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***Ab initio* molecular dynamics study of adsorption and restoration: Si(100):Se**

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Abstract. The adsorption of selenium on the Si(100) 2×1 surface at the coverage of 0.25, 0.50 and 1.0 ML is studied by the *ab initio* molecular dynamics method. It indicates that Si(100): 2×1 will transfer to the buckled 2×2 reconstruction at 0.25 and 0.50 ML, and finally be restored to 1×1 symmetry structure spontaneously induced by the adsorption of Se. The dynamics process of restoration is also simulated, where vibrations of Se atoms with a period of about 0.60 ps are found, and the atoms in dimers vibrate relatively with the same period before the system is annealed. The geometry of the restored 1×1 structure at coverage of 1.0 ML is in good agreement with previous studies.

1. Introduction

Silicon as well as other semiconductors (GaAs, InP) have demonstrated great value, along with their importance in microelectronics and optoelectronics [1, 2], as sources of power (solar cells) for space exploration [3]. The Si(100) surface has attracted renewed interest very recently in connection with porous silicon, where the quasi-one-dimensional columns are terminated by (100)-oriented surfaces. Although the Si(100) surface has been extensively studied in the past decades, there is still some controversy about its symmetry [4]. Investigations of the chemisorption of adatoms on silicon surfaces are also important both technologically and for fundamental physical reasons.

In addition, the idea of surface restoration by adsorbates was nascent in studies of more than a quarter of a century ago. The restored geometries are structurally very simply, yet they represent real solid surfaces. Thus, they are ideally suited for detailed experimental and theoretical studies that critically test our understanding of the physics of semiconductor surfaces. E Kaxiras [5] proposed a set of criteria for choosing adsorbates that can lead to restoration of the ideal bulk-terminated geometry on semiconductor surfaces. According to their studies, the adsorbates should be valence-mending adsorbates (VMA), which can saturate the dangling bonds of substrate. Secondly, in order to guarantee that the resulting structure is stable, the adsorbate in the restored surface must have the same local bonding geometry as in the bulk phase. Furthermore, they predicted the covalent bond radii of the adsorbate should be similar to that of substrate for reducing adsorbate-induced surface stress. Simultaneously, they suggested that Si(100):S and Si(100):Se were likely to fulfill the surface-restoration criteria and investigated these systems with full atomic relaxation included by minimization of the calculated Hellmann–Feynman forces. They found that

both chemical reactivity and induced stress would tend to inhibit formation of Si(100):S, whereas restoration of Si(100) by Se seems more likely.

On the other hand, there has been a recent rising scientific interest on the structural and electronic properties of chalcogen elements (S, Se) on Si(100) 2×1 surfaces [6–10]. In contrast to the calculation work of Kaxiras [5] and later by Kruger [8], T Weser *et al* did not observe an ordered S adlayer when they investigated the behaviour of S on Si(100), experimentally [10]. They also mentioned that annealing of the S/Si(100) 2×1 surface to 325 °C leads to the desorption of the sulphur overlayer and the appearance of the coexisting C(4×4) and 2×1 surface reconstruction, which may be caused by some asymmetrically adsorbed surface reconstruction like the buckled dimer structure on Si(100). A Papageorgopoulos *et al* [6, 7] also studied the system of Si(100):S recently and they find the adsorption of S at room temperature causes the surface restoration of the reconstructed Si(100) 2×1 substrate to its original bulk-terminated surface at 1.0 ML coverage, while it keeps in the 2×1 structure at 0.50 ML. As for the Si(100):Se system, the detailed geometry of the Se-adsorbed Si(100) structure at low coverage has not been reported and the dynamic process of restoration of Si(100) 2×1 to 1×1 structure induced by the chalcogen elements is not clear although some experimental work has also been done on adsorbate-induced restoration of Si(100):Se [9]. From the above discussion it is clear that additional effort on the study of S and Se on Si(100) 2×1 is necessary.

