New structural model for Na_6Si_3 surface magic cluster on the Si(111)-7 × 7 surface

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ABSTRACT

The adsorption of Na atoms on the Si(111)-7 × 7 surface is studied using first-principles calculations. Compared to the Triangle-Trimer model reported previously, we propose a more stable and robust Na_6Si_3 Hexagon-Trimer model which has six Na atoms with hexagon shape and three Si edge adatoms moving inward to form a trimer. The total energy of Hexagon-Trimer model is 0.252 eV lower than that of Triangle-Trimer model and 0.552 eV lower than that of Hexagon model. The simulated STM images of Hexagon-Trimer model are in good agreement with experimental STM observations. The most probable formation process of Hexagon-Trimer model is analyzed. The reaction is catalyzed by a Na atom and the energy barrier is reduced from 0.89 to 0.44 eV. These results have provided a complete picture for the formation mechanism of Na_6Si_3 surface magic clusters on the Si(111)-7 × 7 surface.

1. Introduction

The well-known Si(111)-7 × 7 reconstruction surface with a periodic large unit cell and various dangling bonds offers a promising template for fabricating self-assembled nanoclusters [1–10]. Numerous works have been performed successfully to grow ordered arrays of identical six-atom nanoclusters, so-called surface magic clusters (SMCs), for various elements including Ga [2–4], Al [3,5], In [3,6], Na [7], Pb [8], K [9], and Au [10]. These SMCs are stable above room temperature (RT) in contrast with some metal clusters on a metal surface, which are typically stable only at low temperature (e.g. up to 150 K for Ag clusters on Pt(111) [11]). Among the studies of alkali metals on the Si(111)-7 × 7 surface, the observation of scanning tunneling microscopy (STM) on the growth mechanism of Na nanoclusters reported by Wu et al. [7,12,13] is unique. Below 0.08 monolayer (ML) coverage, Na atoms are strongly bound (adsorption energies ~ −2.2 eV) to the surface and are highly mobile in "basins" around the Si rest atoms forming a two-dimensional gas-like phase at room temperature. However, above the critical coverage of 0.08 ML, stable SMCs are formed which compose of six Na and three Si atoms. Considering the energetic structure of Na clusters and the preferred adsorption site

of single Na atom on the Si(111)-7 × 7 surface, two structural models of Na_6Si_3-SMC have been proposed [7,12]: the Hexagon model (denoted as Hex-model) as shown in Fig. 1(a) and the Triangle-Trimer model (denoted as TT-model [14]) as shown in Fig. 1(b). In Hex-model, six Na atoms form a hexagon in the center of the Si(111)-7 × 7 half unit cell (HUC) and all the Si adatoms do not leave their original positions. However in TT-model, six Na atoms arrange a big triangle and three Si edge adatoms move inward to the center of HUC to form a small trimer. The small Si-trimer is surrounded by the big Na-triangle. The geometry of TT-model has triply degenerate mirror symmetry [7]. Wu et al. [7,9] concluded that TT-model is energetically more favorable than Hex-model based on their theoretical calculations. Despite that TT-model has the lower energy of 0.02 eV/atom than Hex-model and the simulated STM images reproduce the experimental images noticeably better; however, the unusual site-exchange between Na and Si atoms in TT-model is still unclear [7].

In this paper, we use the density functional theory [15] (DFT) to perform a systematic study of the Na atom clustering on the Si(111)-7 × 7 surface. We discover a new Hexagon-Trimer model (denoted as HT-model) of Na_6Si_3-SMC, which has six Na atoms with hexagon shape (same as Hex-model) and three Si adatoms moving inward to the center of the hexagon to form a trimer (same as TT-model). The total energy of this new model is significantly lower than that of TT-model and Hex-model by 0.252 and 0.552 eV, respectively. The simulated STM images of HT-model show good agreement with experimental observations. Moreover, we investigate the plausible formation process of HT-model by using nudged elastic band method [16] and the overall reaction energy barrier is 0.44 eV. We propose a novel reaction pathway of the formation of Na_6Si_3-SMCs

