically favorable one. In calculations μ_{Ag} is set equal to the bulk energy of a single Ag atom in the fcc structure. The choice of the bulk energy as the reference energy of the adatoms has the advantage that it can be shown immediately whether the adatoms wet the substrate or not. If $E_s < \sigma$, then the Ag atoms gain energy by covering the surface rather than forming macroscopic bulklike islands on top of the substrate. In this case, it is concluded that the adatoms wet the substrate.

To introduce the effect of an external electric field, two external uniform charge sheets are placed

parallel in vacuum [21], one at 9 Å above and another at 9 Å below the slab. The electrons in metallic systems will rearrange themselves to give a surface charge which screens off the field. The surface screening charge and the external charge sheets establish an electric field in the vacuum whose magnitude is controlled by the charge density of the charge sheet [21]. Atomic positions for different models (with and without electric field) are fully relaxed.

3. Results and discussions

3.1. Atomic structures

For Ag/W(001) systems the top view and side view of Ag/W(001) c(2×2) substitutional surface alloy are shown in Figs. 1(b) and 2 respectively. Suppose the Ag atoms are removed or replaced by W atoms, the figures will represent W(001) c(2×2) vacancy and the W(001) p(1×1) surface. Removing the surface W atom from the Ag/W(001) substitutional surface results in the structure of Ag on fourfold-hollow site shown in Fig. 1(a). In calculations, all atoms are fully relaxed until the remaining forces acting on each atom are all smaller than 0.01 eV/Å. Due to the symmetric constraint the atoms relax only along the surface normal direction.

In order to study the properties of Ag occupying the vacancy sites of the W(001) surface,

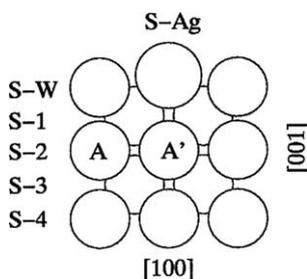


Fig. 2. Side view of fully relaxed structure of Ag/W(001) c(2×2) substitutional surface alloy. W and Ag atoms are represented by small and large circles, respectively. A and A' represent two types of W atoms, of which one is below the surface W atoms, while the other is below the surface Ag atoms.

W(001) c(2×2) vacancy structure is first considered and it is compared with the W(001) p(1×1) surface. Although the W(001) surface is a well studied system, the multilayer relaxation of the surface still remains inconclusive, even for the first layer. The contraction of the first layer spacing of this surface is still controversial, the experimental values range between $5.5 \pm 1.5\%$ and $11 \pm 2\%$ [29–33]. Present calculated atomic relaxations in the percentage change of the interlayer spacings for W(001) p(1×1) surface, W(001) c(2×2) vacancy surface and Ag/W(001) surface are listed in Table 1. Several experimental and theoretical results are quoted for comparison.

The S-2 layer in Ag/W(001) surface and W(001) c(2×2) vacancy surface contains two inequivalent types of atoms [8], of which one (A) is below the surface W atoms while the other (A') is below the Ag atoms or vacancies as shown in Fig. 2. The difference of the positions of inequivalent atoms in S-2 layer along the [001] direction for Ag/W(001) c(2×2) substitutional surface alloy and W(001) c(2×2) vacancy is both 0.05 Å. Therefore, the percentage change of the interlayer spacings given in Table 1 has been averaged for the S-2 layer. The Δ_{12} in Table 1 stands for the change corresponding to the interlayer spacing of the first and second W layer.

The present results show that the surface layer of the W(001) p(1×1) surface contracts by -11.4% , while the deeper layers appears in an oscillatory relaxation of 3.2%, -0.7% and 0.2%. This kind of contractions may be explained by Smoluchowski smoothing effect [35,36]. The Smoluchowski's effect is that when a surface is created by cutting a perfect crystal, the electrons tend to reduce the charge density corrugation near the vacuum region. It means that the charge "flows" from the "hills" (surface W atoms) into the "valleys" formed by the surface atoms. In this way a net positive charge on the "hills" and a negative charge in the "valleys" result, which induces an inward electrostatic forces on the ion cores of the surface atoms and results in the surface W layer contraction.

