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## The Adsorption of Ag and Sb on Ag(111) Surface<sup>1)</sup>

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The adsorption of Ag and Sb atoms on Ag(111) surface was studied by using the extended Hückel theory (EHT) and a cluster model. The possible mechanisms for the layer-by-layer growth of Ag on Ag(111) with Sb as surfactant are discussed. The results are in qualitative agreement with the previous experimental and theoretical results.

### 1. Introduction

There are three modes in crystal growth. One is called Frank-van der Merwe mode, which is a layer-by-layer, or, two-dimensional (2D) growth mode. In this mode, the epitaxial layer being currently deposited is completed before further layers begin to grow on top of it. The second mode is a three-dimensional (3D) or cluster growth mode called Volmer and Weber mode, in which many overlayers grow at the same time, none of them being completed so that the surface exhibits 3D islands. The third one is called Stranski-Krastanov mode which refers to the growth mode of layer-by-layer growth to a few layers followed by islanding.

The goal of epitaxial crystal growth is to achieve atomically flat and defect-free surfaces under the widest possible range of growth conditions. Usually, there exists an intrinsic tending of islanding for the epitaxial layers. One method to get a high quality 2D surface relies on the optimization of the growth conditions to overcome thermodynamic obstacles, such as lowering the growth temperature and increasing the growth rate.

In recent years, great progress has achieved by introducing surface-active species (called surfactants) to modify the growth mode by suppressing the formation of islands without significant levels of incorporation. It has been observed that the preadsorption of suitable surfactants such as As, Sb and Te can change the mode of Ge growth on Si(100) from 3D cluster growth to layer-by-layer growth [1 to 4]. It has also been found that surfactants not only inhibit islanding, but also control the defect structure during the growth of Ge on Si(111) with a monolayer of Sb floating on the surface [5, 6]. The

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mechanisms for the surfactant-mediated layer-by-layer growth of semiconductors on semiconductors are also studied theoretically [7 to 10].

Comparatively, very few studies have been performed on the surfactant-mediated layer-by-layer growth of metal on metal. The growth of Ag on Ag(111) with a submonolayer of Sb as surfactant was studied experimentally by van der Vegt et al. [11]. The growth mode was found to be drastically altered, from 3D to layer-by-layer 2D, by the one-time deposition of Sb at the beginning of the growth process. Experimentally, a model study performed by Rosenfield et al. [12] indicated that the surfactant results in an enhanced density of nuclei, thereby altering the growth mode. Theoretically, Oppo et al. [13] studied the adsorption and surfactant effect of Sb on Ag(111) by using the first-principles all-electron full-potential linear muffin-tin orbitals method. They found that the most stable adsorption for an Sb atom is to substitute one surface Ag atom, and pointed out that the surfactant effect of Sb on Ag(111) is due to Sb adorbates reducing the Ag adatom mobility and thereby giving rise to a high density of Ag islands.

In this paper, the adsorption of Ag and Sb atoms on Ag(111) surface was studied by using the charge self-consistent extended Hückel theory (EHT) and a cluster model. The possible mechanisms for the layer-by-layer growth of Ag on Ag(111) with Sb as surfactant are discussed. The results are in qualitative agreement with previous experimental [11, 12] and theoretical [13] results.

In the framework of EHT [14, 15], a cluster is adopted to simulate the adsorption system. The electron wavefunction is described as the linear combination of atomic orbitals (LCAO), and the Hamiltonian for the system is expressed under the Hückel approximation. The adsorption geometry is determined by the minimization of the total energy, and the adsorption energy is defined by

$$\Delta E = E_{\text{tot}} - E_{\text{surf}} - E_{\text{ad}}, \quad (1)$$

where  $E_{\text{tot}}$  is the total energy of the adsorption system,  $E_{\text{surf}}$  and  $E_{\text{ad}}$  are the energies of the clean surface and the isolated adatom, respectively. The adsorption is possible only for negative  $\Delta E$ .

In the numerical calculation, the 5s orbital for Ag and 5s, 5p orbitals for Sb are chosen as basis functions. The total energy is converged to better than 0.1 meV. The mechanisms for the layer-by-layer growth of Ag on Ag(111) surface with Sb as surfactant are studied in the following three steps.

## 2. Adsorption of Ag and Sb on Ag(111) Surface

In the study of adsorption on Ag(111), several cluster models given in Fig. 1 have been used for simulating the possible adsorption sites of Ag or Sb adatoms. For all the three adatom-cluster geometries in Fig. 1, the substrate clusters contain three layers of Ag atoms and include 13, 7, 7 Ag atoms, as shown in Fig. 1a to c, respectively.  $T_1$  site describes the atop adsorption (Fig. 1a), at which the adatom sits above a first-layer Ag atom. At  $T_4$  site (Fig. 1b), the adatom sits above a second-layer Ag atom.  $H_3$  site (Fig. 1c) is a threefold hollow site at which the adatom sits above a third-layer Ag atom. For each adatom geometry, the optimized position of the adatom is obtained by minimizing the total energy of the system. It is found that the only possible adsorption site for Ag is the  $H_3$  site with a distance of 2.89 Å above the surface, at which the