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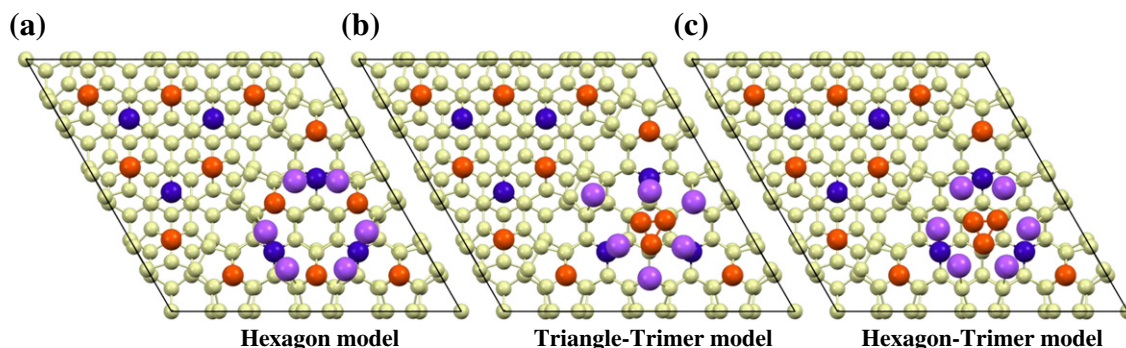
Fig. 1. Three models of Na$_6$Si$_3$-SMC on the Si(111)-7 × 7 surface: (a) Hexagon model, Ref. [9]; (b) Triangle-Trimer model, Ref. [7]; and (c) Hexagon-Trimer model. The white, red, blue, and purple balls represent Si backbone atoms, Si adatoms, Si rest atoms, and Na atoms, respectively.

on the Si(111)-7 × 7 surface catalyzed by additional Na atoms in the system.

Our paper is organized in the following. In Section 2, we briefly describe the computational details of our calculations. In Sections 3.1 and 3.2, we report the adsorption energies of Na atoms and the formation processes of Na$_6$Si$_3$-SMCs. Finally, we summarize our findings in Section 4.

2. Computational details

All the DFT calculations reported here are carried out by using the Vienna Ab-Initio Simulation Package (VASP) [17,18] with the projector augmented wave pseudopotentials [19]. The exchange-correlation functional is treated by the generalized gradient approximation with the Perdew–Burke–Ernzerhof form [20]. The Kohn–Sham wave functions are represented using a plane-wave basis set with a kinetic energy cutoff of 300 eV. In the well-established dimer–adatom–stacking fault model [21,22], a unit cell of the Si(111)-7 × 7 surface consists of a faulted half unit cell (FHUC) and an unfaulted half unit cell (UHUC). Each HUC has nine Si atoms with dangling bonds, which are composed of three corner adatoms, three edge adatoms, and three rest atoms. The (7 × 7) surface is simulated by a repeating unit cell of four atomic bilayers and a vacuum region of about 10 Å. The reconstructed Si(111)-7 × 7 surface contains 396 silicon atoms, and the dangling bonds on the unreconstructed surface are saturated by 49 hydrogen atoms. The Brillouin zone integration is performed with the gamma point only. In all the calculations presented herein, the top three atomic bilayers are fully relaxed, and the bottom bilayer is kept at the bulk positions. The geometry is optimized until the total energy is converged to 10^{-4} eV and all the forces on relaxed atoms are smaller than 25 meV/Å. In order to avoid interactions between the slabs, we have also done the test calculations with the vacuum distance of 15 and 20 Å, the relative energies compared to 10 Å vacuum are within 5 meV per Na atom and thus the vacuum distance of 10 Å is sufficient for this study. We also apply larger size of slabs in the calculation, such as seven silicon bilayers with top five bilayers being relaxed and bottom two bilayers being fixed, and the results are the same.

