Global structural optimizations of surface systems with a genetic algorithm

by

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ABSTRACT

Global structural optimizations with a genetic algorithm were performed for atomic cluster and surface systems including aluminum atomic clusters, Si magic clusters on the Si(111) 7×7 surface, silicon high-index surfaces, and Ag-induced Si(111) reconstructions. First, the global structural optimizations of neutral aluminum clusters Al_n (n up to 23) were performed using a genetic algorithm coupled with a tight-binding potential. Second, a genetic algorithm in combination with tight-binding and first-principles calculations were performed to study the structures of magic clusters on the Si(111) 7×7 surface. Extensive calculations show that the magic cluster observed in scanning tunneling microscopy (STM) experiments consist of eight Si atoms. Simulated STM images of the Si magic cluster exhibit a ring-like feature similar to STM experiments. Third, a genetic algorithm coupled with a highly optimized empirical potential were used to determine the lowest energy structure of high-index semiconductor surfaces. The lowest energy structures of Si(105) and Si(114) were determined successfully. The results of Si(105) and Si(114) are reported within the framework of highly optimized empirical potential and first-principles calculations. Finally, a genetic algorithm coupled with Si and Ag tight-binding potentials were used to search for Ag-induced Si(111) reconstructions at various Ag and Si coverages. The optimized structural models of $\sqrt{3}\times\sqrt{3}$, 3×1 , and 5×2 phases were reported using first-principles calculations. A novel model is found to have lower surface energy than the proposed double-honeycomb chained (DHC) model both for Au/Si(111) 5×2 and Ag/Si(111) 5×2 systems.

CHAPTER 1 GENERAL INTRODUCTION

1.1 Introduction

Recently, the term *nano-technology* has been repeatedly mentioned in both science and engineering communities. Nano-technological research focuses primarily on the manipulation of atoms and molecules, the fabrication of devices, and understanding the properties of new materials. The research will eventually enable scientists and engineers to invent a new machine permitted by the laws of physics in the length scale of nanometer (nm). Atomic clusters or nano-clusters, regarded as a new phase of matter, have been studied not only for their interesting physical and chemical properties but also for their future applications. These nanoclusters can form uniform arrays or nanowires on a semiconductor surface. The detailed structural study of nanoclusters in the free space and on a semiconductor surface is a first step to make the dream of nano-machines feasible.

Naturally, physical systems tend to stay at their most stable states after thermal annealing. The most stable state is defined as the structure of a physical system that has the lowest total energy compared to all other possible structures. The physical properties of the systems could be derived theoretically from the structure with the lowest total energy. However, structural determination for a complex physical system is a big challenge. It would take years even decades of effort to determine the lowest energy structure of a complex system. Conventional methods of structural determination in theoretical studies create candidate structures manually relying on human intuition. Adopting a systematic global structural optimization is an alternative way to solve the problem. Among different global structural optimization methods, the genetic algorithm (GA) is one of the most efficient. Earlier successful applica-

tions of the genetic algorithm have been able to discover new low total energy structures for a number of atomic silicon clusters [1]. The properties of these isomers are calculated and compared well with the experimental data.

The total energy of a system can be calculated within the framework of quantum mechanics. The answer to any given physical system can be obtained by solving the *Schrödinger's* equations and calculating the total energy of that system. Density functional theory (DFT) [2] provides a framework for solving the Hamiltonian (*Schrödinger's* equation) and calculating the total energy of realistic physical systems. Since the valence electrons are mostly responsible for the ordinary physical and chemical properties, the frozen core approximation is adopted. Using a pseudopotential (frozen core approximation) to simulate the effect of nucleus and core electrons, the computational cost is significantly reduced [4, 5]. A useful detailed review of the total energy pseudopotential method can be found in article by Payne, Teter, Allan, Arias, and Joannopoulos [3]. However, for complex systems, the first-principles total energy pseudopotential method is too computationally expensive. The alternative is to calculate the total energy of a system using the tight-binding method. Tight-binding calculations [6], which include the basic features of the electronic structures in the description of the interatomic interaction and are much faster than first-principles calculations, are used to treat more complex problems beyond the capacity of the first-principles calculations. When a system contains hundreds thousands or millions of atoms, classical interatomic potential method is the surviving method that is able to simulate and to calculate the total energy of such a system on contemporary computers.

The correct match between theoretical predictions and experimental observations relies on the correct structure which is calculated theoretically using first-principles methods. Scanning tunneling microscopy (STM) [7] invented by Binnig, Rohrer, Gerber, and Weibel in 1982 is one of the experimental techniques to study the surface by probing the electronic structure of a surface. The Nobel Prize was later awarded to Binnig and Rohrer in 1986. The simulated STM images [8] derived from the calculated electronic structure of a correct surface topology should match the experimental STM images. In this dissertation, we apply the genetic

algorithm technique to study several interesting problems in surface physics. The first is in the area of surface dynamical behavior such as step motion and island growth. Dynamic processes on the Si(111) 7×7 surface have been intensively studied over several decades. Experiments [9] showed that Si magic clusters on the Si(111) 7×7 surface are the fundamental units in mass transport phenomena, step fluctuations, detachment and attachment of Si atoms at step edges, and epitaxial growth. In order to understand these magic clusters, the atomic structures of silicon clusters on the Si(111) 7×7 surface with sizes ranging from 6 to 14 were studied. The second involves stable high-index surfaces which have attracted a lot of research interests because they can be used for the fabrication of quantum scale devices at length scales where lithographic techniques are not applicable. The grooved or faceted morphology of these high-index surfaces can, in some cases, be used as a template for the growth of self-assembled nanowires. Understanding how to control and use the morphology of high-index surfaces for different nanoscale applications depends critically on knowledge of the reconstructions of these surfaces. The last involves the growth of metals on the semiconductor surface: the focus of many studies over the past several decades. Metal-induced reconstructions on semiconductor surfaces play an important role in nanotechnology and semiconductor fabrication. One of the prototypical metal-semiconductor interfaces is the silver-silicon interface. Limited reaction or intermixing between two species reduces the complexity of interface structures between them. However, several aspects of the Ag/Si(111) system remain unresolved and need further investigations.