It has been already established that according to the Smoluchowski smoothing effect the more open the surfaces are, the larger contraction the

Table 1

Layer relaxation given in the percentage change of the unrelaxed interlayer distance for W(001) surface of p(1×1) and c(2×2) vacancy and Ag/W(001) substitutional surface alloy. Available data from other studies are also listed for comparison

	Citation	Δ_{12}	Δ_{23}	Δ_{34}	Δ_{45}
p(1×1)	Present work	-11.4	3.2	-0.7	0.2
	LAPW ^a	-4.02	3.06		
	Expt. ^b	-11 ± 2			
	Expt. ^c	-5.5 ± 1.5			
	Expt. ^d	-10 ± 2			
	Expt. ^e	-6.7 ± 2			
	Expt. ^f	-7 ± 1.5			
c(2×2)-V	Present work	-15.4	0.0	0.2	-0.7
Ag/W(001)	Present work	-12.7	0.8	-0.4	-0.1

^a Ref. [34].

^b Ref. [29].

^c Ref. [30].

^d Ref. [31].

^e Ref. [32].

^f Ref. [33].

layer spacing will be. Therefore the large contraction appears on rough surfaces, while little contraction exhibits on close-packed ones. In the present work the first layer contraction of the W(001) c(2×2) vacancy surface 15.4% which is larger than that of the p(1×1) W(001) is obtained. This result agrees with the above picture because the vacancy surface is more corrugate than the W(001) p(1×1) surface. When the vacancies are occupied by Ag atoms the first W layer contraction for the Ag/W(001) substitutional surface reduces to 12.7%, close to that of the W(001) p(1×1) surface, 11.7%. According to the above picture this is also reasonable. The somewhat larger contraction of 12.7% may be attributed to the more electronegativity of Ag atom than W atom on the Pauling scale. The charge “flows” from the surface W atoms towards the Ag atoms, which results in an additional net positive charge on the surface W atoms, inducing electrostatic forces on the ion cores of the surface W atoms.

Energetically this can be also understood by a simple picture: when atoms decrease the distance due to contracting interlayer spacing between the first and second layer, it will be more favorable in energy by expanding their lateral spacing. Therefore, it can be expected that the W(001) c(2×2) vacancy structure is more stable against the

W(001) p(1×1) structure, because there is a more lateral spacing for atoms in the vacancy array. It is the same case for the Ag/W(001) system. Compared with the W(001) c(2×2) vacancy array, the lateral displacement of surface W atoms will be suppressed when Ag atoms occupy the vacancy site. The contraction for Ag/W(001) therefore reduces to 12.7%.

Next the surface formation energy for Ag atoms adsorbed on the fourfold-hollow site and the surface substitutional site of the W(001) surface is considered. The calculated surface formation energies for W(001) p(1×1) and c(2×2) vacancy as well as for Ag on substitutional site and on fourfold-hollow site of the W(001) surface are listed in Table 2. The surface formation energy per surface atom of Ag on the substitution site is 0.50 eV lower than that of Ag on the fourfold-hollow site,

Table 2

Surface energies (in eV/surface atom) for W(001) surface of p(1×1) (E_s) and c(2×2) vacancy (E_s^{vac}), and surface formation energies (in eV/surface atom) for Ag adsorbed on the fourfold-hollow site (E_s^{fourfold}) and surface substitutional site of the W(001) surface (E_s^{sub})

E_s	E_s^{vac}	E_s^{fourfold}	E_s^{sub}
2.81	2.72	2.70	2.20

which means that the Ag/W(001) substitutional surface alloy is more favorable energetically. Therefore it is expected that Ag on the substitutional sites is more stable than on the fourfold-hollow sites, since bulk Ag is of fcc structure and likes to have a higher coordination. A single Ag adatom on a W(001) surface in the fourfold hollow site has four first neighbors (1NN) of W, while in the substitutional site, it is embedded in an electron density provided by four 1NN W at a distance of $0.866 a$ and four 2NN W at a distance of a , here a is lattice constant. This implies theoretically that Ag/W(001) substitutional surface alloy could be formed.

The surface formation energy of W(001) $c(2 \times 2)$ vacancy is 0.09 eV lower than that of W(001) $p(1 \times 1)$ surface, meaning that the W(001) $p(1 \times 1)$ surface is near-unstable against the formation of W(001) $c(2 \times 2)$ vacancy, as concluded by Singh and Krakauer [2]. It is believed that this near-instability is responsible for the formation of Cu/W(001) substitutional surface alloy [2]. Present calculated surface formation energy of Ag on the vacancy site of the W(001) surface is 0.50 eV lower than that of Ag on fourfold-hollow site of the W(001) surface, which should be the primary reason for the formation of the stable Ag/W(001) substitutional surface alloy.

What is the driving forces for this single layer alloy of Ag with W surface? Whether it is chemical bonding because of the change of electronic environment? In order to answer these questions the electronic structures of Ag/W(001) substitutional surface alloy are investigated in the following.