3. Results and discussion

3.1. Na atom adsorption

In the Si(111)-7 × 7 surface, it is generally believed that the dangling bond determines the chemical reactivity of the surface adsorption. Brommer et al. [23] have applied the concept of "local softness" to quantify the interaction of adatoms and molecules adsorbed at various sites of dangling bond on the Si(111)-7 × 7 surface. The softness depends on the capacity of states to give or receive electrons. However, Cho and Kaxiras [24] have shown a different result that alkali

metals prefer to adsorb on the high-coordination sites surrounding Si rest atoms rather than on the dangling bond sites of Si adatoms or rest atoms. Zhang et al. [25] have also shown that the high-coordination sites are preferable sites for Cu, Ag, and Au atom adsorption on the Si(111)-7 × 7 surface. With this background, in order to understand the formation mechanism of Na$_6$Si$_3$-SMC, we first perform calculations for single Na atom adsorption on the Si(111)-7 × 7 surface. Since clean Si(111)-7 × 7 reconstructed surface has a C$_{3v}$ symmetry, only adsorption sites inside an irreducible region as shown in dashed area of Fig. 2 need to be considered. Six possible adsorption sites (except the dangling bond sites of Si adatoms and rest atoms) are described as follows: (a) site-1: an on-top site which is beside a Si edge adatom and locates between two Si rest atoms; (b) site-2: a H3 site which is at the center of HUC; (c) site-3: a T4 site which is beside a Si rest atom and locates between two Si edge adatoms; (d) site-4: a H3 site which is located between a Si rest atom and an edge adatom; (e) site-5: a T4 site which is beside a Si rest atom and locates between a Si edge atom and a corner adatom; and (f) site-6: a H3 site between a Si rest atom and a corner adatom. As usual the adsorption energy is defined as the total energy of the adsorbed system minus the total energies of the single free Na atom and the Si(111)-7 × 7 surface. Based on this definition, the lower adsorption energy means the stronger interaction. The calculated adsorption energies for the above sites on FHUC and UHUC are summarized in Table 1.

As shown in Table 1, all adsorption energies on UHUC are slightly higher compared with those on FHUC. The energy differences between two HUCs are in the range of 0.058–0.084 eV, which is consistent with previous work [7]. It reveals that Na adsorption behaviors in UHUC are similar to those in FHUC, therefore only the adsorption behaviors in FHUC are discussed hereafter. The most stable sites for Na adatom
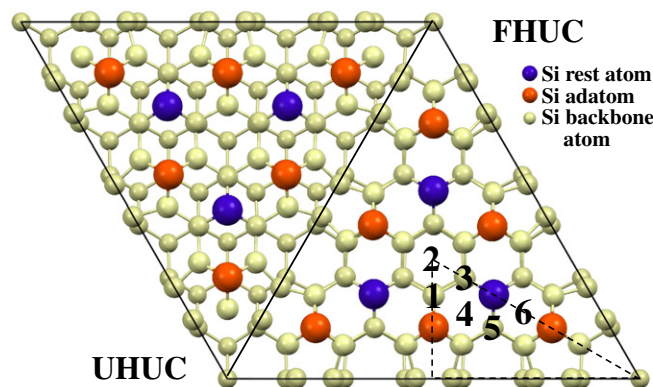

Fig. 2. Different Na adsorption sites on the Si(111)-7 × 7 surface. To make Si backbone atoms on different layers distinguishable, the Si backbone atoms on the first layer are slightly larger and brighter than on second and third layers.

Table 1
The adsorption energies (unit in eV) of single Na atom on six adsorption sites referring to Fig. 2.

	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6
FHUC	−1.769	−1.795	−2.041	−2.150	−2.021	−2.140
UHUC	−1.687	−1.713	−1.973	−2.066	−1.937	−2.082

Table 2
The adsorption energies (unit in eV/atom) of (a) two, (b) three, and (c) six Na atom adsorption on the Si(111)-7 × 7 surface with various configurations referring to Fig. 3.