1.2 Dissertation Organization

The study of each physical system will be presented as a separate chapter in the dissertation.

In Chapter 2, global structural optimizations of neutral aluminum clusters Al_n (n up to 23) were performed using a genetic algorithm (GA) coupled with a tight-binding interatomic potential. Structural candidates obtained from GA search were further optimized using first-

principles total energy calculations. The lowest energy structures of neutral Al_n ($n = 2 - 23$) were reported in this chapter. The results show that the icosahedral structure of Al_{13} serves as the core for the growth of aluminum clusters from Al_{14} to Al_{18} .

In Chapter 3, global structural optimizations of the Si magic clusters on the Si(111) 7×7 surface were performed with a genetic algorithm in combination with tight-binding and first-principles calculations. First-principles calculations show that the Si magic cluster observed in scanning tunneling microscopy (STM) experiment [9] consists of eight Si atoms on the faulted half of the Si(111) 7×7 surface. Simulated STM images of the Si magic cluster exhibit a ring-like feature similar to STM experiments.

Chapter 4 shows that the reconstructions of semiconductor surfaces can be determined using a genetic algorithm. Coupled with highly optimized interatomic potentials, the present approach represents an efficient tool for finding good structural candidates for further electronic structure calculations and comparison with scanning tunnelling microscope (STM) images. The efficiency of the genetic algorithm methods applied to the case of Si(105) will be presented in Chapter 4, along with a database of structures that includes the previously found low-energy models and numerous novel configurations.

In Chapter 5, another stable high index surface, Si(114), has been studied using the global structural optimization method. The genetic algorithm coupled with a highly-optimized interatomic potential for silicon leads to finding a set of possible models for Si(114), whose energies are recalculated with first-principles methods. The most stable structure obtained here without experimental input coincides with the structure determined from scanning tunneling microscopy experiments and first-principles calculations by Erwin, Baski and Whitman [Phys. Rev. Lett. 77, 687 (1996)].

In Chapter 6, the study is extended to the metal-semiconductor interface system which has been studied over the last several decades. Global structural optimizations of silver on the Si(111) surface were performed at various Ag and Si coverages using a genetic algorithm coupled with Ag and Si tight-binding potentials. Selected structures obtained from GA search were further optimized using first-principles calculations. Our calculations showed

that the previous proposed structural models, honeycomb chained (HCC) and honeycomb trimer (HCT), are indeed the lowest energy models for 3×1 and $\sqrt{3}\times\sqrt{3}$ phases, respectively. Moreover, a novel structural model was found to have lower surface energy than the double honeycomb chained (DHC) model for both Ag/Si(111) and Au/Si(111) 5×2 phases. Simulated STM images were also calculated and analyzed to compare with the experimental data. A general conclusion and recommendations of future researches will be presented at the end of Chapter 6.

Environmental dependent tight-binding potentials have been adopted for the global structural optimizations in Chapter 2, 3, and 6, the detailed formalism of tight-binding potentials will be presented in the Appendix.

CHAPTER 2 STRUCTURES OF NEUTRAL ALUMINUM CLUSTERS

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2.1 Abstract

We performed global structural optimizations of neutral aluminum clusters Al_n (n up to 23) using a genetic algorithm (GA) coupled with a tight-binding interatomic potential. Structural candidates obtained from our GA search were further optimized using first-principles total energy calculations. We report the lowest energy structures of neutral Al_n ($n = 2 - 23$). We found that the icosahedral structure of Al_{13} serves as the core for the growth of aluminum clusters from Al_{14} to Al_{18} .

2.2 Introduction

An enormous effort has been invested in understanding the size-dependent structural and physical properties of aluminum clusters [10–21]. It is well accepted that for Al_n ($n \leq 5$) the ground-state structures are planar, and that for Al_n ($6 \leq n \leq 11$) the motifs of lowest-energy structures are all based on the octahedron of Al_6 which serves as the nucleation center for the growth of these clusters. Recent study by Akola *et al.* [20] showed that for medium-sized neutral Al_n ($12 \leq n \leq 23$) clusters, the isomers derived from the Al_{13} icosahedral structure are energetically more favorable compared to those from the decahedral or octahedral structures. Furthermore, their study [21] of anionic aluminum clusters showed that the neutral and anionic clusters share the common lowest energy structures in sizes ranging from 12 to 15. In

addition, for larger anionic clusters, Al_{19}^- , Al_{20}^- and Al_{23}^- , the ground state structures proposed by Akola *et al.* produce the photoelectron spectra in very good agreement with experimental data [21]. To the best of our knowledge, there are no detailed studies on the ground state structures of Al_{16} , Al_{17} , Al_{18} , Al_{21} , and Al_{22} using first-principles calculations.

In this chapter, an unbiased global search for the ground state structures of aluminum clusters with sizes ranging from $n = 6$ to $n = 23$ atoms was performed using a genetic algorithm (GA) coupled with a tight binding (TB) interatomic potential. Low energy candidates obtained from the GA/TB search are further optimized using first-principles total energy calculations. We note that two very recent studies [22–24] have also used a genetic algorithm coupled with classical potentials to search for the lowest energy structures of aluminum clusters. It has been shown that the lowest energy structures under a specific potential model could be obtained with a genetic algorithm. Nevertheless, the classical potentials usually fail to reproduce the correct energy ordering of the isomers compared to first-principles calculations. Therefore, it would be interesting to adopt a more accurate interatomic potential such as tight binding potential to the genetic algorithm for a global optimization. By combining the GA/TB search with first-principles calculations, we have successfully determined the lowest energy structures for Al_n ($n = 6$ to 23). Moreover, we observed a clear growth pattern of Al_n ($n = 3$ to 23).

This chapter is arranged as follows: In Chapter 2.3, we discuss briefly the computational methods. Our results and discussion are presented in Chapter 2.4. Finally, a conclusion is drawn in Chapter 2.5.

