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First-Principle Study for Initial Stage of Ag Adsorption on Ge(001) Surfaces

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For the initial Ag growth on Ge(001) the surface reconstructions are described by performing the first-principle calculations. We found some stable sites of Ag adatom on $c(4 \times 2)$ reconstruction of Ge(001) surfaces. Among them, the most interesting stable site for Ag is substitutional site where Ag replaces the upper dimer Ge atom and the Ge atom places at the bridge site of the Ge-Ag 'dimer'. The other stable site of Ag adatom is the position between the upper and lower side of the dimers and the bridge site of dimer.

Key words: First-principle calculation, Ge(001), silver, metal-semiconductor interface

1. INTRODUCTION

The Ag/Ge(001) system has been interested from the point of view of morphological structures and electrical properties in the interface between a few monolayer of noble metal films and elemental semiconductor surface [1–8]. Silver-induced Ge(001) surfaces in ultra-high vacuum have been investigated from low temperature to room temperature using various instruments. However, there is a discrepancy in the initial growth mode at room temperature among authors [1, 2, 5–7]. Lince *et al.* [1] suggested Stranski-Krastanov (S-K) growth using low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), while Miller *et al.* [2] implied Volmer-Weber (V-W) growth by means of high-energy electron diffraction (HEED), AES and photoemission spectroscopy (PES). However, using scanning tunneling microscopy (STM), there had been the study for surface with high Ag coverage (5-15 Å thickness) [6].

Recently, the initial growth of Ag islands on Ge(001)-2×1 surfaces has been studied at several substrate temperature T_s between 100 K and 300 K by means of STM [7, 8]. At T_s=300 K, Ag predominately grows three-dimensionally (3D) on bare Ge substrates, which is similar to V-W growth. At T_s=100 K, thin two-dimensional (2D) islands which are rectangular and elongate along the Ge dimer-row direction on clean Ge(001) surfaces are formed on the surface at the initial stage of the growth, which corresponds to S-K growth.

For high coverage at room temperature, the LEED [1], HEED [2] and STM [6, 7] results have observed 3D growth islands with Ag(011) plane. However, it has been difficult for previous diffraction studies to provide the structural information on 2D islands such as the Miller indices because the density of 2D islands is low at room temperature. Kushida *et al.* [7] have shown a schematic interpretation of the STM image using grid for 2D islands at room temperature. The apparent width of the 2D islands always occupies approximately three or five times of the Ge dimer-dimer distance. Moreover, they recognized a striped regular modulation in the 2D islands perpendicular to dimer-row direction. They have the period of twice of the Ge dimer-dimer distance where the buckling of the Ge dimers is enhanced. Most of the bright protrusions in the modulation located on the trenches between two dimer-rows because of the periodicity of the modulation which is the same as the period of dimer. Therefore the results from the STM are suggested that the deposition sites of Ag are the trenches between two dimer-rows.

Similarly, at low temperature Komori *et al.* [8] found that the isolated 2D islands apparently occupies three or five dimer rows in the direction the dimer as the island and the period of the dimer-row direction is the twice of the Ge dimer-dimer distance.

So far, there is no theoretical study on the atomic structures and electronic states of the thin Ag islands on Ge(001)-2×1 surface. In fact, it is not known whether the bright areas and the bright points in the STM images describe the Ag atoms or not. Theoretical approaches are necessary to discuss it, but no studies have been carried out on it. The determination of the atomic configuration with the first-principle study would lead to understand the relation between the growth of the thin islands make of Ag and Ge and its electrical properties.

We investigate the surface reconstruction for low coverage of Ag by performing the first-principle calculation using density functional theory and a slab model of the surface based on the results of the STM studies [6–8]. The computational approaches will be helpful to analyze the atomic structure of the two-dimensional islands on Ag-covered Ge(001)

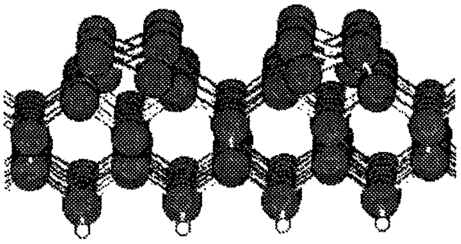


Figure 1: Schematic $c(4 \times 2)$ reconstructed structures of Ge(001) surfaces. The dark balls are Ge atoms, and the bright balls are the saturated H atoms.

Table I: Dimer bond lengths and backing angles for asymmetric dimes of Ge(001) surfaces obtained our calculation, compared with other LDA results and with values extracted from experiment.