	Fig. 3(a)	Fig. 3(b)	Fig. 3(c)
1	−2.151	−2.150	−2.099
2	−2.148	−2.122	−2.057
3	−2.017	−2.051	−2.007
4	−1.997	−2.062	−2.006
5	−2.039	−1.817	−2.010
6			−2.044

are those high-coordination sites (i.e. site-4 and site-6) which interact with two dangling bonds, and the adsorption energies are −2.150 and −2.140 eV, respectively. The second stable sites are T4 sites (i.e. site-3 and site-5) and the corresponding adsorption energies are −2.041 and −2.021 eV, respectively; at these T4 sites, Na atom reacts with one Si rest atom's dangling bond and weakly interacts with two neighboring Si backbone atoms. We notice that for sites 4 and 6 (sites 3 and 5), they are in-equivalent H3 (T4) sites; however their first few neighboring atoms are the same, thus their adsorption energies are only different by 10 (20) meV. For adsorption on top of backbone Si (i.e. site-1), Na atom reacts with one Si edge adatom's dangling bond and one Si backbone atom, the adsorption energy is −1.769 eV. For adsorption on the center of FHUC (site-2), Na atom reacts with three Si backbone atoms, the adsorption energy is −1.795 eV which is similar to the adsorption on site-1. We also calculated the adsorption energies of Na on top of Si rest, edge, and corner adatoms where all are one-dangling-bond sites. The corresponding adsorption energies are −1.924, −1.670, and −1.676 eV, which are higher than the values on high-coordination sites. This result is expected since Na atom reacts more strongly with two dangling bonds than with only one dangling bond; besides, Na atom reacts more strongly with Si rest atom than with Si edge or corner adatom. The present results of single Na atom adsorption are consistent with previous calculations in Ref. [7]. Thus we conclude that the plausible adsorption sites for single Na atom adsorption are more likely to be high-coordination sites: site-4 and site-6.

In order to understand the formation mechanism of Na₆Si₃-SMCs, we further studied the adsorption of two, three, and six Na atoms on the Si(111)-7 × 7 surface. The adsorption configurations are presented in Fig. 3 and the corresponding adsorption energies are listed in Table 2. For two Na atom adsorption, the Na atoms prefer to adsorb on high-coordination sites in two different basins, as shown in Fig. 3(a)-1 and (a)-2. The adsorption energies are −2.151 and −2.148 eV/atom,

respectively, same as the values of single Na atom adsorption on site-4 and site-6. For two Na atoms in the same Si basin as depicted in Fig. 3(a)-3 and (a)-4, the corresponding adsorption energies are −2.017 and −1.997 eV/atom, which are higher than those of single Na adsorption on site-4 by about 0.153 eV. Similarly, for two Na atoms adsorb on site-5 in different basins as Fig. 3(a)-5, the adsorption energy is −2.039 eV/atom, resembling the single Na adsorption on site-5. These results are in good agreement with the previous calculations [26]. The interaction between two Na atoms located in different basins is negligible, and two Na atoms settled in the same basin could lead to a strong repulsive interaction as 0.153 eV per Na atom.

Furthermore, for the adsorption of three Na atoms, the cases for each Na atom separately adsorbs on a different basin as shown in Fig. 3(b)-1 and (b)-2 are found to be energetically the most favorable, the corresponding adsorption energies are −2.150 and −2.122 eV/atom, respectively. In the cases for two Na atoms in one basin and the third Na atom in another basin as shown in Fig. 3(b)-3 and (b)-4, the adsorption energies are higher than those of the cases with each atom adsorbing on different basins by at least 0.060 eV/atom. The case for three Na atoms occupying one basin as shown in Fig. 3(b)-5 has the highest adsorption energy of −1.817 eV/atom, where big repulsive interaction energy of 0.333 eV/atom is found. These results indicate that each Si basin prefers to accommodate at most two Na atoms.

