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Potential Energy Surfaces for H Adsorbed at 4H-SiC{0001} Surfaces

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The constant adsorption energy surfaces for hydrogen adsorbed on Si- and C-terminated hexagonal 4H-SiC{0001} surfaces have been calculated within density functional theory framework. The two unreconstructed and one reconstructed $\sqrt{3} \times \sqrt{3}$ surfaces were taken into account. We show that on all surfaces there is a global energy minimum indicating the most favourable adsorption site corresponding to H atom adsorption on-top of the topmost substrate layer atom. In case of reconstructed surface, there is another small and shallow local minimum. Moreover, the diffusion barrier is much higher at reconstructed surface than at unreconstructed ones.

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1. Introduction

The wide band-gap semiconductor silicon carbide has attracted a great interest during the past decades [1–11] because of number of properties which make it very attractive for many applications in electronic devices. SiC may crystallize in many polytypes. For electronic applications purposes hexagonal 4H-SiC is the preferred polytype. The (0001) surfaces of the hexagonal polytype 4H-SiC are structurally equivalent to the Si(111) surface for which hydrogenation has proved to be the method to produce unreconstructed, extremely flat, H-terminated surfaces [1]. The hydrogen atoms attach to semiconductor dangling bonds thus providing the surface chemically and electronically passivated. Moreover, hydrogen is present in reactor chambers during SiC crystal growth so it can influence both the process and the quality of grown crystals. Several theoretical papers presented research on the electronic and atomic structure of hydrogen adsorbed on Si-rich cubic SiC(001)3×2 surface [10, 12–15].

Our previous paper [16] presented results of our studies of the effect of on-surface and sub-surface adsorption of H atoms on structural and energetic properties of this surface on unreconstructed SiC{0001}. Another important issue is to understand H atoms movements on the surface. Therefore, we calculated the potential energy surface and, consequently, barriers for diffusion for hydrogen atom on flat SiC{0001} surfaces. Polar SiC{0001} surfaces are known to experience many reconstructions either Si- or C-rich. To compare H behaviour on flat and reconstructed surface we carried out similar calculations for H on Si-terminated 4H-SiC(0001)$\sqrt{3} \times \sqrt{3}$ reconstruction.

2. Methods

Our calculations have been performed using density functional theory (DFT) as implemented in Siesta program package [17]. The electron exchange-correlation effects were treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) form of the exchange-correlation functional [18]. The electron ion-core interactions were represented by pseudopotentials of the Troullier–Martins type [19] and the electron wave-functions were expanded into the atomic-orbital basis set using the double-ζ polarized set. The cutoff of 120 Ry was used for the real space mesh. The Brillouin zone integrations were performed applying $(4, 4, 1)$ k-points meshes for 2×2 surface supercell calculations.

According to the tests reported in our previous paper [16], we constructed slabs of 12 Si-C double-layers representing the (0001) and (000$\bar{1}$) surfaces of the 4H-SiC crystal, terminated respectively with Si and C atoms. For brevity, in the following these surfaces will be referred to as Si(0001) and C(000$\bar{1}$). The dangling bonds on the bottom layer atoms of the slabs were saturated by hydrogen atoms. The slabs of such thickness which were separated from their periodic replicas in neighbouring cells by a vacuum region of ≈ 20 Å proved to be sufficient for reproducing surface properties [20]. The atomic positions of the four topmost double Si-C layers of the slab, and of the terminating H atoms on the backside were relaxed until forces on atoms converged to less than 0.02 eV/Å. The positions of atoms of the remaining double Si-C layers have been held fixed. Calculations of potential energy surface were performed in 2×2 supercell for unreconstructed surface and in 1×1 supercell for $\sqrt{3} \times \sqrt{3}$ one.