3.2. Electronic localization function

According to the suggestion of Jarvis et al. [37], in present work electron local function (ELF) is used to investigate the metallic bonds of Ag/W(001) surface alloy and W(001) $c(2 \times 2)$ vacancy. The ELF for (110) plane of both slabs is shown in Fig. 3. The ELF can give a quantitative description about bonding. For the (110) plane of Ag/W(001) substitutional surface alloy the ELF values between Ag and W atoms, shown in Fig. 3(a), range from 0.17 to 0.29, corresponding to a low charge density. This implies that quite weak

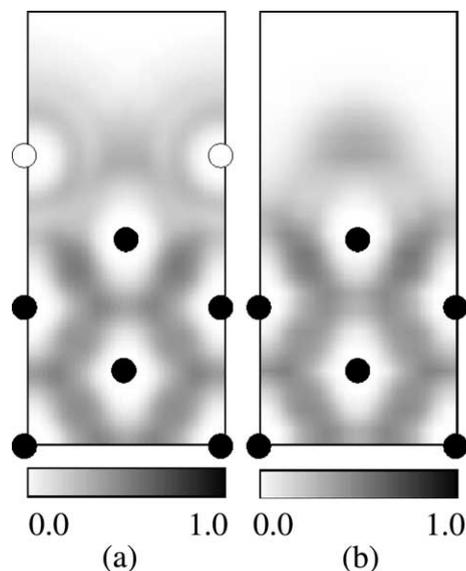


Fig. 3. ELF grey plot of (110) plane of Ag/W(001) $c(2 \times 2)$ substitutional surface alloy (a) and W(001) $c(2 \times 2)$ vacancy (b). The position of Ag and W are represented by white and black circles, respectively.

bonds form between Ag and W atoms. This is consistent with the ELF values of a AgW pseudo-alloy in the bulk, 0.17–0.27. The pseudo-alloy is obtained in this way: one of two W atoms in a bcc cell is replaced by one Ag atom, and its lattice constant is optimized to be 3.22 Å. Of course, such an alloy does not practically exist, therefore, we believe similar interaction should not play an important role in surface alloying of Ag/W(001). By comparison, the values of ELF range from 0.42 to 0.54 in the region among the nearest-neighbor W atoms, which is coincident with the fact that strong metallic bonds exist between W atoms. On the other hand, for the (110) plane of W(001) $c(2 \times 2)$ vacancy, shown in Fig. 3(b), the values of ELF are between 0.46 and 0.55 in the region among the nearest-neighbor W atoms, which indicates not only that strong bonding do exist between W atoms but also that the bonding has almost not been disturbed upon introduction of Ag atoms as the values of ELF keep almost unchanged.

The nearest-neighbour W atoms of Ag in the Ag/W(001) surface alloy are in the second layer in the (110) plane. The distance between the Ag and the nearest-neighbour W is 2.90 Å. Accordingly,

we assume that the strongest interaction between Ag and W should be localized in this plane if any. However, it is also interesting to investigate the ELF for (100) plane because the distance between surface W and Ag is only 3.18 Å. We found an interesting feature in this plane, i.e. a different ELF between surface W and Ag, shown Fig. 4(a). In the region between the surface W and Ag, we found that the ELF seems to be metallic-like, as pointed by an arrow in the figure. However, for the (110) plane, we read the maximum ELF values from the joint line between Ag and W, while we do so for the (100) plane, the ELF values range only from 0.16 to 0.23, somewhat smaller than that of the (110) plane. This is reasonable because the distance between surface W and Ag is longer. The ELF between surface W and Ag seems to be metallic-like since the surface W atom is relaxed to the bulk (12.7% layer contraction), resulting in that the ELF between the surface W atom and its nearest-neighbor W in the second layer is partly mixed into the the ELF between the surface W and Ag. However, when we compare it with the ELF of the W(001) $c2\times2$ vacancy, as pointed by an arrow in Fig. 4(b), it could be concluded that such a metallic-like ELF does not arise from the interaction between Ag and W, rather from the relaxation of the W.

