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A theoretical study of adsorption and the surfactant effect of Sb on the Ag(100) surface

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Abstract. The adsorption and the surfactant effect of Sb on the Ag(100) surface are studied using first-principles calculations. Our calculated results show that the pre-adsorbed Sb atoms act as nucleation centres for the deposited Ag atoms, and surface-substitutional Sb atoms repel on-fcc-site Ag atoms nearby. We suggest that the Sb repulsion network reduces the Ag-adatom mobility and leads to a high density of Ag islands which improve the smoothness of the layer-by-layer growth.

1. Introduction

In general, the epitaxy of ultrathin films proceeds in a complicated fashion depending on the details of the surface energetics and kinetics. Epitaxial films often grow with the formation and growth of isolated three-dimensional (3D) islands, either from the very beginning of the deposition (the island or Volmer–Weber mode), or after the deposition of several (one, two, or three) monolayers in a layer-by-layer mode (the Stranski–Krastanov mode). Recent reports have shown that the use of surfactants can alter the film morphology during the epitaxial growth for both semiconductors [1–4] and metals [5–7]. Here, the surfactant atoms are a monolayer or a submonolayer of foreign atoms on the surface, promoting two-dimensional (2D) layer-by-layer (LBL) growth, as opposed to three-dimensional (3D) island growth.

A smooth layer morphology is often required for many modern electronic devices, but is not thermodynamically and kinetically favourable. One way to tackle this problem is to increase the deposition rate or lower the temperature; however, this leads to poor epitaxial quality at the same time. The surfactant-mediated layer-by-layer growth technique described in this article provides a good way to fabricate the desired film structures. A detailed understanding of the mechanisms involved in the surfactant-mediated growth for both semiconductor and metal systems in heteroepitaxy and homoepitaxy is not only of fundamental interest, but also has technological importance.

In the present study we focus on the problem of homoepitaxy of Ag(100) after submonolayer pre-deposition of Sb, which has recently been reported on by van der Vegt *et al* [8]. They observed that the pre-deposition of Sb on the clean surface improved the smoothness of the layer-by-layer growth. But the mechanism of the action of Sb in the Ag/Ag(100) growth remains unclear [8]. In this paper, the adsorptions of Sb and Ag on clean and Sb-covered Ag(100) are studied using first-principles calculations. An explanation of the action of Sb is given on the basis of our calculations.

This paper is organized as follows. Section 2 contains a brief description of the first-principles method used. In section 3 we present the calculated results and detailed discussion, and we give our conclusions in section 4.

2. The model and method

In this paper, the discrete variational X_α (DV-X_α) method is used in the calculation of the adsorptions of Sb and Ag on clean and Sb-covered Ag(100) surfaces. The DV-X_α method that we used is a first-principles molecular cluster approach based on local-density-functional (LDF) theory. The matrix elements of the Hamiltonian and the overlap are evaluated by a numerical integration technique on a grid of about 800 points per atom. In the DV method, the atomic wave functions ϕ are generated numerically from the same LDF solutions for the free atoms, and are used as basis functions. The molecular wave functions and eigenvalues are determined using the self-consistent charge (SCC) approximation to the potential. More details of this method have been given in reference [9]. The frozen-core approximation is used for Ag and Sb, except that the Ag 4d and Sb 4d electrons are treated fully in the self-consistent iterations. The Hedin–Lundqvist exchange–correlation terms [13] are adopted in the potential. This cluster approach has proved to be a very good one in studying the adsorptions on transition metal surfaces [10–12].

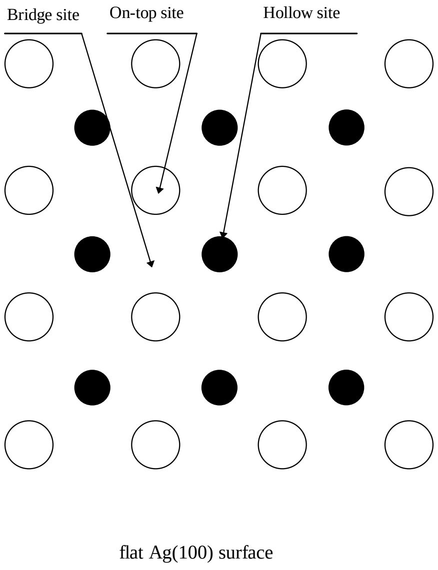

Figure 1. A top view of the Ag(100) flat surface structure. The various adsorption sites are indicated by arrows. The empty circles represent the first-layer atoms and the filled circles represent the second-layer atoms.