2.3 Computational Methods

Genetic algorithm (GA) has been successfully used in global structural optimizations of C_{60} [25] and medium-sized silicon clusters [1]. The genetic algorithm used in present study is a variant derived from that used by Deaven and Ho [25] and is described as follows: In generation zero, a population pool of $p = 30$ structures for a given cluster size are generated by

means of putting n atoms randomly in a simulation cubic box with a appropriate length. The structures are relaxed to their local minima using a tight-binding potential with the steepest descent method. The detailed formalism of tight-binding potential used is presented in the Appendix. In each subsequent generation, three types of operations (i.e., mating, mirror, and rotation, which will be described later) are used to generate 15 new structures: 12 from mating, one from the mirror operation, and two from the rotation operation. Then, 15 new structures are relaxed to their nearest local minima by tight-binding calculations. The population pool is updated if the newly relaxed isomers have energies lower than those in the pool and their structures are not identical to any isomer inside the population pool. The structural optimizations with a genetic algorithm were proceeded up to 800 generations. Finally, the energetically favorable isomers retained in the population pool are further optimized using first-principles total energy calculations.

Here we describe the three types of genetic algorithm operations i.e., mating, mirror, and rotation, for creating new structures. In the mating operation, both parents A and B are randomly rotated about their centers of mass which are set to be the origin. Then, by simply cutting the parents structures through the plane of $z = 0$ and permuting the lower-halves (atoms below the plane of $z = 0$) of the parent structures A and B, two new offspring structures C and D can be created. If the number of atoms in the new structure does not match that in the parent, parents A and B are shifted along the z -axis in order to achieve the correct number of atoms. In the present study, two structures from the population pool are picked as parents and a child structure is generated by mating lower-half of parent A with upper-half of parent B. In the mirror operation, a parent structure is picked from the population pool and rotated randomly about its center of mass which is set to be the origin. A offspring is created simply by duplicating the lower-half into the upper-half. The new upper-half is shifted along the z -axis to reach a appropriate distance between two halves. Finally in the third operation, *rotation*, a parent structure is picked from the population pool and rotated randomly about its center of mass which is set to be the origin. A child structure is created by rotating the upper-half in a random angle, while the bottom half is held.

In order to maintain the diversity in the population pool, it is crucial to have a structural comparison algorithm when updating the population pool. Before describing the procedures of the structural comparison algorithm, we will first define the translation-rotation operation below.

Translation-rotation (T-R): The translation-rotation operation rotates the cluster to a certain orientation defined by any three chosen atoms in a cluster. First, we perform a translation to make the first chosen atom as the origin. Next, we perform a rotation on the cluster in order to make the line connecting the first and second atoms oriented along the z -axis. Last, we perform another rotation to make third atom lies on the $x - z$ plane.

Having described the T - R operation, we now elaborate on the algorithm to compare two clusters A and B with size of N atoms. For cluster A, we picked only three atoms and then perform the T - R operation to set its orientation. For cluster B, a total number of $N(N - 1)(N - 2)$ sets of 3-atom coordinates could be chosen to perform the T - R operation. If cluster B is identical to cluster A, there should be a particular set of coordinates in B whose values are identical to those of the 3 chosen atoms in A after the T - R operation. For each set of choices of 3-atom coordinates in cluster B, we performed the T - R operation and calculate the deviations between the positions of these atoms and the corresponding atoms in cluster A. If the maximum deviation is less than $0.35 \text{ \AA}$, then the two structures are regarded as identical. A similar algorithm to perform the structural comparison between two clusters could also be found in the study by Curotto *et al.* [28].

At the end of the global minimum structure search, as many as $p = 30$ structures remain as possible candidates. The selected candidates are further optimized using first-principles total energy calculations. First-principles calculations were done using Vienna *Ab initio* Simulation Package (VASP) [29], which is based on density functional theory, and uses ultrasoft pseudopotentials and plane waves basis. Local density approximation is used for the exchange-correlation functional, and spin-polarization is also calculated. The kinetic energy cutoff is set to be 170 eV. The structural optimization is done with the conjugate gradient algorithm and without symmetry until the forces on the atoms are less than $0.001 \text{ eV/\AA}$. For

clusters containing less than 15 atoms, the length of supercell is set to be 15 Å. For Al₁₅, Al₁₆, Al₁₇, Al₁₈, and Al₁₉ to Al₂₃, the lengths of supercell are 16, 17, 17, 18, and 19 Å, respectively.

2.4 Results and Discussion

2.4.1 Small neutral Al_n clusters (2 ≤ n ≤ 12)

We have performed structural optimizations for aluminum clusters Al₆ to Al₂₃ with a genetic algorithm. The energies presented in this chapter are all done using first-principles calculations. The lowest energy isomers for Al₂ to Al₁₂ are shown in Fig. 2.1. For small clusters containing up to 5 atoms, the structural characteristic of the lowest energy isomers are planar which is in agreement with several other first-principles studies. [14, 15, 17, 18]

For clusters containing 6 to 10 atoms, the geometries transform into a three-dimensional motif and the growth pattern is based on the octahedron of Al₆. The most stable isomer for Al₉ has the structural characteristics of Al₆ with three capped atoms on one side of the octahedron as shown in Fig. 2.1(h). The lowest energy isomer for Al₁₀ is the one where there is one more capped atom on Al₉.

For Al₁₁ and Al₁₂, the structures start to form motifs similar to an icosahedron of Al₁₃. For Al₁₁, the result is similar to the anionic cluster Al₁₁⁻ identified in the study of Rao and Jena [17]. For Al₁₂, we found that two low energy structures are very close to those obtained by removing one atom from an ideal icosahedron of Al₁₃ as shown in Fig. 2.1(k) and (l). The lowest energy isomer shown in Fig. 2.1(k) has larger distortion than the one shown in Fig. 2.1(l). The energy difference per atom between the two isomers is 7.36 meV/atom. However, both isomers have the icosahedral origin of Al₁₃ shown in Fig.2.2(a) [11, 14–18, 20, 21].