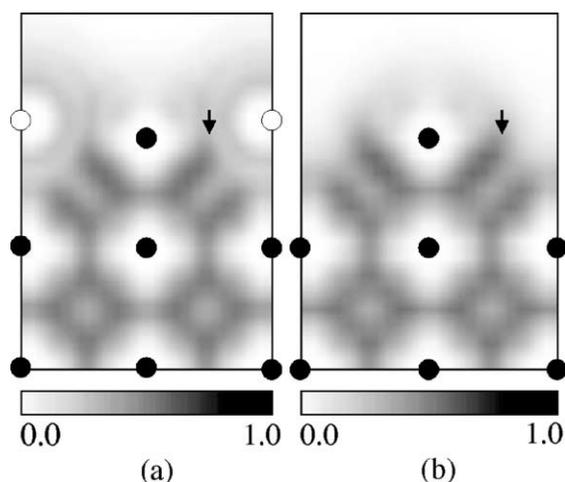


Fig. 4. ELF grey plot of (100) plane of Ag/W(001) $c(2\times2)$ substitutional surface alloy (a) and W(001) $c(2\times2)$ vacancy (b). The position of Ag and W are represented by white and black circles, respectively.

In brief, the ELF pattern demonstrates clearly that there is, if any, only weak chemical bonding between Ag and W atoms, consisting well with the conclusions for Cu/W(001) substitutional surface alloy by Singh and Krakauer [2].

3.3. Surface charging effect

From above analysis chemical bonding could be excluded from the mechanism of the formation of Ag/W(001) substitutional surface alloy, it is natural to ask which driving forces account for the surface alloying. It is noted that Ag is more electronegative than W and it will cause significant charge transfer between Ag and surface W upon the Ag adsorption and will induce charge redistribution [38–40]. It is interesting to know if the depletion of electrons from W atom of Ag/W(001) is a driving force for surface alloying of Ag on W(001) surface even though Ag does not alloy with W in the bulk.

In the following the effect of surface charging on surface alloying is considered exclusively without any chemical bonding involved. It is well known when a metallic system is subjected to an external electric field the electrons will rearrange themselves yielding a surface charge to screen out the field so that the electric field cannot penetrate into the metal bulk. For a typical metal, the screening charge is mainly distributed in the top layer. In this respect surface charging is equivalent to a surface subjected to an external electric field.

An external electric field imposing on the surface will perturb the surface states and then affect surface morphology. There have been several investigations reported in which an external electric field is intentionally applied in order to examine its influence on the surface. Since an external electric field can change the surface morphology [3,21,41], it is interesting to know whether or not the surface charge can stabilize the Ag/W(001) when Ag atoms deposit on the vacancy sites of W(001) surface, and whether or not the surface charging effect is an exclusive driving force for surface alloying of immiscible metals.

In order to simulate the electron depletion of W, an external electric field is added on the W(001) $c(2\times2)$ vacancy. In the present calculation

this is accomplished by setting two external uniform charge sheets at the middle of the vacuum, which is just like putting the slab at the middle of a capacitor. The strength of the electric field and also the amount of surface charging can be controlled by the charge density of the charge sheet. It is obvious that in this way only the physical charge transfer is involved.

Che et al. [21] have concluded that an external electric field can really stabilize the W(001) $c(2 \times 2)$ vacancy structure, which implies surface charge transfer might stabilize the Ag/W(001) substitutional surface alloy too. Therefore, the difference in charge distribution of the surface W atoms between the system of Ag on the W(001) vacancy site i.e. Ag/W(001), and the system of W(001) vacancy surface is calculated. The later is obtained by removing Ag from the Ag/W(001) while the positions of all W atoms are kept the same for both systems, i.e., corresponding to those that optimize the energy of the Ag/W(001) substitutional surface alloy. The pseudocharge difference in charge density obtained in this way is plotted in the (100) plane and shown in Fig. 5(a). The cross in the figure represents the position of the surface W atoms. The solid curves represent charge added, while the dotted curves represent the charge removed. Note that in both sides (left and right) of Fig. 5(a) there are considerable charges added around the Ag atoms, since the pseudocharge difference here is shown for two

systems: one with Ag atom and the other without. For comparison, the pseudocharge difference in charge density between the W(001) $c(2 \times 2)$ vacancy with an external electric field of 3 V/\AA and that without the external electric field is also calculated in the same way, that is, the positions of all W atoms of the system without the electric field are kept to the same as the system with an external electric field of 3 V/\AA . The corresponding pseudocharge difference of the surface W atom is shown in Fig. 5(b), also for the (110) plane. Again, the dotted curves indicate charge reduction.

