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Rotation of Ge ad-dimers on Ge(0 0 1)

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Abstract

Structural calculations of the Ge ad-dimer rotation on Ge(0 0 1)-2 × 1 and Ge(0 0 1)-c(4 × 2) surfaces were performed by ab initio and semiempirical methods. Besides the two (already known) stable adsorption sites on top of the substrate dimer rows (angles between substrate dimer bond and ad-dimer bond are 0° and 90°, respectively) a new local minimum was found. The angle between the substrate dimer bond and the ad-dimer of this local minimum is about 45°. This theoretical result might explain the observation of the so-called A/B Ge ad-dimers on Ge(0 0 1). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Si(0 0 1) and Ge(0 0 1) surfaces, and in particular their growth modes, are of great scientific and technological interest. Adsorption of Si and Ge dimers on these surfaces is an important aspect because the dimers act as nucleation sites in epitaxial growth. There are four plausible adsorption sites for Si and Ge ad-dimers on Si(0 0 1). Two of these configurations (A and B) consist of isolated dimers directly adsorbed on top of the substrate rows and the other two configurations (C and D) are isolated dimers lying in the trough between the substrate rows. The dimer bond of these ad-dimers can be parallel to the substrate dimer bonds (A and C) or perpendicular to the substrate dimer bonds (B and D). An A or C-type ad-dimer (non-epitaxial orientation) has to rotate to an epitaxial configuration (B or D) in order to achieve nice epitaxial growth. The activation barriers for the rotation of on-top Si ad-dimers on the Si(0 0 1) surface have been found to be 0.70 ± 0.08 eV (B to A) and 0.64 ± 0.09 eV (A to B) [1]. For Si and Ge ad-dimers on Ge(0 0 1) also dimers having some intermediate "A/B" configuration are found [2–4]. It is not yet clear whether these A/B features represent an on-top dimer in a (meta)stable configuration or if it is simply a result of a rapid back and forth rotation between A and B configurations.

In this paper we have studied the rotation and stability of Ge ad-dimers on Ge(0 0 1)-(2 × 1) and Ge(0 0 1)-c(4 × 2) using ab initio and semiempirical calculations.

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2. Theoretical modeling of Ge dimer adsorption and rotation

The Ge ad-dimer (positioned on top of the substrate dimer rows) rotation on Ge(0 0 1)2 × 1 was investigated using ab initio calculations. All the calculations were performed using the GAMESS program [5]. Convergence is reached when the density change between two consecutive SCF cycles is less than 10^{-5} Ry in absolute value. Total energy convergence criterion and force convergence criterion are 10^{-5} Ry and 10^{-4} (Ry/a.u.). The geometries of the adsorption sites were determined by minimizing the energy with respect to the nuclear coordinates of the Ge adatoms and its nearest neighboring Ge atoms while keeping the remaining Ge and H atoms at their bulk position. The bulk Ge–Ge distance was taken as 2.44 Å [6]. Hydrogen atoms are used to saturate the Ge dangling bonds. Unrestricted shell Hartree–Fock energies are used in the calculation. The calculations were performed by using the SBK (Stevens–Basch–Krauss–Cundari) effective core potential and the basis set for Ge and H atoms [7]. $Ge_{17}H_{16}$ clusters were used to simulate adsorption and rotation of Ge ad-dimers on Ge(0 0 1)2 × 1. The Ge(0 0 1) surface dimers were non-buckled. The adsorption energy per Ge-adatom (E_b) was determined as an algebraic sum of the full energies of (1) cluster without Ge adatoms – E_{tot} ($Ge_{15}H_{16}$), (2) germanium atom – E_{tot} (Ge) and (3) cluster with an ad-dimer – $E_{tot}(Ge_{15}H_{16} + 2Ge)$:

$$E_b = -[E_{tot}(Ge_{15}H_{16}) + 2 \times E_{tot}(Ge) - E_{tot}(Ge_{15}H_{16} + 2 \times Ge)]/2. \quad (1)$$

A negative E_b value is indicative for a possible adsorption site.