In the present calculations, the model cluster of Ag_{25} is adopted to simulate the flat (100) surface of Ag (see figure 1). Thus a natural first step is to calculate the adsorption of Sb on the Ag(100) surface. We investigate the different adsorption sites described in section 3.1. For the calculation of the subsurface adsorption, we employ the cluster $Ag_{36}Sb$ (see figure 2). The adsorption energy of an adatom is defined as

$$E_{\text{adatom}} = -(E_{\text{t}} - E_{\text{clean}} - E_{\text{atom}}) \tag{1}$$

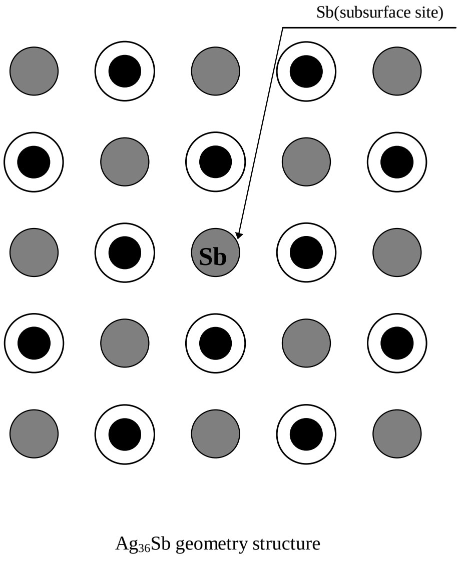

Figure 2. A top view of the cluster $Ag_{36}Sb$ geometry structure. The Sb atom at the subsurface adsorption site is indicated by an arrow. The empty circles represent the first-layer Ag atoms, shaded circles represent the second-layer Ag atoms, and filled circles represent the third-layer Ag atoms.

with E_t, E_{clean}, and E_{atom} being the total energies of the adsorbate-covered cluster, of the clean one, and of the free atom. The vertical positions of the adsorbates are optimized by minimizing the total energy of the cluster. The substrate sites have been frozen unless especially needed. The binding energies of various dimers on the Ag(100) surface are calculated and described in section 3.1. The binding energy of a dimer on the surface is given by

$$E_b = E_{dimer} - (E^1_{adatom} + E^2_{adatom}) \tag{2}$$

where E_{dimer} is the total adsorption energy of the dimer on the surface, and E^1_{adatom}, E^2_{adatom} are the adsorption energies of one adatom in a dimer. A dimer is said to be bound if the binding energy is positive in sign. The larger the binding energy, the more stable the dimer. The interaction between the surface-substitutional Sb and on-surface Ag atom nearby is calculated by varying the distance between them while their vertical positions are separately optimized. The degree of convergence of the self-consistent iterations, measured by root mean square (rms) changes in the charge density, is set to be 10^{-4}, which allows the total energy to converge to 10^{-4} eV. The cluster size chosen here is sufficient to achieve the convergence of adsorption energies within 0.06 eV.

3. Results and discussion

3.1. Adsorption sites and binding energies

For the Sb/Ag(100) system, we have studied three kinds of adsorption: on-surface, surface-substitutional, and subsurface adsorption. For the adsorptions of Sb on the Ag(100) surface, we investigate three different adsorption sites, namely on-top, bridge, and hollow sites, respectively (see figure 1). The calculated results for various adsorption sites for the Sb/Ag(100)

Table 1. Adsorption energies of Sb on Ag(100) for various adsorption sites. E is the adsorption energy, and h is the vertical height of the adatom from the Ag(100) surface (a negative value of h indicates a subsurface site).

Adsorption site		E (eV)	h (au)
On-surface site	Hollow site	4.20	3.87
	Bridge site	3.01	4.67
	On-top site	2.02	5.07
Surface-substitutional site		4.87	0.12
Subsurface site		3.35	−3.87

system are given in table 1. As seen from the table, the most favoured on-surface adsorption site is the hollow one, while adsorption at the substitutional one is greatly favoured over on-surface fcc adsorption. Thus, the most energetically favoured adsorption site is the surface-substitutional one. For an unannealed starting surface, most Sb atoms occupy the on-surface hollow sites at the start of the Ag deposition at room temperature. Because there exists an energy barrier to the vacancy formation, the establishment of substitutional adsorption is hindered. For an annealed starting surface, the Sb atoms can occupy energetically favoured surface-substitutional sites due to there being enough thermal activation.

For a good surfactant, segregation is a necessary condition. If there is not enough segregation, the surfactant atoms will be buried in the layers that grow initially, and cannot influence the growth mode of subsequent layers. We have studied the energetics of the segregation of Sb on an Ag(100) surface. In order to study whether Sb can be incorporated into the bulk of Ag, we calculated the adsorption energy for Sb at a subsurface site, which is below one overlayer of Ag (see figure 2). As seen from table 1, this site is energetically disfavoured as compared to the surface-substitutional and on-surface hollow ones. So, we can conclude that Sb can segregate to the surface, and is not incorporated into the bulk of the Ag.