Clearly Fig. 5(a) and (b) show different behaviors of surface charge depletion induced by Ag atom and by an external electric field. It is found that except for the region near the surface W atom and the region around Ag atoms, the pseudocharge difference is almost zero, meaning reasonably no change in charge density, which is expectable since for the W(001) $c(2 \times 2)$ vacancy the effect of the electric field has been well screened out, while for the Ag/W(001) substitutional surface alloy at most there are only weak interactions between Ag and W. Therefore, the surface charge transfer for both cases exists only near the topmost layer and has no effect on the charge in the inner layers. These plots show how the charge density on the surface W atom changes when Ag is deposited in the vacancy site and when an external electric field is imposed. For the case of W(001) vacancy array, the charge depletion under an external electric field of 3 V/\AA is localized only on the top of the surface W atom (hill) to screen the field which cannot penetrate into the bulk more than one layer, as shown in the Fig. 5(b). However, for the case of Ag/W(001) substitutional surface alloy, the charge transfer between Ag and W appears with a different distribution, corresponding to that the W atoms seem to be embedded in the Ag environment. Therefore, it may account for a different mechanism for surface alloying, compared with the stability of the W(001) $c(2 \times 2)$ vacancy under an external electric field.

3.4. Surface state shift

In order to further reveal the origin of surface alloying the detailed electronic structures are in-

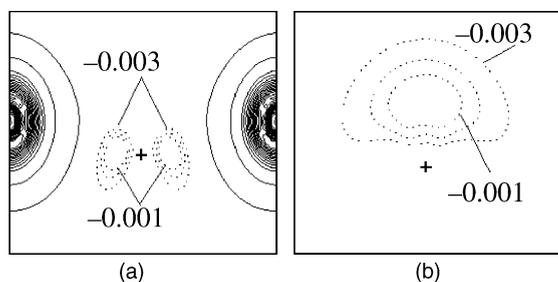


Fig. 5. The difference in charge density of the surface W atoms between Ag on the W(001) vacancy site and the W(001) vacancy surface (a), and between with and without an external electric field for $c(2 \times 2)$ vacancy (b). Dotted lines represent charge decrease, while solid lines represent charge increase. The cross represents the position of W atoms. The adjacent contours are separated by 0.001 e/au^3 .

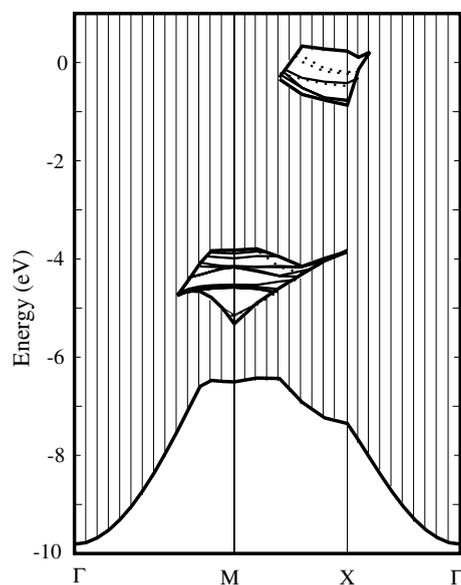


Fig. 6. Surface band structure of the Ag/W(001) substitutional surface alloy (—) and the W(001) $c(2 \times 2)$ vacancy (\cdots). The shaded area represents the bulk W band structure projected onto the SBZ.

vestigated. The surface band structure of Ag/W(001) substitutional surface alloy is calculated and shown in Fig. 6. In this figure the band structure of bulk bcc W projected onto the SBZ is given by the shaded areas and the Fermi level has been set to be at zero. There are two pockets in the projected bulk band, one of them is near the Fermi level, and the other is about 4 eV below the Fermi level. The surface states are represented by solid lines for Ag/W(001) substitutional surface alloy and dotted lines for W(001) $c(2 \times 2)$ vacancy array.

From Fig. 6 it can be seen that surface states in the lower pocket are mainly contributed by Ag as shown by solid lines, except for states near the edge of this pocket. It is found the surface states in the pocket near the Fermi level have upwards dispersion along XM and only small dispersion along X Γ . In order to explore the origin of these surface states, the density of states projected on the surface W atom both for the Ag/W(001) substitutional surface alloy and the W(001) $c(2 \times 2)$ vacancy array at point X of SBZ are calculated and shown in Fig. 7. Again, the solid lines are for Ag/

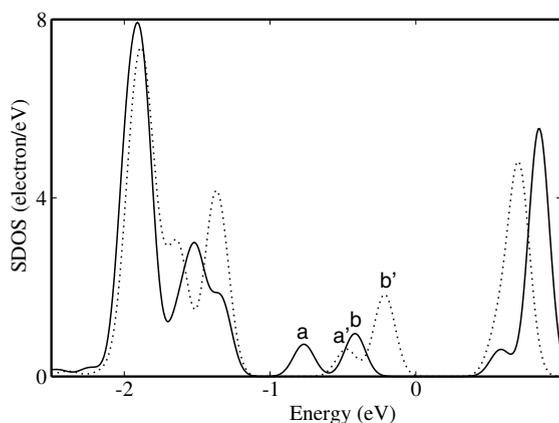


Fig. 7. The surface density of states of the surface W atom for the Ag/W(001) substitutional surface alloy (—) and the W(001) $c(2 \times 2)$ vacancy array (\cdots). Symbols *a*, *b* and *a'*, *b'* label surface states. Fermi level is set at $E = 0$.