3. Results

In order to obtain constant potential energy surface H atom was placed in various sites on the surface. Hydrogen's x and y-coordinates were kept frozen while z-coordinate and the substrate were allowed to relax. There were used 25 evenly distributed sites in 1/4 of 2×2 supercell on unreconstructed surfaces and 100 sites

on reconstructed $\sqrt{3} \times \sqrt{3}$ surface. For each point the adsorption energy $E_{\rm ads}$ was calculated. The adsorption energy is defined as follows: $E_{\rm ads} = E^{\rm H/SiC} - E^{\rm SiC} - E^{\rm H}$, where $E^{\rm H/SiC}$, $E^{\rm SiC}$, and $E^{\rm H}$ are total energies of surface with adsorbed hydrogen, clean surface, and free H atom, respectively. This definition yields the lower adsorption energy for the more favourable energetically adsorption site.

Results of such calculations are given in Fig. 1. Our previous calculations [16] showed that hydrogen atoms are attached on top of the surface atoms saturating either Si or C dangling bonds. The minima observed at all plots correspond to the same case, i.e. H on top of the topmost substrate layer atom. The lowest adsorption energy (the strongest bond) equal to -4.81 eV is observed for hydrogen on C(000$\bar{1}$) surface. On Si(0001), H atom is less strongly bound with $E_{\rm ads} = -4.10$ eV [16]. In both cases constant energy surfaces reveal threefold symmetry characteristic for hexagonal surfaces.

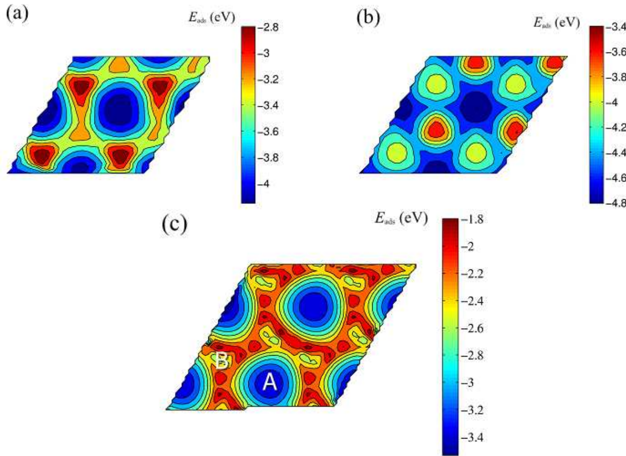

Fig. 1. Constant adsorption energy $E_{\rm ads}$ surfaces $\sqrt{3} \times \sqrt{3}$ or hydrogen adsorbed at Si-terminated (a), C-terminated (b) and Si-terminated $\sqrt{3} \times \sqrt{3}$ (c) surfaces.

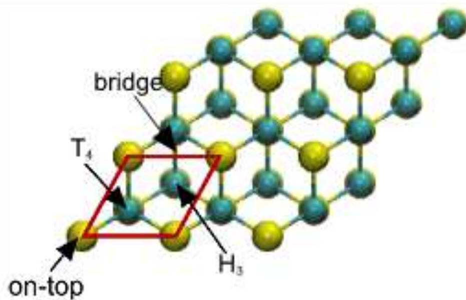

Fig. 2. High-symmetry adsorption sites on 4H-SiC{0001} surfaces. Top view of the surface with 1×1 supercell indicated in red. Blue/yellow balls represent Si or C atoms depending on the termination considered.

The observed maxima are related to the high--symmetry adsorption sites H3 and T4 on hexagonal semiconductor surfaces (Fig. 2). At the Si(0001) surface the main energy maximum is for hydrogen adsorbed in T4 site, where C atom from the second layer is just below H atom. There, the adsorption energy equals to -2.65 eV. In the second maximum, when H is at the H3 site (over the C atom from the third layer) $E_{\rm ads} = -3.19$ eV. On the C(000$\bar{1}$) opposite situation is observed: main maximum exists for hydrogen at H3 site with adsorption energy equal to -3.47 eV. There is the second maximum when H atom is placed at T4 site and $E_{\rm ads} = -3.9$ eV. The energy barrier that H atom should overcome passing from one minimum to the other is higher on Si(0001) and equals to 0.7 eV. At C(000$\bar{1}$) surface the barrier for diffusion is lower and amounts to 0.5 eV.