Table 2. Binding energies of dimers on the Ag(100) surface. E is the binding energy; a negative E-value indicates repulsion between two atoms in a dimer.

	Ag–Ag	Ag–Sb	Sb–Sb
E (eV)	0.45	0.97	−0.22

The binding energies of Ag–Ag, Ag–Sb, Sb–Sb dimers on the Ag(100) surface are studied, where the atoms are at the nearest-neighbouring fcc sites. The vertical positions of two adatoms in a dimer are separately optimized. The calculated results are summarized in table 2. The binding energies of Ag–Ag and Ag–Sb dimers on the Ag(100) surface are 0.45 eV and 0.97 eV, respectively. Therefore, the Sb atoms preferentially stay among the Ag islands. There is a repulsion between the two Sb atoms at the nearest-neighbouring fcc sites, and the repulsive energy is 0.22 eV, which helps to form a uniform distribution of Sb atoms over the Ag(100) surface.

Zhang and Lagally suggested a general model (ZL's model) for metal systems [14]. ZL's model is based on the inequality $V_{\mathrm{A-A}} > V_{\mathrm{A-S}} \gg V_{\mathrm{S-S}}$ connecting the adatom–adatom, adatom–surfactant, and surfactant–surfactant bond strengths ($\mathrm{A} = \text{adatom}, \mathrm{S} = \text{surfactant}$).

The applicability of this model has been confirmed for Cu/In/Cu(100) homoepitaxial growth [15, 16]. Here, our results show that the above assumption of ZL is not satisfied for the Ag/Sb/Ag(100) system. So, a new explanation of the effect of Sb is needed.

Table 3. Adsorption energies of Ag on clean and Sb-covered Ag(100). Clean: Ag on Ag(100); Sb-covered: Ag on Sb:Ag(100), where Sb stays at the surface-substitutional site, as a nearest neighbour. E is the adsorption energy, and h is the vertical height of the adatom from the Ag(100) surface.

	Clean	Sb-covered
E (eV)	2.6	2.39
h (au)	3.47	3.87

In order to illustrate the effects of adsorbed Sb atoms on the growth mode of Ag, we studied Ag adsorption on clean and Sb-covered Ag(100) surfaces. Here the Sb atom stays at the surface-substitutional site. The adsorption energies are summarized in table 3. Our results show that Ag has a higher adsorption energy on the clean surface than on the Sb-covered Ag(100) surface. Thus it is energetically preferable for Ag to be sited on one of the clean portions of the surface, while the proximity of a surface-substitutional Sb atom is unfavourable. Furthermore, we calculated the energies of the repulsion between the surface-substitutional Sb and nearby on-fcc-site Ag atoms. Two adsorption sites of Ag on the substitutional Sb-covered surface—either as a nearest neighbour to Sb, or as a next-nearest neighbour—are studied. The resulting repulsion energies are given in table 4. From this table, we see that the surface-substitutional Sb atoms repel on-surface Ag atoms nearby. So, the deposited Ag atoms tend to avoid such Sb atoms, and aggregate to form small islands between them. The enhanced island density can improve the smoothness of the layer-by-layer (LBL) growth. The adsorption of Sb on Ag(111) has been studied by Oppo *et al* using first-principles calculations [17]. By comparing the characteristics of the adsorption of Sb on the two different surfaces, we can conclude that the Sb atoms favour substitutional sites energetically, and repel the on-fcc-site Ag atoms nearby on both (111) and (100) surfaces.

Table 4. The energies of the repulsion between the on-fcc-site Ag and surface-substitutional Sb atoms. nn: nearest neighbour; nnn: next-nearest neighbour. E is the repulsion energy.

	nn	nnn
E (eV)	0.21	0.11

3.2. The surfactant mechanism and the additional barrier ΔE

On the basis of the calculated results given above, we give an explanation for the effect of Sb being different from that predicted by ZL's model for the Ag/Sb/Ag(100) system.

For the unannealed surface, most pre-adsorbed Sb atoms occupy fcc sites. Since $V_{\mathrm{Ag-Ag}} < V_{\mathrm{Ag-Sb}}$, after the Ag atoms are deposited the Sb atoms will be the centres of nucleation for the deposited atoms. Many small islands centred at the Sb atoms are formed in the early stages of growth, which is in agreement with experimental observation [8]. After the small islands are formed, the repulsion effect of surface-substitutional Sb atoms begins to take effect. Ag atoms arriving at the small islands will diffuse to the edges of the islands and leave them rapidly due to the repulsion. Thus a smooth first layer is grown, and an almost uniformly distributed repulsion network of the surface-substitutional Sb atoms is formed. From the second layer on, the repulsion network starts to take effect. For the annealed surface, the pre-adsorbed Sb atoms occupy the surface-substitutional sites, and build a repulsion network at the start of the deposition.