W(001) substitutional surface alloy and dotted lines for W(001) $c(2 \times 2)$ vacancy array. It is confirmed from the figure that the surface states just below the Fermi level at X point are localized at the surface W atom. Compared with the surface states of the surface W atom in the W(001) $c(2 \times 2)$ vacancy array, the surface states of the surface W atom in the Ag/W(001) substitutional surface, labeled by *a* and *b* respectively, have similar behaviors and are little affected by the existence of Ag except for shifting the surface states downward. It can be understood from this picture: due to the existence of Ag at the vacancy site of W(001) and induced charge transfer, the surface potential has been changed and the surface W atom experiences a different electronic environment. This results in a downward shifting of the occupied surface states, which can be clearly seen from Figs. 6 and 7. The occupation of Ag on the W(001) vacancy site leads to significant consequences in the electronic structure near the Fermi level. This mechanism is similar to the origin of the reconstruction of W(001) $c(2 \times 2)$ -M₅, that is, compared with the instability of the W(001)(1 \times 1) surface, small displacements of surface W parallel to the surface result in the surface state splitting and shifting to lower energy, leading to a more stable structure [42].

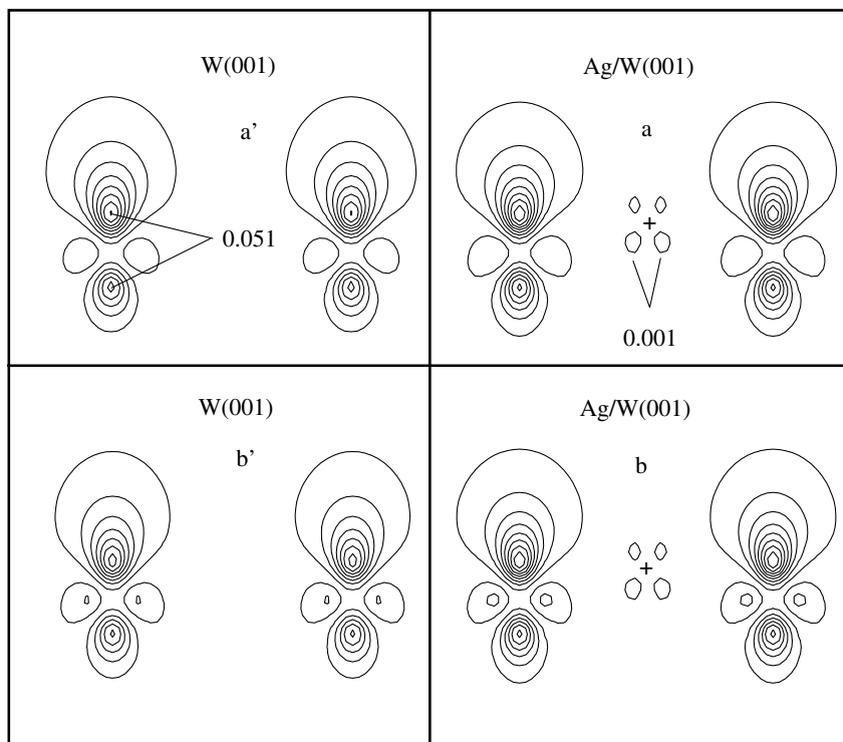


Fig. 8. Contours of charge density of the surface states, a' , b' and a , b , at X point of SBZ for $c(2 \times 2)$ vacancy and Ag/W(001) substitutional surface alloy, respectively. The adjacent contours are separated by $0.005 e/\text{au}^3$.