From the above study of one, two, and three Na atom adsorption on the Si(111)-7 × 7 surface, we conclude the following two points: (1) Na atom prefers to adsorb on high-coordination sites, as site-4 or site-6; and (2) one Si rest atom basin could contain at most two Na atoms. For the SMC of six Na atom adsorption on the Si(111)-7 × 7 surface, previous STM study [7] indicated that Na atom transfers charge to the nearest Si adatom and making it brighter in the filled
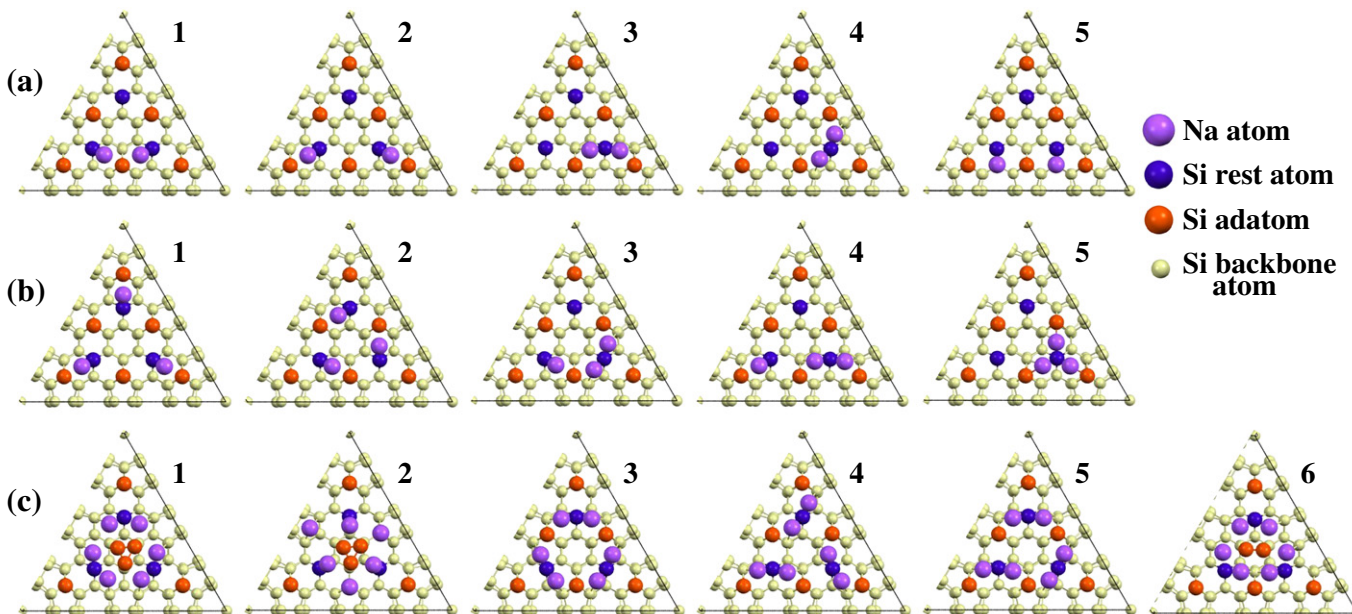

Fig. 3. The configurations of (a) two; (b) three; and (c) six Na atom adsorption on the Si(111)-7 × 7 surface. Here only FHUC is represented.