First the bond lengths of the equilibrium geometry of the $Ge_{15}H_{16}$ cluster (Fig. 1) that reflects the Ge(0 0 1)-(2 × 1) are determined. The bond length of the symmetric surface dimer, $D_{Ge1-Ge1}$, is 2.40 Å, whereas the bond length between dimer atom and an atom in the germanium layer beneath, $D_{Ge1-Ge2}$, is 2.45 Å. The value of 2.40 Å for the Ge-dimer bond length is in good agreement with the results obtained recently by Stigler et al. [8], $D_{Ge1-Ge1} = 2.38$ Å.

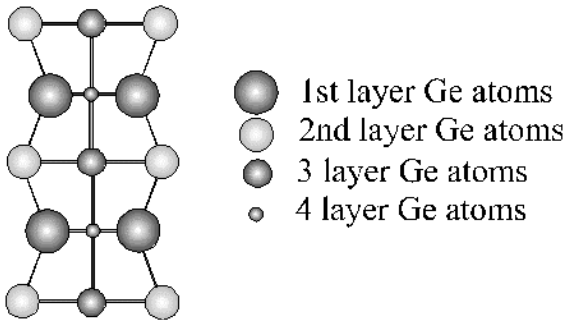

Fig. 1. Ball and stick model of the $Ge_{15}H_{16}$ cluster used in the calculation. Hydrogen atoms are not shown.

Then, the Ge ad-dimer was placed on the surface dimers of the Ge(0 0 1)2 × 1 surface in a symmetrical way with respect to axis of symmetry (C2) of the $Ge_{15}H_{16}$ cluster. The position of the center of mass of the Ge ad-dimer was located on the axis of symmetry (C2) of the $Ge_{15}H_{16}$ cluster. Subsequently all the coordinates of the ad-dimer and surface dimers were optimized.

The dependence of the Ge ad-dimer adsorption energy on the Ge(0 0 1) surface with respect to the rotation angle between ad-dimer bond and substrate dimer row direction are shown in Fig. 2. As

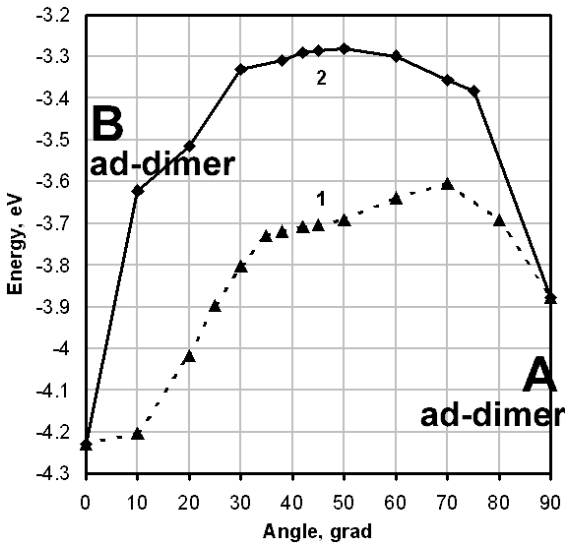

Fig. 2. Energy barriers for ad-dimer rotation. The dotted line (curve 1) refers to the dissociative and the solid line (curve 2) refers to the non-dissociative pathway, respectively.

can be seen in Fig. 2 there exists two metastable minima at 0° and 90°. The minimum at 0°, which corresponds to epitaxial ad-dimer (B-dimer), is the most stable one. This result is in perfect agreement STM data [4]. This structure is characterized by an increased ad-dimer bond length (2.83 Å, i.e. 1.16 times larger than the bulk Ge–Ge bond length). The epitaxial Ge ad-dimer tightly bonds with the Ge surface atoms, whereas the bonding with his dimer partner is somewhat weaker.

The non-epitaixal ad-dimer at 90° (A-dimer) has a smaller dimer bond length (2.52 Å, i.e. only 1.03 times larger than the bulk Ge–Ge bond length) and in the same time it has also a longer bond length between the ad-dimer atoms and surface atoms. So for the A ad-dimer the dimer bond is stronger, but the bonding with the substrate is weaker (see Table 1).