In Fig. 8 the charge density of these states a and b is plotted and compared with a' and b' of W(001) $c(2 \times 2)$ vacancy array. It confirms that they are very localized at the surface W atom with large lumps of their charge density extending into the vacuum region. These surface states are found to be of the characters of atomic orbital $d_{3z^2-r^2}$. This kind of polarized states should be sensitive to an external electric field normal to the surface and sensitive to the surface charging. It is found that these states include almost no any component from Ag, supporting again the fact that there is no chemical bonding between Ag and W. Therefore this leads to the conclusion that the deposition of Ag on the W(001) vacancy site will split out the surface states of the W(001) $c(2 \times 2)$ vacancy array further, lower the energy of states and stabilize the Ag/W(001) substitutional structure. This factor might account for the formation of Ag/W(001) substitutional surface alloy.

3.5. Au, Cu on W(001) and Ag, Au, Cu on Mo(001)

Au and Cu are isoelectronic with Ag, while Mo is isoelectronic with W, it could be expected when they are deposited on the W(001) or Mo(001) surface, they will be shown similar behavior. In this work the surface formation energy for the Au and Cu on the W(001) as well as Ag, Au and Cu on the Mo(001) surface is calculated. All comparable features are found to be similar. The surface states near the Fermi level are localized at the surface W or Mo atoms and have similar response to the adsorption of atoms of fcc noble metals on the W(001) and Mo(001) $c(2 \times 2)$ vacancy sites. The surface energy of Au (Cu) substituting W or Mo on W(001) or Mo(001) surface is calculated and the similar features are obtained. Surface formation energies of these noble metals on the fourfold-hollow sites and surface substitutional

Table 3

Surface energies (in eV/surface atom) for Mo(001) surface of p(1×1) (E_s) and c(2×2) vacancy (E_s^{vac}), and surface formation energies (in eV/surface atom) for noble metals adsorbed on the fourfold-hollow site (E_s^{fourfold}) and surface substitutional site of the W(001) and Mo(001) surface (E_s^{sub})

System	E_s	E_s^{vac}	E_s^{fourfold}	E_s^{sub}
Au/W(001)			2.44	1.98
Cu/W(001)			2.60	2.11
Mo(001)	2.25	2.20		
Ag/Mo(001)			2.21	1.78
Au/Mo(001)			1.99	1.55
Cu/Mo(001)			2.15	1.78

sites of Mo(001) or W(001) surface are listed in Table 3. It is observed that the surface formation energies of the noble metals on the surface substitutional sites are smaller than those on the fourfold-hollow sites, which demonstrates that these substitutional surface alloys could be formed. The Mo(001) p(1×1) is also found to be near-unstable against the Mo(001) c(2×2) surface vacancy. The calculated results show that the mechanism for the formation of these substitutional surface alloys may be similar to that of Ag/W(001) substitutional surface alloy, since there is weak chemical bonding between these adsorbates and their substrates either.

4. Conclusions

We have presented a study based on first principles calculations for surface alloying of immiscible metals which do not like to alloy in the bulk. The calculations for surface formation energy show that noble metals such as Ag, Au and Cu would like to occupy the vacancy sites of the W(001) or Mo(001) surface to form the substitutional surface alloys. For the Ag/W(001) substitutional surface alloy, the calculated electronic local function (ELF) values between Ag and W atoms range from 0.17 to 0.29, by comparison, that values range from 0.42 to 0.54 in the region among the nearest-neighbor W atoms. This means that there are only relatively weak bonds between Ag and W atoms. Due to different electronegativity between Ag (Au and Cu) and W (Mo) which

will induce charge transfer between them, we analyze the effect of surface charge transfer on the Ag/W(001) substitutional surface alloy. It is well known that an external electric field will induce a screening charge distributed mainly on the top surface layer. In order to exclude the chemical factor in the case, we simulate the surface charge transfer by imposing an external electric field on the W(001) c(2×2) vacancy array. It is found from the calculated pseudocharge difference in distribution that the behaviors of surface charge depletion induced by Ag and by the electric field are different. The alternative replacement of surface W with Ag changes the electronic environment of surface W, leading to the downward shift of the surface states localized on the W atoms, and lowering the corresponding energy. Thus, it could be concluded that the surface state shift might be primarily involved in the surface alloying of immiscible metals.

Acknowledgements

This work was supported by the National Natural Science Foundation of China.