In this work, we investigate the system of Si(100):Se by the *ab initio* molecular dynamics (MD) method, which was first proposed by R Car and M Parrinello [11]. At different coverage, 0.25, 0.50 and 1.0 ML, the adsorption of Se on Si(100) 2×1 is investigated. Asymmetry structures of the Se-adsorbed Si(100) surface are obtained at low coverage, while a restored structure is also obtained at the coverage of 1.0 ML, which is in good agreement with previous studies.

2. Method and model

The scheme of *ab initio* molecular dynamics combines the MD technique for the computation of statistical properties of classical systems with the first principles treatment of inter-atomic forces due to the quantum electronic system, as provided by density functional theory [11]. Details of the method have been given in [12, 13]. Norm-conserving pseudopotentials [14, 15] are used in the calculation.

We use a periodically repeated slab made up of six layers of Si(100), each containing a 2×2 cell (see figure 1); in the bottom plane the silicon dangling bonds are saturated with hydrogen atoms as in most previous studies. The surface unit cell has horizontal dimensions 7.68 Å and perpendicular dimension of 16.97 Å. The vacuum thickness in the slab is 8.8 Å, which is large enough for being adsorbed by a layer of Se atoms. During the simulation of adsorption and restoration, we always moved five layers, while we kept fixed the sixth Si layer and all the H atoms. The energy cut-off for the plane-wave expansion is chosen at 8 Ryd with 2629 plane waves used in the calculation. A 16 Ryd cut-off was also used to check the reliability of the structure optimization.

A symmetry (2×1) reconstruction structure is also chosen as an original state of the silicon substrate in the simulation. The symmetric silicon dimer bond length and the inward relaxation of first layer are 2.30 and 0.35 Å respectively under our simulation, which are consistent with the previous calculated Si(100) 2×1 symmetric dimer model [16] with corresponding parameters of 2.24 and 0.33 Å. A symmetric Si(100) 2×1 substrate is used in most recent works about the chalcogen and silicon interface although the presence of asymmetric dimers in a large temperature range are outlined. In addition, the studied models

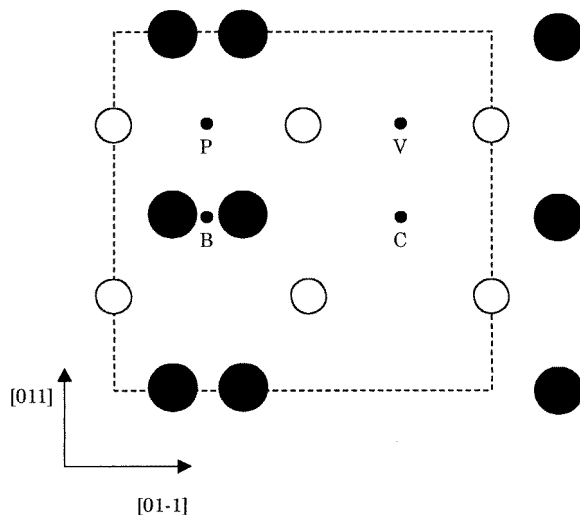


Figure 1. Top view of 2×2 cell of the Si(100) 2×1 reconstructed surface. Black circles correspond to the first silicon layer, and the white circles correspond to the second silicon layer. The small black points refer to high symmetry sites: cave (C), valley (V), pedestal (P) and bridge (B).

are all heated to more than 200 K during the simulation, which allows the Si substrate to continue to reconstruct with the adsorption of Se. Furthermore, it is well known that group-VI elements are adsorbed on Si(100) in bridge sites and cave sites, as can be expected from simple chemical considerations [8], so the bridge site is preferred at 0.25 and 0.50 ML, while bridge sites and cave sites are studied at 1.0 ML rather than other sites according to previous studies.

3. Results and discussion

3.1. Adsorption of Se at 0.25 and 0.50 ML

First, the adsorption of selenium on the Si(100): 2×1 surface at 0.25 ML coverage is investigated. As in the previous discussion, an Se atom is put at one bridge site in a 2×2 cell of the Si(100) 2×1 reconstruction surface (figure 1). The system is annealed slowly towards 0 K after heating to more than 200 K. During that process, the spontaneous formation of buckled (2×2) geometry from the Si(100) 2×1 symmetry structure is found, while one of the Si dimers is destroyed by the adsorbed Se atom. A view of the atomic geometry is shown in figure 2(a), and the corresponding parameters are indicated in figure 3(a) and 3(b). The bond lengths of Si–Se are 2.34 and 2.55 Å respectively, where the higher Si atom is a little closer to the Se atom. The height difference between two Si atoms is about 0.49 Å (see figure 3(a)). The Se atom has also a displacement of 0.31 Å in the [01-1] direction. The angle between two Se–Si bonds is about 117.9°.