state images. However, the three protrusions of STM images are observed on the edges of each HUC on the Si(111)-7 × 7 surface. By combining previous STM observations [7] and current DFT results, it reveals that Na atom could not appear on the corner sites as site-6, all six Na atoms should directly adsorb on site-4 and its symmetry-related sites which are preferential sites for Na atoms to form a hexagon shape in HUCs as the Hex-model [9] shown in Fig. 1(a). In Ref. [9], the adsorption energy of Hex-model is only 0.02 eV/atom higher than TT-model and it could be treated as a precursor state of Na_6Si_3-SMCs. In our point of view, considering the adsorption results of Na atoms, TT-model is unnatural; since the configuration with three Na atoms on top of Si rest atoms is unfavorable. We propose a new model of Na_6Si_3-SMC on the Si(111)-7 × 7 surface, in which six Na atoms adsorb on favorable positions of site-4 and its symmetry-related sites to make hexagon shape as Hex-model does and three Si adatoms move inward to the center of the hexagon to form a trimer as TT-model does. Therefore this new model is named as Hexagon-Trimer model (HT-model). As listed in Table 2, the adsorption energies of HT-model (Fig. 3(c)-1), TT-model (Fig. 3(c)-2), and Hex-model (Fig. 3(c)-3) are −2.090, −2.057, and −2.007 eV/atom, respectively. In total energy, HT-model is the most stable one which is 0.252 eV lower than TT-model and 0.552 eV lower than Hex-model. The above results show that the most plausible and reliable model of Na_6Si_3-SMC is HT-model. Interestingly, one can find other two configurations, as shown in Fig. 3(c)-4 and (c)-5, which have adsorption energies of −2.006 and −2.010 eV/atom, respectively, extremely close to Hex-model. It reveals that two Na atoms in the same basin can revolve freely around Si atom either clockwise or anti-clockwise with almost the same speed. Additionally, as in Fig. 3(c)-6, for the configuration with six Na atoms keeping hexagon shape and only two Si edge adatoms moving toward the center of HUC, its total energy is 0.222 eV lower than Hex-model, and only 0.078 eV higher than TT-model.

To corroborate the above results, we simulated the STM images by an integration of the local density of states and compared them with experimental STM observations (see Fig. 3(a) and (b) of Ref. [7]). Fig. 4(a) and (b) are the simulated STM images of TT-model and HT-model, respectively. The filled and empty states are integrated from Fermi level to −2.0 and +0.8 eV, respectively. Both the filled and empty state images are characterized by three protrusions near the positions of Si edge adatoms. For filled state images, that of TT-model is approximately triangular and that of HT-model is a distorted hexagon; nevertheless, three edge protrusions (the big white spots) always appear in these two models. For empty state images, splitting and extended outward features are observed in both models. In

general, the simulated STM images of TT-model and HT-model well reproduce the experimental observations.

3.2. Na-SMC formation processes

To investigate the formation mechanism of HT-model on the Si(111)-7 × 7 surface, we calculated the energy barriers of various reaction pathways by using nudged elastic band method [16] and the energy barrier profiles are shown in Fig. 5. Since Hex-model (Fig. 3(c)-3) can be treated as the precursor state of Na_6Si_3-SMCs [9], we first select this model as the initial state. Comparing Fig. 1(a) and (c), intuitively one may think that three Si edge adatoms can move inward to form HT-model directly. However, based on our calculations, when a Si edge adatom moves straight to neighboring on-top site beside the center of HUC, it has to overcome a large energy barrier of 1.71 eV (for two Si edge adatoms moving simultaneously, the energy barrier is increased to 2.54 eV). Therefore Si edge adatoms could not simply move inward to form HT-model, and this reaction pathway can simply be discarded. We then find another formation process as shown in Fig. 5(a), the initial state is taken to be the configuration of Fig. 3(c)-5 which has almost the same adsorption energy as Hex-model does. For one Si edge adatom diffuses from edge site (Fig. 5(a)-1) to neighboring H3 site (Fig. 5(a)-3), the energy barrier is 0.59 eV (i.e. 10^4 hoppings/s at RT), then it diffuses to T4 site beside the center of HUC (Fig. 5(a)-5) with an energy barrier of 0.37 eV. Compared to the above selected pathway, the total energy barrier in this process is decreased from 1.71 to 0.89 eV. However, the Si edge adatom is still hard to move inward through this high energy barrier pathway.