References

- [1] G.A. Attard, D.A. King, Surf. Sci. 188 (1987) 589.
- [2] D. Singh, H. Krakauer, Surf. Sci. 216 (1989) 303.
- [3] P. Hu, A. Wander, L. Morales de la Garza, M.P. Bessent, D.A. King, Surf. Sci. Lett. 286 (1993) L542.
- [4] J. Tersoff, Phys. Rev. Lett. 74 (1995) 434.
- [5] J.L. Stevens, R.Q. Hwang, Phys. Rev. Lett. 74 (1995) 2078.
- [6] E. Bauer, H. Poppa, G. Todd, F. Bonczek, J. Appl. Phys. 45 (1974) 5164.
- [7] E. Bauer, H. Poppa, G. Todd, P.R. Davis, J. Appl. Phys. 48 (1977) 3773.
- [8] G.A. Attard, D.A. King, Surf. Sci. 222 (1989) 360.
- [9] S.H. Overbury, D.R. Mullins, J. Vac. Sci. Technol. A 7 (1989) 1942.
- [10] H. Takahashi, M. Sasaki, S. Suzuki, S. Sato, T. Abukawa, S. Kono, J. Osterwalder, Surf. Sci. 304 (1994) 65.
- [11] A. Derraa, M.J.G. Lee, Phys. Rev. B 53 (1996) 10348.
- [12] H. Wormeester, E. Hüger, E. Bauer, Phys. Rev. B 57 (1998) 10120.
- [13] P. Liu et al., Phys. Rev. B 67 (2003) 155416.
- [14] Z. Song et al., J. Phys. Chem. B 107 (2003) 1036.
- [15] See e.g. J.W.M. Frenken, R.L. Krams, J.F. van derVeen, Phys. Rev. Lett. 59 (1987) 2307.

- [16] C.L. Fu, K.M. Ho, *Phys. Rev. Lett.* 63 (1989) 1617.
- [17] A.D. Becke, K.E. Edgecombe, *J. Chem. Phys.* 92 (1990) 5397.
- [18] B. Silvi, A. Savin, *Nature* 371 (1994) 683.
- [19] A. Savin, R. Nesper, S. Wengert, T.F. Fässler, *Angew. Chem. Int. Engl.* 36 (1997) 1808.
- [20] L. De Santis, R. Resta, *Surf. Sci.* 450 (2000) 126.
- [21] J.G. Che, Z.Z. Zhu, C.T. Chan, *Phys. Rev. Lett.* 82 (1999) 3292.
- [22] P. Hohenberg, W. Kohn, *Phys. Rev.* 136 (1964) B864.
- [23] L. Hedin, B.I. Lundqvist, *J. Phys. C* 4 (1971) 2064.
- [24] D.R. Hamann, M. Schlüter, C. Chiang, *Phys. Rev. Lett.* 43 (1979) 1494;
G.B. Bachelet, M. Schlüter, *Phys. Rev. B* 25 (1982) 2103.
- [25] S.G. Louie, K.M. Ho, M.L. Cohen, *Phys. Rev. B* 19 (1979) 1774.
- [26] See, e.g., C.T. Chan, K.M. Ho, K.P. Bohnen, in: W.N. Unertl (Ed.), *Handbook of Surface Science*, Elsevier, Amsterdam, 1996 (Chapter 3).
- [27] D.D. Johnson, *Phys. Rev. B* 38 (1988) 12807.
- [28] C.T. Chan, K.P. Bohnen, K.M. Ho, *Phys. Rev. B* 47 (1993) 4771.
- [29] B.W. Lee, A. Ignatiev, S.T. Tong, M.A. Van Hove, *J. Vacuum Sci. Technol.* 14 (1977) 291.
- [30] J. Kirschner, R. Feder, *Surf. Sci.* 79 (1979) 176.
- [31] P. Heilmann, K. Heinz, K. Müller, *Surf. Sci.* 89 (1979) 84.
- [32] L.J. Clarke, L. Morales De La Garza, *Surf. Sci.* 99 (1980) 419.
- [33] R. Feder, *Surface Sci.* 103 (1981) 75.
- [34] I.G. Batirev et al., *Surface Sci.* 417 (1998) 151.
- [35] R. Smoluchowski, *Phys. Rev.* 60 (1941) 661.
- [36] M.W. Finnis, V. Heine, *J. Phys. F* 4 (1974) L37.
- [37] E.A.A. Jarvis, A. Kristensen, E.A. Carter, *Surf. Sci.* 487 (2001) 55.
- [38] Ruqian Wu, A.J. Freeman, *Phys. Rev. B* 52 (1995) 12419.
- [39] P.J. Feibelman, *Surf. Sci.* 313 (1994) L801.
- [40] M. Kuhn et al., *Surf. Sci.* 341 (1995) L1011.
- [41] J.G. Che, C.T. Chan, *Phys. Rev. B* 67 (2002) 125411.
- [42] D. Singh, H. Krakauer, *Phys. Rev. B* 37 (1988) 3999.