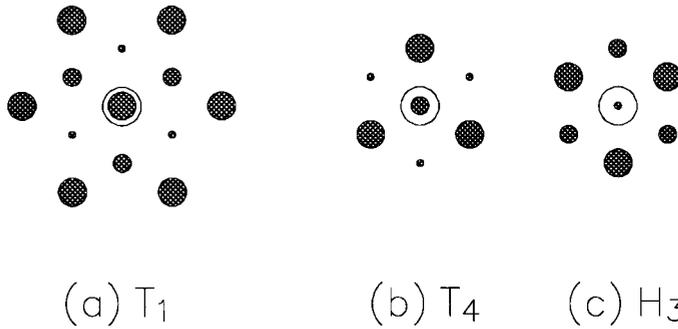


Fig. 1. Top view of the cluster models used for the adsorption of Ag or Sb. a) The model for atop adsorption ( $T_1$ ); b) the model for the adsorption at  $T_4$  site; c) the model for the adsorption at  $H_3$  site. The large solid circles, middle-sized solid circles and small-sized solid circles represent the atoms on the first, second and third layer, respectively. The empty circles represent the adatoms approaching the surface from above the surface

adsorption is very weak. The adsorption energy is only  $-0.15$  eV. Therefore, the deposited Ag atom can move easily on the clean Ag(111) surface and the surface diffusion length should be very large. This might be the reason of the observed 3D growth mode of Ag on clean Ag(111). Comparatively, the only possible adsorption site for Sb is  $T_4$  site at the height of  $2.17$  Å from the surface, at which the adsorption energy is  $-1.64$  eV.

### 3. Substitutional Adsorption of Sb on Ag(111)

An alternative adsorption site of Sb on Ag(111) considered is the substitutional adsorption as depicted in Fig. 2a. The substrate cluster in Fig. 2a also contains 13 Ag atoms. We consider an Sb atom substituting a surface Ag atom, and consider different possible adsorption sites near the Sb atom for the kicked-out Ag atom. The calculations show that the kicked-out Ag atom could not be adsorbed at the sites ( $T_1$ ,  $T_4$  and  $H_3$ ) near the Sb atom, i.e., when an Ag atom approaches the surface from far above these sites,

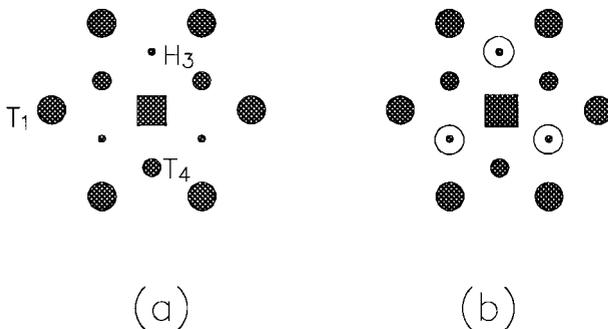


Fig. 2. Top view of the cluster models used for a) the substitutional adsorption of Sb on Ag(111) surface and b) the study of the surface segregation of Sb during the deposition process of Ag on Ag(111). The large solid circles, middle-sized solid circles and small-sized solid circles represent the atoms on the first, second and third layer, respectively. The solid square represents the Sb atom which substituted an Ag atom, and the empty circles represent the adlayer Ag atoms

the total energy became higher. Therefore, the kicked-out Ag atom will migrate to and be adsorbed at a  $H_3$  site on clean portions of Ag(111) surface or at the edge of an Ag island (or step). In this case, the adsorption energy is  $-3.57$  eV, which is more stable than in the case of adsorption on  $T_4$  site. For the same reason, the subsequently deposited Ag atoms can also not be adsorbed near the Sb atom. They also favor to be adsorbed at  $H_3$  sites on clean portions of Ag(111) surface or at the edge of an Ag island (or step) already formed. As a consequence, the adsorbed Sb atoms in the substitutional configurations will reduce the surface mobility of Ag by increasing the diffusion barrier for Ag adatoms approaching the Sb centers. The presence of substitutional Sb should therefore favor the growth of small-sized Ag islands. If the island density is high, one expects that they coalesce into a single layer.

#### 4. Surface Segregation of Sb Atoms

A good surfactant should have strong surface segregation properties. In order to check the surface segregation of Sb, a cluster model shown in Fig. 2b, which contains 16 atoms (15 Ag atoms and one Sb atom), is adopted to simulate the case when the deposited Ag atoms cover the Ag:Sb alloy surface. If the buried Sb atom is replaced by one of the overlayer Ag atom, the replaced Sb atom will find another most stable position. Comparing the three possible sites, i.e.  $T_1$ ,  $T_4$  and  $H_3$ , we found that the empty  $H_3$  site left by the Ag atom is the only stable one for the replaced Sb atom. The stable position for the Sb atom is almost at the original Ag position. The energy gain of this process is 1.93 eV. So we conclude that Sb atoms will segregate to the surface layer when they are buried under the epitaxial layer, instead of being incorporated.

#### 5. Conclusions

In conclusion, the chemisorption of Ag and Sb atoms on Ag(111) surface and the possible mechanisms for the layer-by-layer growth of Ag on Ag(111) with Sb as surfactant are studied by using the extended Hückel theory (EHT) and a cluster model. The following results are achieved. 1. The adsorption of Ag on clean Ag(111) surface occurs at  $H_3$  site and is very weak, while the adsorption of Sb occurs at  $T_4$  site and is relatively strong. 2. The most strong adsorption for Sb is to substitute one of the surface Ag atoms, therefore, the adsorption of Sb atoms will favor the formation of an Sb:Ag alloy surface. 3. When Ag atoms are deposited on the alloy surface, they prefer to adsorb on clean portions or at the edge of an Ag island (or step) already formed. So the presence of substitutional Sb atoms would reduce the surface mobility of Ag and favor the growth of small-sized Ag islands, thereby promotes the layer-by-layer growth. 4. When the Sb atoms are buried under the epitaxial Ag layer, they will change their positions with the surface Ag atoms and therefore a new Sb:Ag alloy surface is formed. So the Sb atoms always float on the epitaxial layer front.

These results are qualitatively in agreement with experimental [11, 12] and theoretical [13] results.

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