Our results for small clusters are consistent with the studies of Jones [15] and Rao *et al.* [17] for sizes ranging from 2 to 10. For Al₁₁ and Al₁₂, the structures obtained from present study are nearly identical to those proposed by Rao and Jena [17]. The small differences in Al₁₁ and Al₁₂ between our results and previous results may be attributed to different pseudopotentials

and exchange-correlation energy functional used in the studies.

2.4.2 Medium-size neutral Al_n clusters ($13 \leq n \leq 23$)

The six low energy isomers of Al_{13} are shown in Fig. 2.2. The lowest energy isomer is the icosahedron shown in Fig. 2.2(a). The energetic ranking of the three isomers shown in Fig. 2.2(a), (b), and (d) is in agreement with that of Akola *et al.* [20]. We found that a new isomer named distorted icosahedron shown in Fig. 2.2(c) is the third lowest energy isomer. As we will see later, this isomer becomes another important building block beside the icosahedral isomer as the cluster increases in size. For clarity, we denote it as "1516" with the numbers indicative of the number of stacking atoms in each layer, and following this numeration we denote the icosahedron as "15151".

For Al_{14} , the low energy isomers contain either one of the building elements from Al_{13} . Some isomers of Al_{14} can be obtained by capping one atom on the icosahedron of Al_{13} as shown in Fig. 2.3(a) and (b). The difference in (a) and (b) is the positions of capped atoms. The lowest energy isomer is a capped icosahedron on one of its faces, whereas the second lowest energy isomer is a capped atom on one bond of the icosahedron as shown in Fig. 2.3(b). Other low energy isomers shown in Fig. 2.3(c) and (f) are found to be one capped atom on the decahedron. Structures with one capped atom on a distorted icosahedron (denoted "1516") at different positions as shown in Fig. 2.3(d) and (e) are energetically not favorable.

For Al_{15} , the first five low energy isomers also contain the two distinct bases of Al_{13} . The lowest energy isomer is the symmetric bi-capped icosahedron which is in agreement with the study of Akola *et al.* [20]. The other isomers can be named as the adjacent bi-capped icosahedron shown in Fig. 2.4(b), the non-adjacent bi-capped decahedron shown in Fig. 2.4(c), the adjacent bi-capped distorted icosahedron shown in Fig. 2.4(d), and the adjacent bi-capped decahedron shown in Fig. 2.4(e). Other than capping, the atoms can also be embedded into the structure. A stacking layer of 16161 shown in Fig. 2.4(f) is obtained by embedding two atoms into the outer surface of the icosahedral Al_{13} . From Al_{12} to Al_{15} , the growth motif starts to appear.

For Al_{16} , the low energy isomers grow in the same manner as Al_{14} and Al_{15} . Basically, three atoms will cap on the surface of Al_{13} isomers in different ways. The lowest energy isomer we found for Al_{16} is the one with a capped atom near either one of the two capped atoms in Al_{15} , forming two adjacent capped atoms and a individually capped atom as shown in Fig. 2.5(a) and (b). It shows that one of the atoms is partially embedded into the icosahedral surface. Other isomers along with the relative energies to the lowest energy structure are shown in Fig. 2.5 as well.

For Al_{17} , the lowest energy structure consists of four capped atoms on an icosahedron, with two sets of two adjacent atoms capping on opposite symmetric positions as shown in Fig. 2.6(a). This is a novel structure and has not been reported in the literatures. The other isomers of Al_{17} are also shown in Fig. 2.6 in order to have a clear comparison.

For Al_{18} , the lowest energy structure shown in Fig. 2.7(a) is formed by capping one more atom to the lowest energy isomer of Al_{17} shown in Fig. 2.6(a). One isomer proposed by Ahlrichs [16] shown in Fig. 2.6(g) is obtained by removing five corner atoms from the decahedron of Al_{23} shown in Fig. 2.9(f). Note that motifs derived from the icosahedron of Al_{13} have better energies than those derived from the decahedron of Al_{13} . In this regard, the icosahedron is the preferred nucleation center for Al_{14} to Al_{18} .

For Al_{19} , the lowest energy isomer is the one with five adjacent atoms and a individually atom capping on the decahedron as shown in Fig. 2.8(a), which is the second lowest anionic isomer in the study of Akola *et al.* [21]. Another low energy isomer (61516) is shown in Fig. 2.8(b), while the most well-known isomer of Al_{19} is the double icosahedron (1515151) as shown in Fig. 2.8(c) which could also be classified as 6 adjacent capped atoms on one side of an icosahedron. This double icosahedron structure is not the lowest energy structure according to first-principles calculations. The other well-known geometrically magic isomer is the octahedron as shown in Fig. 2.8(d). We found that numerous isomers have energies lower than the well-known double icosahedron shown Fig. 2.8(c). Here, we can clearly see that the geometrically magic cluster is not always necessarily the energetically favorable motif.

For Al_{20} , the lowest energy structure shown in Fig. 2.8(e) has one atom embedded into

the double icosahedron of Al_{19} . The structure (denoted "1515161") is prolate in shape and its internal structure is a hybrid between an icosahedral stacking and hexagonal pyramid. This structure is also the lowest energy anionic isomer of Al_{20}^- [21].

For Al_{21} , the lowest energy structure among our calculations is shown in Fig. 2.8(f). This structure of Al_{21} is obtained by capping one atom on the side of Al_{20} shown in Fig. 2.8(e).

The low energy structures of Al_{22} and Al_{23} are shown in Fig. 2.9. For Al_{22} , the first two low energy isomers as shown in Fig. 2.9(a) and (b) are close in energies. A noteworthy feature is that by adding one more atom on second lowest energy isomer of Al_{22} in Fig. 2.9(b), we obtain the lowest energy isomer of Al_{23} shown in Fig. 2.9(d). This lowest energy isomer of Al_{23} is also the lowest energy anionic cluster [21]. In fact, we found several structures have energies lower than that of the icosahedron and that of the decahedron as shown in Fig. 2.9(f) and (g), respectively. One of those low energy isomers is shown in Fig. 2.9(e).