The question is now: are there, besides the A and B configurations, other metastable ad-dimer positions on top of the substrate rows? STM data [2–4] for Ge and Si on Ge(0 0 1) reveal that there is an additional feature on top of the substrate rows labeled A/B dimer. Therefore we study the rotation process of the Ge ad-dimer on the substrate dimer row of Ge(0 0 1). We consider both the rotation process from the epitaxial position (B dimer) to the non-epitaxial position (A dimer) and vice versa. The energy of the ad-dimer versus the ad-dimer rotation angle is shown in Fig. 2.

The curve labeled 1 refers to the ad-dimer rotation process where the dimer bond dissociation is included. With increasing rotation angle the ad-dimer bond length increases up to 3.2 Å at a rotation angle of 20°. Ad-dimer dissociation is expected to occur near 20°. The curve labeled 2 illustrates the rotation process, where the ad-dimer height with respect to the surface increases. At the same time the bond length between the ad-dimer atoms decreases. Both processes (curves 1 and 2) induce a small buckling of the surface dimers (buckling angle does not exceed 8°). The energy barrier to go from the epitaxial position (B dimer) to the non-epitaxial position (A dimer) including dissociation of the ad-dimer is about 0.6 eV, whereas the energy barrier for the reverse process is only about ~0.3 eV (curve 1). The energy barrier for the non-dissociative rotation from epitaxial position to non-epitaxial position is about 0.9 and 0.6 eV for the reverse direction (curve 2). The rotation process that includes dissociation of the ad-dimer is therefore more favorable than the rotation process that does not include dissociation.

Experimental data [2–4] provide some evidence for the existence of a metastable intermediate state of a Si and Ge ad-dimer during its rotation on Ge(0 0 1). STM data reveal that the A–B dimers are 0.1–0.2 Å lower than the B-dimer. On the contrary, in the above calculations both intermediate A/B dimer and A-dimer lie higher than B-dimer for both curves in the Fig. 2. Hence the model considered above does not explain the existence of an intermediate A/B dimer on Ge(0 0 1).

Next we consider the rotation of a Ge ad-dimer on Ge(0 0 1)-c(4 × 2). Because this system is more complicated then the previous one, we have used a semiempirical method. The semiempirical calculations were performed by the MOPAC program [9] using the MNDO-PM3 approach [10]. In these calculations we have used $Ge_{53}H_{44}$ clusters (Fig. 3a, b). The coordinates of the first two Ge layers, as well as ad-dimer height and ad-dimer bond length were optimized. The bond lengths of the equilibrium geometries of the $Ge_{53}H_{44}$ clusters that reflects the Ge(0 0 1)-(2 × 1) and Ge(0 0 1)-c(4 × 2) surfaces are determined. The surface dimer bond

Table 1
Structural parameters of adsorbed Ge dimers on Ge(0 0 1)-(2 × 1) as obtained by ab initio calculations. α is the angle between the ad-dimer bond and the substrate dimer row

System	Angle (α) (grad)	Adsorption energy (E_b) (eV)	Ad-dimer bond length (Å)	Ad-dimer–substrate bond length (Å)	Substrate dimer bond length (Å)
B dimer	0	4.23	2.83	2.49	3.03
A dimer	90	3.88	2.52	2.79	2.52