Different hydrogen atom behaviour is observed on reconstructed Si-terminated $\sqrt{3} \times \sqrt{3}$ surface (Fig. 1c). Similarly to unreconstructed surfaces, the constant energy surface experiences a deep minimum related to the H atom bound on top of the topmost Si atom which is indicated by letter A at the plot. In this case, the adsorption energy equals to -3.40 eV.

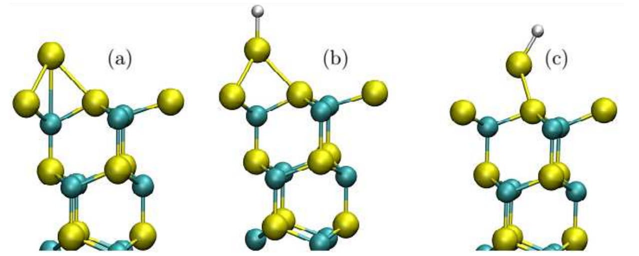

Fig. 3. Final atomic configuration for clean reconstructed surface (a), hydrogen adsorbed in the main minimum (b), and the second minimum (c) on reconstructed 4H-SiC(0001) $\sqrt{3} \times \sqrt{3}$ surface. Yellow, cyan, and white balls represent Si, C, and H atoms, respectively.

Another type of minimum indicated by letter B at the plot is much smaller and shallower with $E_{\rm ads} = -2.54$ eV. Looking at the atomic positions corresponding to the minima (Fig. 3) it can be easily noticed that in both cases hydrogen atom is bound to the topmost surface silicon. In the most favourable situation, topmost silicon remains in the same T4 position as on the clean surface with the bond length to the nearest Si atom equal to 2.44 Å. The H-Si bond length is 1.53 Å. It is similar to that on unreconstructed Si(0001) surface where it ranges from 1.52 to 1.55 Å depending on the H coverage. In the second minimum the topmost Si atom with H attached on is shifted to the H3 site. At clean surface, the H3 site for Si atom is less favourable energetically by ≈ 0.5 eV. The energy difference for hydrogen adsorption at these two positions is even bigger and amounts to 0.84 eV. Nevertheless, the local geometry remains almost unchanged: the bond length between Si atoms is 2.45 Å and between

the H atom and underlying Si atom 1.54 Å. In the path of the lowest energy for H atom passing from site A to B the barrier of 1.16 eV should be overcome. Then, there is another barrier for H going from B to another A of 0.6 eV.

4. Summary

In this work, the *ab initio* method was applied to calculate constant energy surfaces for hydrogen atom adsorbed on 4H-SiC{0001}. Two unreconstructed and one reconstructed surfaces were taken into account. In general, hydrogen is bound more strongly to the unreconstructed surfaces but there is higher barrier for diffusion on reconstructed $\sqrt{3} \times \sqrt{3}$ surface. Our calculations show deep and wide minima on all surfaces corresponding to H atom adsorbed on-top of the topmost substrate layer atom. Hydrogen is bound more strongly to the C-terminated surface with adsorption energy equal to -4.81 eV. On the Si-terminated surface E_{ads} is higher by about 0.7 eV. On both surfaces, the differences between maximal and minimal values of adsorption energy are similar and amount to about 1.4 eV. The barriers for diffusion are 0.7 eV and 0.5 eV on the Si(0001) and C(000$\bar{1}$) surface, respectively. In case of reconstructed Si-terminated $\sqrt{3} \times \sqrt{3}$ surface, there are two types of minima of adsorption energy. Both of them correspond to H adsorption on top of the same topmost Si atom but in deeper minimum Si is placed at the T4 site while in the other at the H3 site. The adsorption energies in those minima are -3.40 and -2.54 eV. The barrier for diffusion is much higher at reconstructed surface and equals 1.16 eV.

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