The bond length of the remaining Si dimer, which is not adsorbed by Se, is about 2.35 Å (see figure 3(b)), which is slightly shorter than 2.38 Å, a previous *ab initio* MD result of a buckled clean Si(100) c(4×2) or p(2×2) reconstructed structure [17], and the same as the nearest neighbour distance in the bulk. The buckling height difference and tilt angle of the

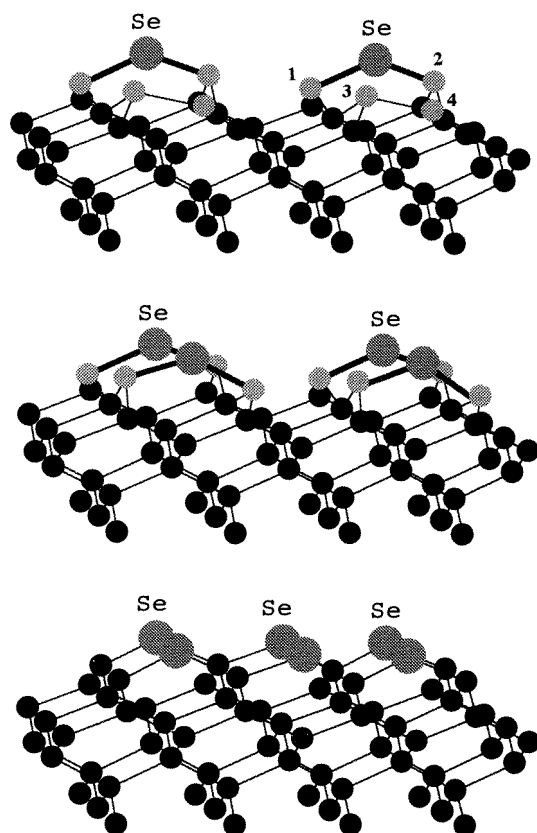


Figure 2. A view of geometric structures of the Se-adsorbed Si(100) surface at 0.25 ML (a), 0.50 ML (b) and 1.0 ML (c). Se atoms are represented by bigger grey circles. The black circles represent Si atoms, while those of the outermost layer at 0.25 and 0.50 ML are shown in grey ones.

dimer are 0.65 \AA and 15.5° respectively, which are also very similar to that of the previous clean $p(2 \times 2)$ structure, 0.66 \AA and 15.9° [17]. It indicates that adsorbed Se atoms affect the neighbour dimers little, which means that the remaining Si dimer is almost the same as that on the clean surface. The second layer Si atoms are also a little distorted in the $[01\bar{1}]$ direction. This results in the second atoms being closer to each other by about 0.22 \AA under the lower outermost Si atom of the remaining dimer and closer by 0.18 \AA under the lower Si atom bonded with the Se atom.

Moreover, we investigate the geometry of the Si surface while both bridge sites are adsorbed by Se atoms in a 2×2 cell. It is also heated to more than 200 K and annealed towards 0 K finally. A view of the atomic geometry is shown in figure 2(b). This results in an adsorbed Se chain with a zigzag displacement of 0.39 \AA in the $[01\bar{1}]$ direction, only 0.08 \AA larger than that of 0.25 ML. The local adsorption geometry of Se is almost as the same as that of 0.25 ML, which is suggested to be ascribed to the small interaction between adsorbed Se atoms and can be understood by the previous discussion on the remaining dimer structure at 0.25 ML with a clean surface. The second layer of Si atoms is also pulled closer by 0.20 \AA under the lower Si atoms bonded with Se atoms.