In order to find a pathway with lower energy barrier, we propose another plausible reaction process to describe the formation of HT-model. According to previous works [7,26], the energy barrier of single Na atom diffusing within a basin is 0.14 eV. In addition, hopping between different basins in the same HUC and crossing the unit cell boundary are characterized by energy barriers of 0.36 and 0.42 eV, respectively. As shown in Fig. 5(b), we also find that in Hex-model, a Na atom can diffuse along the dimer row and its energy barrier is 0.33 eV. Consequently, this indicates that a Na atom can freely diffuse on the Si(111)-7 × 7 surface. This forms a complete network pathway on the surface with energy barrier less than 0.42 eV. If we start from Hex-model with one additional Na atom diffusing along the boundary to the site beside Si edge adatom (see Fig. 5(c)-1), this additional Na atom can promote this Si edge adatom moving to neighboring H3 site (Fig. 5(c)-3) with a low energy barrier of 0.44 eV
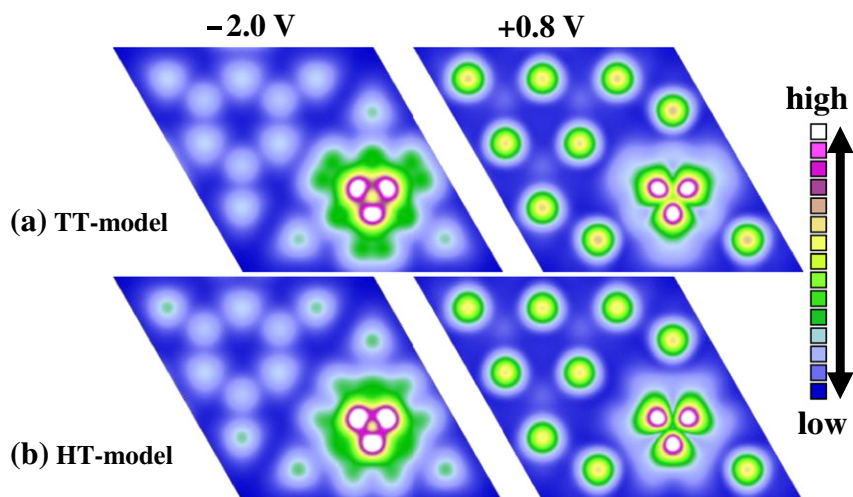