When the deposited Ag atoms enter this network, they will be repelled by the Sb atoms around them, and will tend to avoid the repulsive Sb centres and aggregate to form many small islands between these Sb atoms. The island density N satisfies the following scaling relation:

$$N \sim r^{\lambda} \exp(\lambda \beta E_{\mathrm{surf}})$$

where r is the deposition rate, and $\beta = 1/kT$. In two dimensions, $\lambda = 1/3$, and in one dimension $\lambda = 1/4$ [18]. Therefore, an increase of N implies an increase of the diffusion barrier E_{surf} under the same growth conditions. It is the repulsion network that leads to an increase of E_{surf} on average. The experimental result shows that the growth mode of Ag/Sb/Ag(100) also depends on the Sb coverage; this proves that an increase of E_{surf} is a global effect of the surfactant network. For the interacting system, there are many microscopic diffusion barriers; the value of the measured diffusion barrier E_{surf} must result from some complex averaging of all of these, and does not refer to any microscopic process in particular [19].

A necessary condition for layer-by-layer growth is that the interlayer mass transport is rapid. One can imagine the surfactants to exhibit enhanced interlayer mass transport achieved by some means. In order to assess the interlayer mass transport occurring during the growth quantitatively, Meyer *et al* introduced a ratio factor $R_{0,\mathrm{c}}/R_{1,\mathrm{c}}$ [20]:

$$\frac{R_{0,\mathrm{c}}}{R_{1,\mathrm{c}}} = \left(\frac{h_0}{h_1} + \frac{2\exp(\Delta E/KT)}{R_{1,\mathrm{c}}}\right)^{1/2} \tag{3}$$

where $R_{1,\mathrm{c}}$ is the critical radius of the first-layer island (the radius of the first-layer island at the onset of second-layer nucleation), $R_{0,\mathrm{c}}$ is a measure of the spacing between the centres of first-layer islands, h_0 and h_1 are the probabilities of hopping on the substrate and the first-layer island respectively, the additional barrier ΔE is the difference between the hopping barriers on the terrace and step edges, and $\Delta E = E_{\mathrm{step}} - E_{\mathrm{surf}}$. The ratio $R_{0,\mathrm{c}}/R_{1,\mathrm{c}}$ is close to 1 for smooth growth, and larger than roughly 1.5 for 3D island growth.

It is clear from equation (3) that there exist multiple possibilities for decreasing the value of $R_{0,\mathrm{c}}/R_{1,\mathrm{c}}$. In a pure system, $h_0 = h_1$; thus, the most efficient way to decrease the value of $R_{0,\mathrm{c}}/R_{1,\mathrm{c}}$ is to increase the growth temperature. Because low-temperature layer-by-layer growth is often desired, the next choice is to reduce ΔE. There are two ways to reduce ΔE. One way is to reduce the step-edge barrier E_{step}, and the other is to increase the terrace barrier E_{surf}. An increase of the terrace barrier E_{surf} will induce enhanced island density. It is apparent that either a reduced E_{step} or an enhanced island density (or both) can enhance the interlayer mass transport. In the Ag/Sb/Ag(100) system, surfactant Sb atoms stay preferentially at the surface-substitutional site, and build a repulsion network. It is the repulsion network that leads to an increase of the average diffusion barriers for the Ag atoms on the terraces, E_{surf}, and the enhanced island density. An enhanced island density has been observed in experiments [8].

4. Summary and conclusions

We have studied the adsorption of Sb and the surfactant effect for the Ag/Sb/Ag(100) system using first-principles calculations. Our results show that the Sb atoms act as nucleation centres for Ag atoms deposited on the Ag(100) surface. The surface-substitutional Sb atoms repel nearby on-surface Ag atoms, and build a repulsion network. On the basis of our calculated results, we propose a repulsion model to illustrate the surfactant behaviour of Sb in the Ag/Sb/Ag(100) system as discussed above, which is different from ZL's model.

For the Ag/Sb/Ag(100) system, Sb surfactants increase the terrace barrier E_{surf} as a result of the repulsive interaction network. In this metal system, Sb surfactants can segregate effectively, which is a necessary condition for surfactants.

Our calculated results also show that the additional barrier ΔE is an essential physical quantity in determining the film growth mode. Only if ΔE becomes smaller will smooth growth be induced. Increasing E_{surf} has been proved to be an effective way of achieving this.

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