Among the lowest energy structures for Al_{13} to Al_{23} obtained from the present study, the structures of Al_{16} , Al_{17} , Al_{18} , Al_{21} , and Al_{22} are novel, while the structures for Al_{13} to Al_{15} , Al_{19} , Al_{20} and Al_{23} are in agreement with those reported in the literature [21]. We also show that the geometrically magic isomers of Al_{19} and Al_{23} are not necessarily the energetically favorable ones.

2.4.3 Relative stabilities

Studies of fragmentation pathways and dissociation energies provide useful information for understanding the stability of the clusters. It has been found that clusters which frequently appear in the fragmentation products are likely to be relatively stable clusters. The energy needed to dissociate a neutral n -atom cluster into m -atom and $(n-m)$ -atom clusters is given by

$$\Delta E_{nm} = E_m + E_{n-m} - E_n, \quad (2.1)$$

where E_m is the total energy of the cluster with m atoms. The cohesive energies per atom are plotted against the size of the cluster in Fig. 2.10(a), and the fragmentation energies for the energetically most favorable channels obtained from Eq. (2.1) are plotted in Fig. 2.10(b).

We note that for the fragmentation of the neutral clusters, the most dominant channel is the evaporation of *one* atom from the cluster. This result is in agreement with the study of Al_n (n up to 15) by Rao *et al.* [17]. The relative stable isomers from our present study are found to be $n = 7, 13, 16, 20$, and 22 , as one can see from the plot of Fig. 2.10(b).

2.5 Conclusion

We have performed global structural optimizations for aluminum neutral clusters Al_n , n up to 23 atoms. The low energy isomers of Al_2 - Al_{23} are obtained based on first-principles calculations. Novel lowest-energy structures for Al_{16} , Al_{17} , Al_{18} , Al_{21} , and Al_{22} have been determined from first-principles calculations. From the fragmentation energy analysis, the size of the relative stable clusters are found to be $n = 7, 13, 16, 20$, and 22 .

We have also studied the growth motif for Al_n ($2 \leq n \leq 23$). For n from 2 to 5, the structures are planar. For n from 6 to 10, the structures become three dimensional with additional capped atoms on the octahedron of Al_6 . For n from 11 to 13, the clusters start to form the icosahedral-like motif. The growth pattern from Al_{14} to Al_{18} is mainly based on the mechanism of capping extra atoms on the icosahedron of Al_{13} . For $n \geq 19$, the structures undergo additional structural transformations. The lowest energy isomer of Al_{19} consists of five adjacent atoms and a individually atom capping on the decahedron isomer of Al_{13} as shown in Fig. 2.8(a). Al_{20} and Al_{21} share the same motif of capping atoms on the double icosahedron. For $n \geq 22$, the aluminum clusters begin to grow into a different motif.

2.6 Acknowledgement

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Figure 2.1 (a) to (k): The lowest-energy isomers of neutral Al_2 to Al_{12} . (l) is the lowest energy isomer of Al_{12}^- . The numbers in the parentheses and under the structures are relative energies per atom (in meV/atom) with respect to that of the lowest energy isomer of the same size.

Figure 2.2 Low energy isomers of Al_{13} . The numbers under the structures are the relative total energies per atom (in meV/atom) with respect to that of the lowest energy isomer.

Figure 2.3 Low energy isomers of Al_{14} . The numbers under the structures are relative energies per atom(in meV/atom) with respect to that of the lowest energy isomer.

Figure 2.4 Low energy isomers of Al_{15} . The numbers under the structures are relative energies per atom(in meV/atom) with respect to that of the lowest energy isomer.

Figure 2.5 Low energy isomers of Al_{16} . The numbers under the structures are relative energies per atom (in meV/atom) with respect to that of the lowest energy isomer.

Figure 2.6 Low energy isomers of Al_{17} . The numbers under the structures are relative energies per atom(in meV/atom) with respect to that of the lowest energy isomer.

Figure 2.7 Low energy isomers of Al_{18} . The numbers under the structures are relative energies per atom (in meV/atom) with respect to that of the lowest energy isomer.

Figure 2.8 (a), (b), (c), and (d) are isomers of Al_{19} . (e) is the lowest energy isomer of Al_{20} ; (f) is the lowest energy isomer of Al_{21} . The numbers under the structures are relative energies per atom (in meV/atom) with respect to that of the lowest energy isomer of the same size.

Figure 2.9 (a), (b), and (c) are isomers of Al_{22} ; (d), (e), (f), and (g) are that of Al_{23} . The numbers under the structures are relative energies per atom (in meV/atom) with respect to that of the lowest energy isomer of the same size.

Figure 2.10 (a) The cohesive energy v.s. size of the cluster. (b) The fragmentation energy ($\Delta E_{nm} = E_m + E_{n-m} - E_n$) v.s. size of the cluster.

CHAPTER 3 GLOBAL STRUCTURAL OPTIMIZATION OF SILICON MAGIC CLUSTERS ON THE SILICON (111) 7×7 SURFACE

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3.1 Abstract

We performed global structural optimization using a genetic algorithm in combination with tight-binding and first-principles calculations to study the structures of the magic clusters on the Si(111) 7×7 surface. Our calculations show that the magic cluster observed in scanning tunneling microscopy (STM) experiment [9] consists of eight Si atoms on the faulted half of the Si(111) 7×7 surface. Simulated STM images of our Si magic cluster exhibit a ring-like feature similar to STM experiments.

3.2 Introduction

Magic clusters on semiconductor surfaces [9, 30–32] may play an important role in the fabrication of surface nanostructures with uniform size and shape distribution. These magic clusters are energetically stable entities on the substrate and are able to diffuse as a whole. Formation of Si magic clusters on the Si(111) 7×7 surface has been studied by Hwang *et al.* [9] using scanning tunneling microscopy (STM). They showed that Si magic clusters on the Si(111) 7×7 surface are the fundamental units in mass transport phenomena, step fluctuations, detachment and attachment of Si atoms at step edges, and epitaxial growth. More recently, magic clusters and ordered arrays of magic clusters formed upon deposition

of Al, In, and Ga on the Si(111) 7×7 surface have also been observed experimentally using STM [30–32].