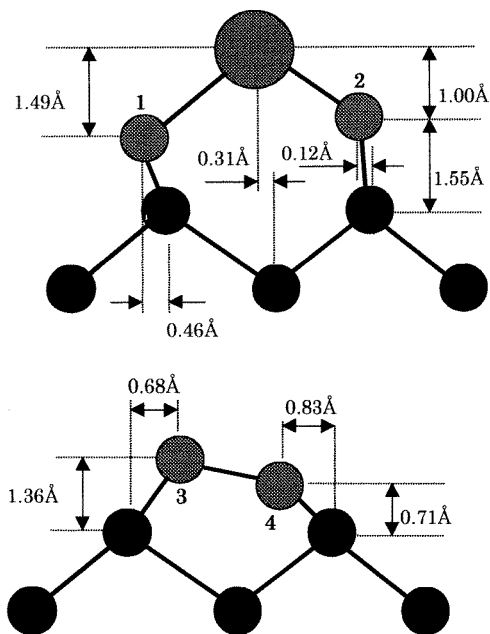


Figure 3. Local adsorbed geometric configuration at 0.25 ML. (a) Destroyed silicon dimer. (b) Remaining dimer. The Se atom is represented by bigger grey circles. The black circles represent Si atoms, while those of the outermost layer are shown in grey ones labelled with numbers consistent with figure 2(a).

3.2. Restoration to Si(100)1×1

At coverage of 0.25 and 0.50 ML, Se-induced restoration of Si(100) from 2×1 to 1×1 does not occur in the simulation. We continue to increase the coverage of Se by putting four Se atoms at bridge and cave sites in a 2×2 cell of Si(100) 2×1 reconstruction surface and simulate the dynamics process of restoration to the 1×1 surface. It is very difficult to simulate the real dynamics process of adsorbate-induced restoration because it is coupled with the diffusion of adsorbate. To simplify it, the silicon dimers are lengthed by 0.78 Å and Se atoms are put 1.4 Å over bridge and cave sites initially. In this case, the closest distance between Si and Se atoms is 0.28 Å shorter than Si–Se bond length, which will heat the system when it is relaxed. The temperature of the system increases to 300 K within 0.02 ps by the relaxing of the strong interaction between Si and Se, and it is annealed towards 0 K slowly in the following procedure. The changes of bondlength of Si dimer and adsorption height of Se at bridge site and cave site related to time are shown in figure 4(a) and figure 4(b), respectively. The vibration periods of Si atoms at different sites are very close to each other, although it is a little longer at the bridge at the beginning because the distance between Se and Si atoms is a little longer at the cave site. Evolution of dimer distance is consistent with that of Se atom height, which is about 0.60 ps. It is suggested that the vibration amplitudes of dimers and Se atoms should be much smaller in the real adsorption and restoration process, but the period, which is a characteristic of the corresponding bond, is supposed to be of the same order as our simulation work.

A view of the atomic geometry of the final restoration structure is shown in figure 2(c) and corresponding parameters are indicated in figure 5. The bond of the dimer is destroyed