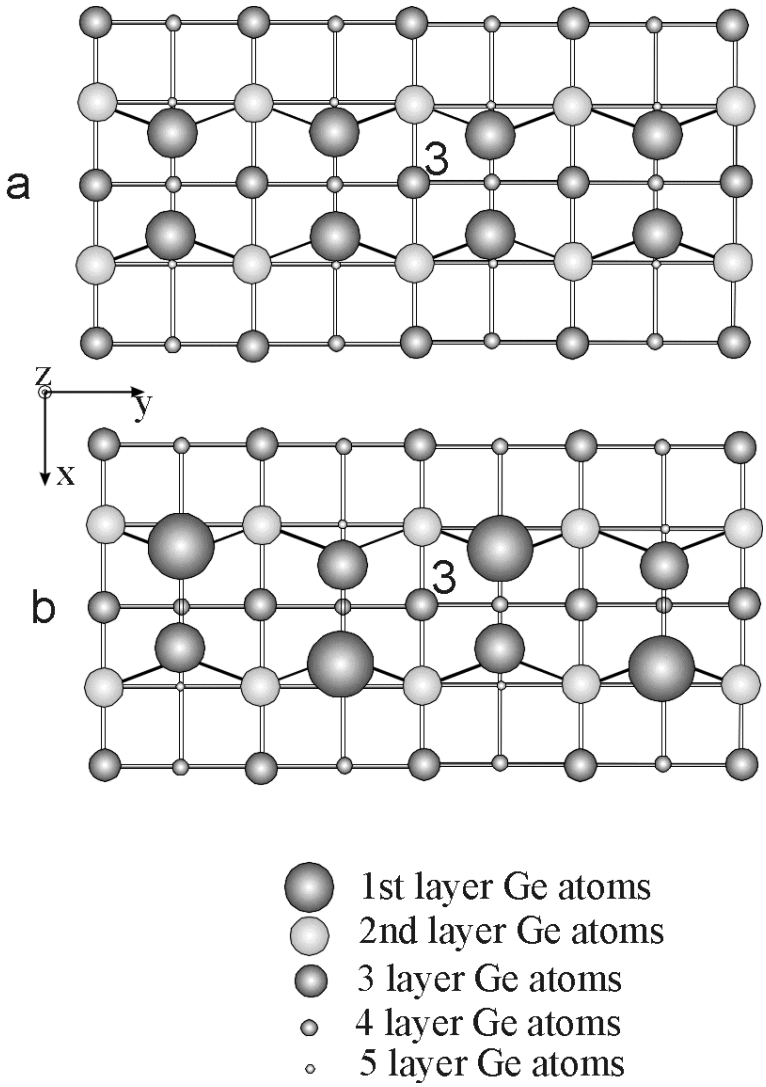

Fig. 3. The c(4 × 2) (a) and (2 × 1) (b) reconstructions of the Ge(0 0 1) surface ($Ge_{53}H_{44}$ cluster). The larger circles denote upper dimer atoms. The label (3) refers to the stationary atoms in the third layer.

length $D_{Ge1-Ge1}$, is 2.61 Å for the Ge(0 0 1)-(2 × 1) surface, and the surface dimer bond length $D_{Ge1-Ge2}$, is 2.39 Å for the Ge(0 0 1)-c(4 × 2) surface. A value 2.39 Å for the asymmetric Ge-dimer bond length is in good agreement with the results obtained recently by Stigler et al. [8], $D_{Ge1-Ge1}$ = 2.38 Å.

The results of Ge ad-dimer rotation (without dissociation) on Ge(0 0 1) surfaces are shown in Table 2 and in Fig. 4. All curves in Fig. 4 refer to the non-dissociative rotation process. First we have repeated the calculations for the ad-dimer on Ge(0 0 1)-(2 × 1) surface. Two minima at 0° and 90° are obtained for the Ge(0 0 1)-(2 × 1) surface. (see curve 1 in Fig. 4). Moreover, we carried out the calibration calculation using the same cluster ($Ge_{15}H_{16}$) and the same methodology as used in the ab initio calculation (see curve 3 in

Table 2
Structural parameters of adsorbed Ge dimers on Ge(0 0 1)2 × 1 as obtained by semiempirical calculations. α is the angle between the ad-dimer bond and the substrate dimer row. The Ge ad-dimer height (*h*) is the distance between the center mass of the ad-dimer and atom (3) in the third layer (see Fig. 3)

System	Energy E_b (eV)	Angle (α) (grad)	Ge ad-dimer height (*h*) (A)	Ad-dimer bond length (Å)	Ad-dimer–substrate bond length (Å)	Substrate dimer bond length (Å)
Ge/Ge(0 0 1)2 × 1						
B dimer	5.52	0	4.42	2.43	2.40	2.39
A dimer	6.46	90	3.08	2.42	2.39	2.37
Ge/Ge(0 0 1)4 × 2						
B dimer	5.04	0	4.02	2.39	2.40, 2.31	2.51
A–B dimer	6.31	~47	4.09	2.35	2.46, 2.49	2.41
A dimer	5.33	90	4.38	2.39	2.42	2.39