	Dimer bond length (Å)	Buckling angle (degree)	Reference
LDA	2.47	21	this work
LDA	2.46	14	14)
LDA	2.41	19	15)
LDA	2.51	19	13)
X-ray	2.44	21	16)
X-ray	2.55	19±1	17)

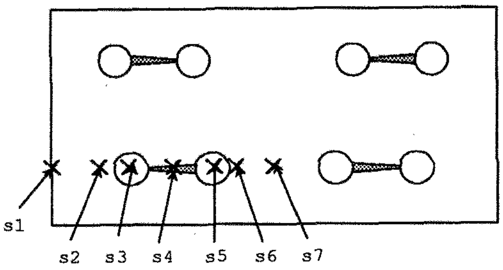


Figure 2: Top view of the $c(4 \times 2)$ surface unit cell. The open circles describe the Ge atoms. The Ag deposition sites are indicated by capitals from s1 to s7.

Table II: Total energies for the Ag-induced reconstruction E_{Ag} (eV/*unit cell*) for various deposition sites on the $c(4 \times 2)$ Ge surface. x coordinate is referred to the $c(4 \times 2)$ unit cell, i.e. a_1=15.86 Å.

Position	x	E_{Ag} (eV/*unit cell*)
s1	0.0	0.00
s2	0.125	0.86
s3	0.175	0.85
s4	0.25	0.00
s5	0.315	0.86
s6	0.375	0.66
s7	0.5	0.00

surfaces obtained by the experiments such as STM studies.

2. CALCULATION METHODS

The present calculations were based on the density functional theory within the local density approximation [9]. We used the exchange-correlation potential in the Ceperley-Alder form [10,11] and the norm-conserving pseudopotentials [12,13]. Wavefunctions were expanded in terms of the plane-wave basis set with a cutoff energy of 18 Ry. We used four k points in the Brillouin zone integration. The theoretical lattice constant for bulk Ge considered in this work is 5.60 Å. The supercell consists of five layers of Ge, the vacuum region equivalent to five atomic layers and a layer of H atoms terminating the Ge dangling bonds at the bottom surface. At each deposition, the upper three substrate layers and the adatom height, that is, the z coordinate of it, are fully relax, while the lower layers and the x and y coordinate of the adatom are kept fixed.

The four dimers in the topmost layer form the $c(4 \times 2)$ surface reconstruction in our calculations [see Fig. 1]. We reproduced that Ge dimer-rows form a zigzag structure for $c(4 \times 2)$ reconstruction. In the relative energies of the Ge(001) high-order reconstructions, we also reproduced that the most stable structure turned out to be the $c(4 \times 2)$ reconstructed surface, which could support the result obtained by Yoshimoto *et al.* [14] and not Needels *et al.* [15]. We obtained asymmetric dimers as well, with a dimer bond length of 2.47 Å and a buckling angle of 21°. Our result for a dimer length and a buckling angle for Ge(001) surface and a comparison with other results are given in Table I. Our calculated $c(4 \times 2)$ structure reproduced fairly well those obtained by X-ray diffraction [17,18] and nearly agrees with other results from LDA [14–16].

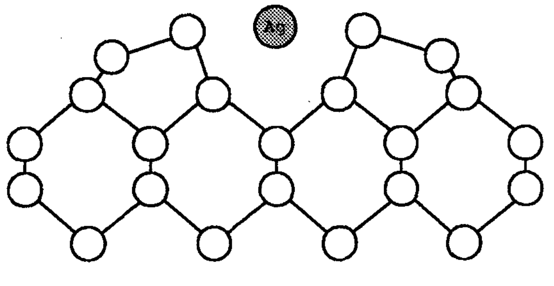


Figure 3: Atomic placement of deposition site s7. The open circles represent Ge atoms and the gray circle represents Ag adatom.

3. RESULTS AND DISCUSSIONS

We first investigated the total energy for the Ag-induced reconstruction along the dimer direction as shown in Fig. 2. At each deposition, the calculation started from the configuration where an adatom height is 0.75 Å above the surface. Table II summarizes the resulting energies for Ag-induced reconstruction at each deposition site. In each $c(4\times2)$ unit cell we find the minimum sites: s1, s4 and s7 in Fig. 2. The sites of s1 and s7 are the long-bridge sites, the trenches between two dimer-rows. The site s1 is the lower dimer long-bridge site, and the site s7 is the upper dimer long-bridge site, which is shown in Fig. 3. The site s4 is the short-bridge site. When the Ag adatom deposits on the dimer at the site s4, its Ge dimer bonds are broken. This is described in Fig. 4. Though the site s4 is not expected for the Ag-induced reconstruction model based on the STM images [7,8], the site s4 is one of the stable deposition site extracted from our calculations.

We discuss the configurations in which Ag deposits on the Ge(001) surface. For the long-bridge site, the substrate atoms are reconstructed. The buckling angle for the dimers which sits side by side with the deposited Ag atom is 14° at the site s7, which means that the deposition of the Ag weakens the buckling of their dimers. However, Komori *et al.* [8] have discussed that slight enhancement of asymmetric dimers can be seen even on the second neighbor dimer rows from 2D islands. In our calculations, the Ag is single adatom and not islands. So we consider that the enhancement of asymmetric dimers derives from other factor or the enhancement does not arise in the deposition of the single Ag atom on $c(4\times2)$ Ge surface.