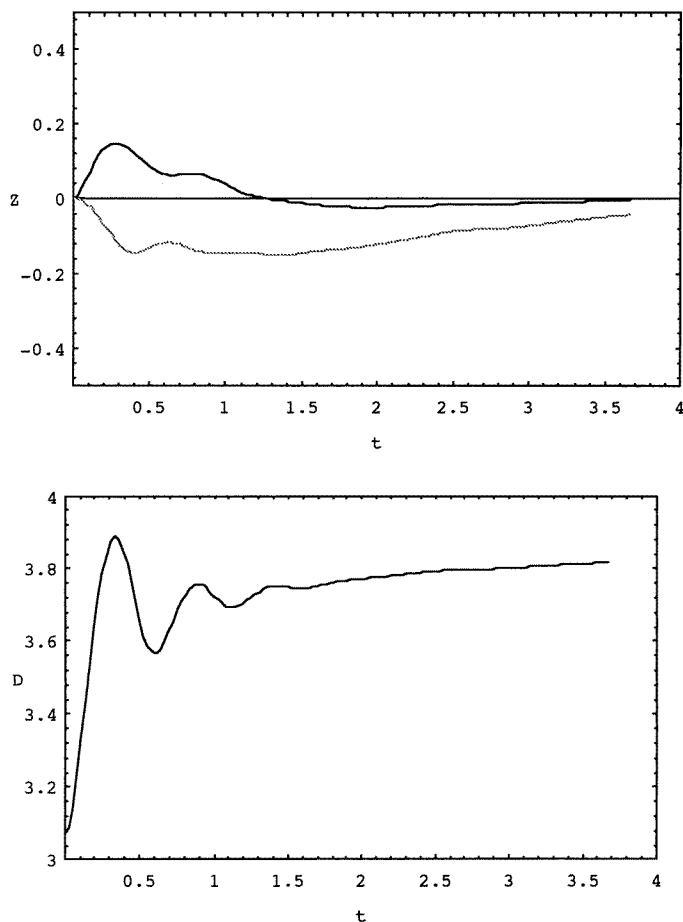


Figure 4. (a) Evolution of heights of Se atoms at bridge site (black curve) and cave site (grey curve). (t in ps and Z in Å.) (b) Evolution of Si dimer distance. (t in ps and D in Å.)

finally and the distance between corresponding Si atoms is about 3.81 Å in the restoration structure, very close to the crystal constant of Si, 3.84 Å, and the Se atoms at different sites are also fixed to almost the same height at last, which is less than 0.05 Å different, after being vibrated in different ways. The Si–Se bond length is 2.28 Å and the angle between Se–Si bonds is 113.6°.

As to the restored Si(100) surface, the geometric configuration is very close to the ideal Si(100) surface, which has bond length of 2.34 Å and bond angle of 109.4°. The Si bond length of restored Si(100) in our studies is 2.30 Å, and the bond angle is 113.2°. They are in good agreement with previous theoretical studies [5], which reported that the Se-induced Si(100) restoration structure has a bond length of 2.34 Å and bond angle of 110.2°. The displacement of Si atoms in the [011] direction is less than 0.014 and 0.002 Å at the two topmost layers with respect to the ideal lattice planes, which is slightly shorter than corresponding results in [8], which gives the displacement of 0.075 Å, 0.017 Å and 0.006 Å at the three topmost layers. This indicates that Se is an ideal adsorbate to lead the restoration of the Si(100) surface.

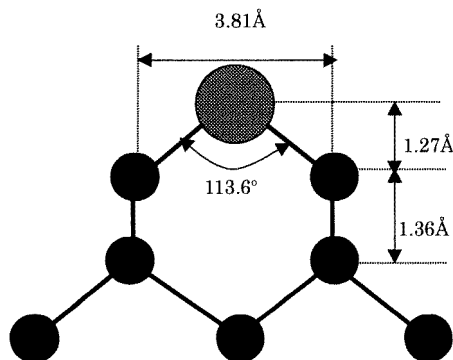


Figure 5. Local adsorbed geometric configuration at 1.0 ML. The Se atom is represented by a grey circle and Si atoms are shown in black ones.

4. Summary

The structural and electronic properties of chalcogen elements (S, Se) on Si(100) 2×1 surfaces have attracted interest recently as well as S and Se being suggested as the ideal adsorbates to lead the restoration of the Si(100) surface. We studied the detailed geometry structures of the Se-adsorbed Si(100) surface structure at different coverage and simulated the dynamics process of restoration of Si(100) 2×1 to 1×1 induced by adsorption of Se atoms. A summary of important results is as follows.

(i) At the coverage of 0.25 and 0.50 ML, Se-adsorbed Si(100) has a buckled structure rather than a symmetric one. The local adsorption structures of Si(100):Se are very similar to each other at 0.25 and 0.50 ML.

(ii) Si(100) 2×1 is restored to the 1×1 structure spontaneously when Se atoms are adsorbed at 1.0 ML, and vibrations of Se atoms and Si atoms of the top layer with a period of around 0.6 ps are found during the dynamics process. It is confirmed that Se is an ideal adsorbate to restore the Si(100) surface, and the final restored Si(100) structure is in good agreement with previous studies.

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