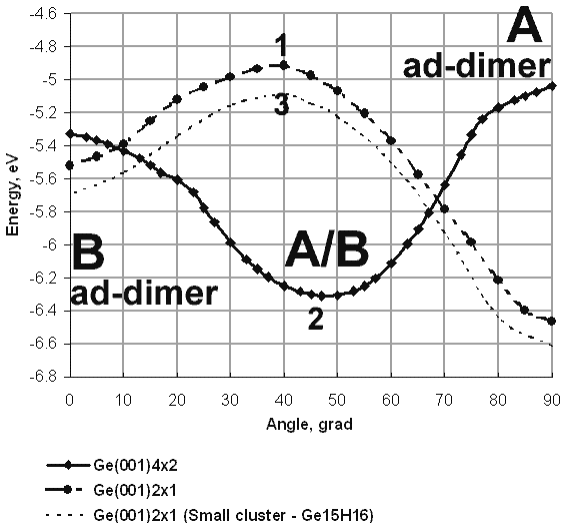

Fig. 4. The energy diagram for a Ge ad-dimer rotating on top of a dimer substrate row using a semiempirical calculation. (1) Ge(0 0 1)-(2 × 1) surface modeled by $Ge_{53}H_{44}$ cluster (dash-dotted line labeled 1); (2) Ge(0 0 1)-c(4 × 2) surface modeled by $Ge_{53}H_{44}$ cluster (solid line – curve 2); (3) Ge(0 0 1)-(2 × 1) surface modeled by $Ge_{15}H_{16}$ (dotted line labeled 3).

Fig. 4). The convergence of E_b for various cluster sizes (curves 3 and 1) suggests that the absolute values will not change by more than about 0.2 eV for larger cluster representations of the surface. Whereas, the value of potential energy between the small and larger cluster models along the rotation path is not changed by more than about 0.02 eV. The energy barrier for the Ge ad-dimer rotation from B to A configuration is ~0.6 eV, even in the small cluster model. The computational results between the large and small cluster is shown to be qualitatively consistent with each other.

In contrast to the ab initio results the A ad-dimer is more favorable than the B ad-dimer. The energy barrier for the rotation from A to B is ~1.4 eV, and the barrier for the reverse direction is about 0.6 eV. In the MNDO-PM3 calculations the bonding energy are higher and the bond length are smaller as compared to the ab initio calculations. Next we have considered the Ge ad-dimer rotation on Ge(0 0 1)-c(4 × 2). The curve of Ge(0 0 1)-c(4 × 2) in Fig. 4, exhibits only one minimum at ~47°. The adsorption site at an angle ~47° is characterized by a significant buckling of the substrate dimers. The buckling angle of the substrate dimers is about 38°, the bond length of the ad-dimer is 2.35 Å and the ad-dimer lies about 0.3 Å lower than the B ad-dimer on Ge(0 0 1)-(2 × 1) surface. This is in agreement with the experimental data [4], which reveal that the B ad-dimer is about 0.1–0.2 Å higher than the intermediate A/B dimer.

The adsorption site with the lowest energy turns out to be the A configuration for the semiempirical calculation and the B configuration for the ab initio calculation. The ab initio result is in agreement with STM data [4]. The energy of the B type dimer on Ge(0 0 1) surface is underestimated in the

MNDO-PM3 calculations. So, the only possibility for the existence of a stable position for a Ge ad-dimer on Ge(0 0 1)-c(4 × 2) surface near 47° comes from the semiempirical calculation. The large dimer buckling (38°) is necessary to stabilize the A/B dimer formation.

3. Conclusions

We have investigated the rotational mode of Ge ad-dimers on top of the substrate dimer rows of Ge(0 0 1) by using ab initio calculations. The calculations are in favor of a dissociative rotational process rather than a non-dissociative process. The B type ad-dimer site is the most stable adsorption site on Ge(1 0 0)-(2 × 1). Besides the A and B type adsorption sites also another local minimum near 47° was found using semiempirical calculations. This theoretical result might explain the occurrence of A/B dimers on Ge(1 0 0). The formation of these A/B dimers goes along with a strong buckling (38°) of the substrate dimers. Thus, the transition from a B type dimer to an A–B type dimer may be accompanied by a local transformation of the (2 × 1) to c(4 × 2) reconstruction.

Acknowledgements

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