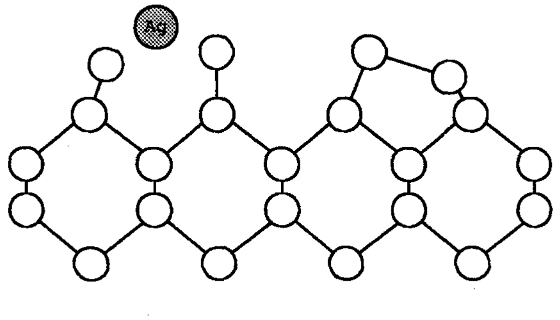
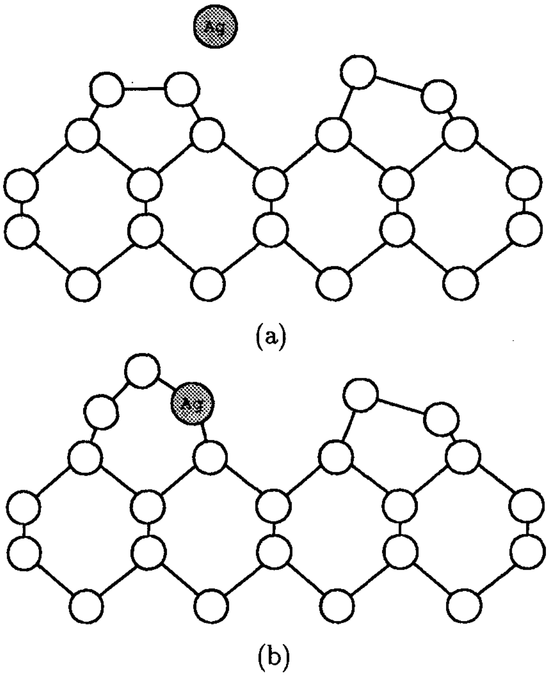


Figure 4: Atomic placement of deposition site s4. The open circles represent Ge atoms and the gray circle represents Ag adatom.



(a)

(b)

Figure 5: Atomic placement of deposition site s6; (a) on the dimer site, (b) the substitutional site. The open circles represent Ge atoms and the gray circle represents Ag adatom.

At the site s6, the dimer turned out to be symmetric dimer by inducing Ag atom [see Fig. 5(a)]. However, when the adatom height is approximately equal to the height of the upper dimer atom, we found that the Ag atom replaces the upper dimer Ge atom and the Ge atom places at the short-bridge site of the Ge-Ag 'dimer' [see Fig. 5(b)]. We call this a substitutional site. Comparing with the energy for the position at which the Ag atom places on the dimer shown in Fig. 5(a), the substitutional site is more stable than the site of the Ag deposition on the dimer shown in Fig. 5(a). The total energy of the substitutional site is slightly higher than that of site a1, a4 and a7. Therefore we can propose that this substitute site is metastable site when the Ag atom is induced on the $c(4\times2)$ Ge(001) reconstruction. In addition, we confirmed that the Ag adatom could also replace the lower dimer Ge atom at site s2.

The structure parameter is as follow. The atomic distance between Ag and Ge atoms are 2.33~2.40 Å. The bond length between the Ge atom replaced by Ag and the Ge atom of the lower dimer is 2.32 Å. This is shorter than the bond length of Ge bulk. The Ge atom of the lower dimer and the induced-Ag atom are approximately symmetric position. For other surface dimer, the dimer bond lengths and buckling angles are 2.48~2.50 Å and 19~21°. This is slightly different from the clean $c(4 \times 2)$ surface.

This is the candidate of the structure of the enhanced buckling dimer image. Moreover, we suggest that the substisutional structure prevents the migration to the topmost short-bridge site when the Ag adatom deposits on the long-bridge site between Ge dimers. So the substitution affects strongly the migration of the Ag adatom; the sites of s1, s7 and s4 are no more equivalent for a hopping motion. However, it remains to demonstrate that the phase is transformed into the mixed Ge-Ag structure. These features will be helpful to analyze the atomic structure of the 2D islands on Ag-covered Ge(001)-2×1 surface.

4. SUMMARY

We found some stable sites of Ag adatom on Ge(001)-2×1 reconstructed surface using the first-principle total energy calculations. The most stable sites of Ag adatom are the short-bridge and long-bridge sites between the Ge dimers. Moreover, we suggested that the interesting metastable site for inducing Ag atom is substitutional site where Ag replaces the upper or lower dimer Ge atom and the Ge atom places at the bridge site of the Ge-Ag 'dimer'.

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