−2.0 V   **+0.8 V**

(a) TT-model

(b) HT-model

high

low

Fig. 4. The filled (−2.0 V) and empty (+0.8 V) state images for Na_6Si_3-SMCs on the Si(111)-7 × 7 surface obtained from (a) TT-model; and (b) HT-model. The indicator of the intensity of charge density is displayed at the right side.
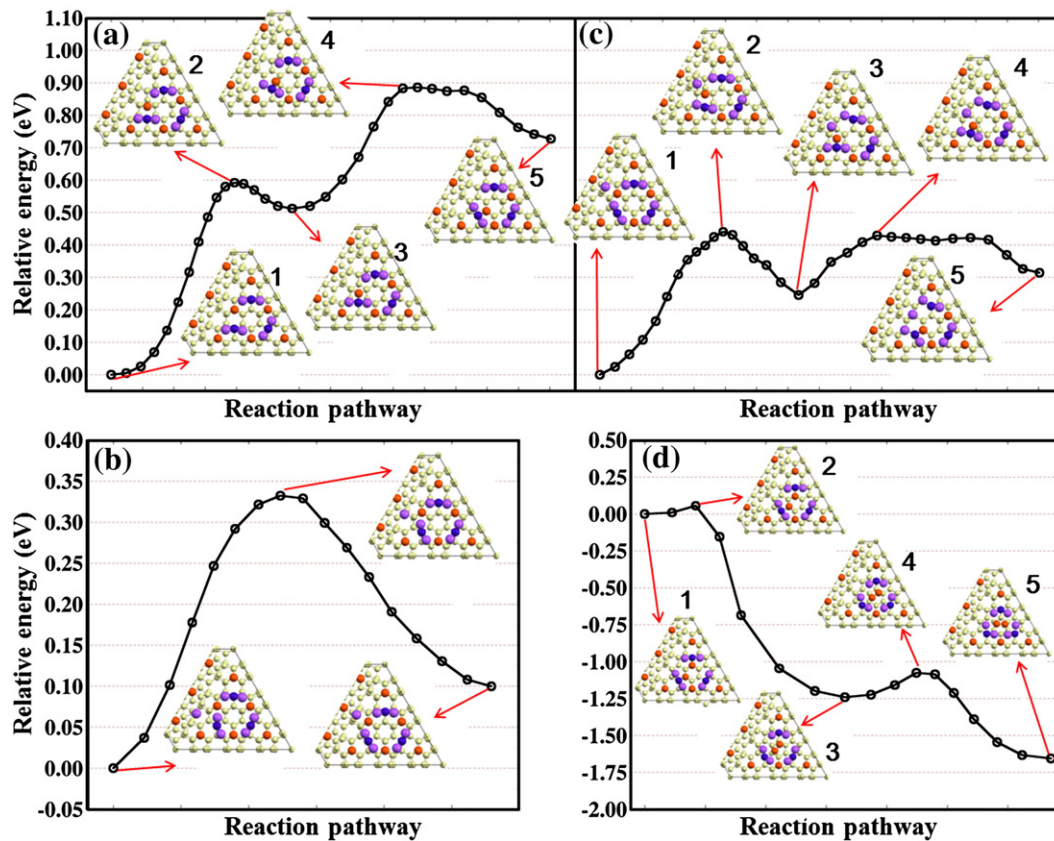
Fig. 5. The energy barrier profiles for various reaction pathways. The white, red, blue, and purple balls represent Si backbone atoms, Si adatoms, Si rest atoms, and Na atoms, respectively.

(i.e. 10^6 hoppings/s at RT); the reason is that this additional Na atom reacts with the top Si backbone atom neighboring Si edge adatom and this weakens the bonding between these two Si atoms. Then diffusing Si adatom can easily move from H3 site to T4 site beside the center of HUC (Fig. 5(c)-5) and the energy barrier is only 0.18 eV. Meanwhile this additional Na atom moves to the original position of Si edge atom, then it could easily diffuse back to the boundary of HUC, and the energy barrier is only 0.12 eV. Therefore, the reaction of diffusing a Si adatom (from edge site to T4 site) is catalyzed by a Na atom and this self-catalysis mechanism could help to reduce the energy barrier. Another Si edge adatom could also move to the T4 site (in the neighborhood of the center of HUC, as shown in Fig. 5(d)-1) through the process of Fig. 5(c). These two Si atoms form a Si dimer (Fig. 5(d)-3) with a small energy barrier of 0.06 eV. The Si dimer rotates 60° with the energy barrier of 0.16 eV, and forms the final state (Fig. 5(d)-5, which is the same as Fig. 3(c)-6). In the end, the last Si edge adatom could move inward to form a Si trimer in the center of HUC. From the above discussion, it nicely explains the formation process of HT-model. As a result, we have proposed a novel reaction pathway with self-catalysis by Na atoms to describe the formation mechanism of HT-model on the Si(111)-7 × 7 surface.

4. Conclusion

In this work, we propose a new structural model of Na_6Si_3-SMC on the Si(111)-7 × 7 reconstruction surface. This new Hexagon-Trimer model (HT-model) is more stable by 0.252 eV than the TT-model reported by Wu et al. [7]. In addition, a reasonable and reliable reaction pathway is proposed for the interpretation of HT-model formation mechanism. One additional Na atom cooperated into reaction process could help to reduce the reaction energy barrier from 0.89 eV to 0.44 eV, this enhances the reaction probability enormously

and one can expect to form the Na-SMCs at room temperature. Moreover, the simulated STM images of HT-model are in good agreement with the experimental STM observations. Combining these results, we conclude that HT-model is the most plausible model for Na_6Si_3-SMCs on the Si(111)-7 × 7 surface.

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