While STM studies give valuable information about the overall shape and the size of the magic clusters on the Si(111) 7×7 surface, the images from STM cannot provide exact determination of the detailed atomic structure of the magic clusters. A comprehensive understanding of the structural and dynamical properties of the magic clusters on the surfaces would be very important for precise manipulation of nanostructures assembly on semiconductor substrate and for studying the properties of these assembled nanostructures.

In this chapter, we focus on determining the structures of the Si magic clusters on the Si(111) 7×7 surface as a first step towards understanding their atomic structures, electronic properties, and future applications. Global structural optimization is developed and performed using genetic algorithm (GA) coupled with the environment-dependent Si tight-binding (TB) potential [6]. The detailed formalism of tight-binding potential is also presented in Appendix. The low energy candidates selected from the GA optimizations were further relaxed using first-principles total energy calculations. Simulated STM images were calculated to compare with experimental observations.

The STM studies by Hwang *et al.* showed that Si magic clusters appear on the faulted half of the Si(111) 7×7 unit cell, and are approximately 1.5 Å higher than the Si adatoms of the Si(111) 7×7 surface [9]. The mirror symmetry of the (7×7) reconstruction along the $[\bar{1}\bar{1}2]$ direction is broken due to the presence of the cluster. The empty state STM image shows six or three protrusions of nearly equal brightness forming a ring-like structure [9]. The spacing between adjacent protrusions is much larger than the length of the Si-Si bond, indicating that the cluster probably contains more than six Si atoms. The size of the magic cluster is estimated to be between 9 and 15 Si atoms by Hwang *et al.* Dynamical studies show that these magic clusters diffuse as a unit and are still observable up to a temperature of 500° C. While the magic clusters diffuse on the surface, the detachment of those clusters leave the surface intact. This experimental information is very useful for guiding the design of our atomic structure search strategy as described below.

3.3 Methods

The genetic algorithm (GA) has been used successfully in global structural optimization for isolated clusters [1, 25]. In Chapter 2, such a genetic algorithm has been applied to the structural optimizations of aluminum clusters as well. Very recently, we have also successfully applied the genetic algorithm to study the reconstructions of high-index silicon surfaces [26, 27]. In this Chapter, a new version of the genetic algorithm is developed to study the atomic structure of the magic cluster on the Si(111) 7×7 surface. We note that the total number of atoms involved in a Si(111) 7×7 substrate is too large for performing such global minimum search using tight-binding potential. Obviously, the total number of the atoms involved in the GA operations needs to be reduced. Since the magic clusters are found to be located on one half of the 7×7 unit cell, our GA optimization is performed only on a half unit cell of the 7×7 reconstruction together with the dimers at the boundary between the faulted and the unfaulted halves of the (7×7) reconstruction as shown in Fig. 3.1. We also note that the bonding between the magic cluster and the substrate involves mostly the top substrate atoms since diffusion of the magic cluster leaves the surface reconstruction intact. Therefore, only one Si bilayer is used to model the substrate in order to further reduce the number of atoms involved in the GA optimization. The bottom layer of the slab and the Si dangling bonds at the edge of the unit cell are passivated by hydrogen atoms. The final modeling substrate is shown in Fig. 3.1.

Once the substrate is chosen, the procedures of our genetic algorithm are as follows. We generate ten geometries as initial population ($p=10$) by randomly placing a specific number of Si atoms n on the half unit cell and then relaxing the structure to a local minimum. The relaxation is done using tight binding potential with the steepest descent method. In each subsequent generation, four distinct geometries are randomly picked from the population pool. Then twelve new geometries are generated from the four parents through the mating operation described below. These children geometries are then relaxed to their nearest local minima. The population of ten geometries in the pool is updated if any child geometry has

Figure 3.1 The top view (upper) and the side view (lower) of the half unit cell Si(111) 7×7 substrate used in the genetic algorithm. The three adatoms (labeled with A) and the three rest atoms (labeled with R) involved in the GA mating process are those in gray and black, respectively, whereas the atoms which are not involved in the GA operation are shown in white. Big white circles are the Si atoms, whereas the small circles are the H atoms. The Si dangling bonds at the edges and at the bottom of the unit cell are passivated with hydrogen.

different structure and lower energy than any of those in the present population pool. The genetic algorithm was implemented up to 400 generations.

The mating operation produces a child geometry C from the two given parent geometries A and B as follows. For each of the parent geometry, the atoms in the cluster along with three rest atoms and three adatoms (the dark and grey atoms in Fig. 3.1) on a half unit cell substrate are chosen to be mated. The centers of mass of these chosen atoms in both geometries are then calculated and both parents are cut through the centers of mass with randomly chosen parallel planes. The child geometry C is created by assembling the right half of the chosen atoms in the parent A and the left half of the chosen atoms in the parent B. The resultant atomic configuration of this child C is placed back on the substrate which has three rest atoms and three adatoms removed as illustrated in Fig. 3.1. During the mating process, the number of atoms in the resultant child C is forced to be the same as that in its parents.

We note that the energy calculations using a one-bilayer substrate cannot differentiate between faulted half and unfaulted half of the Si(111) 7×7 substrate. Therefore, the candidate geometries obtained from the genetic algorithm described above are further optimized using TBMD by augmenting the structures with a two-bilayer full Si 7×7 substrate. The bottom layer of the substrate is passivated by H, and this two-bilayer full Si 7×7 substrate contains 200 Si atoms and 49 H atoms with a periodic boundary condition parallel to the surface. Two individual optimizations of each structure are done by putting the cluster on either the faulted half or the unfaulted half of the substrate. Finally, the best geometries obtained from genetic algorithm and TBMD optimizations are further studied by first-principles total energy calculations using the same full Si 7×7 substrate. First-principles calculations in this work have been done using the PWscf package [33], which is based on density functional theory [2] under local density approximations and uses pseudopotential and plane wave basis. The Ceperley-Alder functional [34] parameterized by Perdew and Zunger [35] is used for the exchange-correlation energy functional. The kinetic energy cutoff is set to be 12 *Ry* and Γ -point is used in the Brillouin zone sum. A vacuum layer of 12 Å is used in the calculations.

Moreover, the structures are optimized until the forces are less than 0.025 eV/Å.

3.4 Results and Discussion

We have performed global structural optimization for Si clusters on Si(111) 7×7 for sizes ranging from $n=6$ to $n=14$. The lowest energy structure of each size is showed in Fig. 3.2 where only the faulted half of the 7×7 unit cell is shown for clarity. In all structures, one of the substrate adatoms is found to be incorporated into the Si cluster. This incorporation will leave three back-bond atoms unbonded and the Si cluster will subsequently anchor itself to these back-bond atoms. This structural feature justifies the necessity of including the three adatoms and the three rest atoms of the substrate in our GA mating operation. For $n=6$, the structure obtained by placing six Si atoms at the bright spots as indicated in the STM experiment [9] is not stable according to our first-principles calculations. Instead, our genetic algorithm for $n=6$ found that a six-member ring with an extra Si atom at the center is the lowest energy structure as shown in Fig. 3.2(a). The bonds between one of the substrate adatoms and the corresponding three back-bond atoms are broken and the adatom is bonded with the deposited atoms. Another noteworthy feature is that for $n < 12$ the cluster exhibits a nearly planar geometry on the surface, whereas for $n \geq 13$ the cluster starts to show a three-dimensional growth.

In order to determine the size n of the magic cluster observed in experiments and to study the relative stability of different sizes of Si clusters on the Si(111) surface, we calculated the surface energy per cluster atom E_s as follows:

$$E_s = \frac{E - E_{sub} - nE_{bulk}}{n} \quad (3.1)$$

where E is the total energy of the cluster on the Si(111) 7×7 substrate, E_{sub} is the energy of the Si(111) 7×7 substrate, and E_{bulk} is the energy of bulk Si (per atom) in crystalline diamond structure. We first checked the surface energy ordering of different-sized clusters on the surface using tight-binding calculations. We found that the energy ordering is the same regardless the choice of substrate, i.e, half unit cell or the full 7×7 substrate, and the thickness

of the substrate. This result indicates that the reduced Si substrate we used in our GA global search is sufficient for the present study. The plots of surface energies versus the size of the Si cluster obtained from the tight-binding calculation and first-principles calculations are shown in Fig. 3.3(a) and (b), respectively. The plots show that Si cluster on the faulted half of the 7×7 substrate is energetically more favorable than that on the unfaulted half. This agrees with STM observations that statistically more magic clusters reside on the faulted half than on the unfaulted half of the Si(111) 7×7 surface. We found that there is a sharp dip in the surface energy at $n=8$, which is the most stable Si cluster on Si(111) 7×7 among the sizes that we considered. By comparing Fig. 3.3(a) and (b), we found that our tight-binding Si potential can reproduce the overall trend of the surface energies versus size of the Si cluster.

Our calculations suggest that the magic Si cluster on Si(111) 7×7 surface should correspond to the $n = 8$ structure as shown in Fig. 3.2(c) (as well as Fig. 3.4). This structure is energetically most favorable when compared with the other structures. The presence of this magic cluster ($n = 8$) minimizes its own dangling bonds while saturating that of the clean Si(111) 7×7 reconstruction surface, and does not introduce extra strained bonds or 5-fold Si coordination. We calculated simulated STM images using our atomic model of the Si magic cluster and compare it with experimental STM image. The simulated STM images are calculated according to the theory of Tersoff and Hamann [8] by tracing the height profile of constant tunneling current to produce a three-dimensional surface, which is then projected onto the xy -plane to produce our simulated STM images. Our calculated empty state images with a bias of +1V for $n = 8$ and 9 are shown in Fig. 3.4. Both simulated empty state images show a ring-like feature. Within the ring, one circular bright spots and two elongated spots can be found for $n = 8$, while there are six bright spots for $n = 9$. The experimental image shows three spots, whereas the other STM image shows six equally bright spots in Fig. 1(b) and 1(c) of the article by Hwang, Ho, and Tsong¹. The difference between the two experimental images was attributed to tip effects. We note that our lowest energy $n =$

¹Surface Science, **514**, Ing-Shouh Hwang, Mon-Shu Ho, and Tien-Tzou Tsong, *Dynamic behavior of Si magic clusters on Si(1 1 1) surfaces*, Page 309-318, (2002).

8 structure has actually two degenerate states, one is shown in Fig. 3.4, and the other is the mirror image of the first one along the $[11\bar{2}]$ direction. We have done TBMD simulation of our $n = 8$ structure at elevated temperature, we found that there can be flipping between the two degenerate $n = 8$ states. Due to the time-averaging of the two states, the experimental STM image would have a total of six spots instead of three as shown in Fig. 1(c) of the article by Hwang, Ho, and Tsong¹. However, there may be interactions between the STM tip and the magic cluster such that one of the degenerate geometry is pinned, and hence the experiments can also observe three spots instead of six for certain STM tips as shown in Fig. 1(b) of the article by Hwang, Ho, and Tsong¹. Apart from the ring, both our simulated images show three additional spots due to the three unsaturated atoms of the Si clusters, which are not observed in STM experiments [9]. It is possible that the three additional spots were not resolved by experiments due to the finite size of the STM tip and shadowing effects at the edge of the cluster on the surface.

3.5 Conclusion

In summary, we have performed global structural optimization using genetic algorithm to search for the ground state structures of Si clusters on the Si(111) 7×7 surface for $n = 6$ up to 14. We found that Si clusters prefer to reside on the faulted half of the 7×7 substrate for all the sizes studied. When the Si cluster contains 13 atoms or more, it begins to exhibit three-dimensional growth. Placing six Si atoms according to the experimental bright spot positions does not produce a stable structure. Instead, our study suggests that the structure with $n=8$ as shown in Fig. 3.2(c) (as well as Fig. 3.4) could be the magic cluster observed in STM experiments [9].

3.6 Acknowledgement

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Figure 3.2 The geometries of clusters with sizes ranging from $n=6$ to 14 obtained by the genetic algorithm. The Si atoms in the cluster are colored red, while the three adatoms and the three rest atoms in the substrate that are involved in mating process are colored blue and green, respectively. The geometries shown are optimized with a full 7×7 unit cell. For clarity, only the faulted half of the Si(111) 7×7 surface is shown in the figure.

Figure 3.3 The surface energy per cluster atom calculated by (a) the tight-binding potential method, and (b) by first-principles calculations. The curve with circles (square) corresponds to the Si cluster being placed on the faulted (unfaulted) half of the Si(111) 7×7 substrate.

Figure 3.4 Top: The positions of the cluster atoms for $n=8$ (left) and $n=9$ (right), the adatoms, and rest atoms on the Si(111) 7×7 are indicated and are colored in the same way as that in Fig. 3.2. Bottom: The simulated STM images of the $n=8$ Si cluster (left) and $n=9$ Si cluster (right) with a bias of +1V.

CHAPTER 4 FINDING THE LOWEST ENERGY STRUCTURE OF SILICON (105) WITH A GENETIC ALGORITHM

A paper published in Surface Science¹

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4.1 Abstract

In this chapter we show that the reconstructions of semiconductor surfaces can be determined using a genetic procedure. Coupled with highly optimized interatomic potentials, the present approach represents an efficient tool for finding and sorting good structural candidates for further electronic structure calculations and comparison with scanning tunnelling microscope (STM) images. We illustrate the method for the case of Si(105), and build a database of structures that includes the previously found low-energy models, as well as a number of novel configurations.

4.2 Introduction

The determination of atomic structure of crystalline surfaces is a long-standing problem in surface science. Despite major progress brought by experimental techniques such as scanning tunnelling microscopy (STM) and advanced theoretical methods for treating the electronic and ionic motion, the commonly used procedures for finding the atomic structure of surfaces still rely to a large extent on one's intuition in interpreting STM images. While

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these procedures have proven successful for determining the atomic configuration of many low-index surfaces, in the case of high-index surfaces their usefulness is limited because the number of good structural models for high-index surfaces is rather large, and may not be exhausted heuristically. An illustrative example is Si(5 5 12), whose structure has been the subject of intense dispute [36–39] since the publication of the first atomic model proposed for this surface [40]. While the structure of Si(5 5 12) may still be an open problem, there are other stable surfaces of silicon such as (113) [41] and (105) that required a long time for their structures to be revealed. In this chapter, we focus on Si(105) and show that there is a large number of low-energy models for this surface.

The high-index surfaces attract a great deal of scientific and technological interest since they can serve as natural and inexpensive templates for the fabrication of low-dimensional nanoscale structures. Knowledge about the template surface can lead to new ways of engineering the morphological and physical properties of these nanostructures. The main technique for investigating atomic-scale features of surfaces is STM, although, as pointed out in a recent review, STM alone is only able to provide "a range of speculative structural models which are increasingly regarded as solved surface structures" [42]. With few exceptions that concern low-index metallic surfaces [43, 44], the role of theoretical methods for structural optimization of surfaces has been largely reduced to the relaxation of these speculative models. However, the publication of numerous studies that report different structures for a given high-index silicon surface [36–40] indicates a need to develop methodologies capable of actually searching for the atomic structure in a way that does not predominantly rely on the heuristic reasoning associated with interpreting STM data. Recently, it was shown that parallel-tempering Monte Carlo (PTMC) simulations combined with an exponential cooling schedule can successfully address the problem of finding the reconstructions of high-index silicon surfaces [45]. The PTMC simulations, however, have a broader scope, as they are used to perform a thorough thermodynamic sampling of the surface systems under study. Given their scope, such calculations [45] are very demanding, usually requiring several tens of processors that run canonical simulations at different temperatures and exchange config-

urations in order to drive the low-temperature replicas into the ground state. If we focus only on finding the reconstructions at zero Kelvin (which can be representative for crystal surfaces in the low-temperature regimes achieved in laboratory conditions), it is then justified to explore alternative methods for finding the structure of high-index surfaces.

Here, we address the problem of surface structure determination at zero Kelvin, and report a genetically-based strategy for finding the reconstructions of elemental semiconductor surfaces. Our choice for developing this genetic algorithm (GA) was motivated by its successful application for the structural optimization of atomic clusters [1, 25] and for Si magic clusters on the Si(111) 7×7 surface [see Chapter 3]. Like the study using PTMC method by Ciobanu and Predescu [45], the genetic algorithm in present study also circumvents the intuitive process when proposing candidate models for a given high-index surface. Except for the periodic vectors of the surface unit cell [which can be determined from scanning tunnelling microscopy (STM) or from low-energy electron diffraction (LEED) measurements], no other experimental input is necessary. An advantage of the genetic algorithm over most of the previous methodologies used for structural optimization is that the number of atoms involved in the reconstruction, as well as their most favorable bonding topology, can be found within the same genetic search. Since the interactions are modelled by empirical potentials, it is generally desirable to check the relative stability of different model structures using higher-level calculations based on density functional theory. Here we test the genetic algorithm on the (105) surface, which, at least in conditions of compressive strain, is known to have a single-height rebonded step structure SR [46–50]. The PTMC study [45] indicates that the SR structure is the lowest surface energy even in the absence of strain, although there are several other reconstructions with very similar surface energies. It is interesting to note that the number of reported reconstructions for the (105) orientation has increased very rapidly from two (models SU and SR [46–48]), to a total of fourteen reported in the literature [45, 49]. While the set of known reconstructions has expanded, the most favorable structure has remained the SR model –in contrast with the first reported model [51], but in agreement with more recent studies [46–48].

Figure 4.1 The mating operation $\mathcal{O} : (A,B) \rightarrow C$. From two candidate surface structures A and B, the upper portions (5 Å -thick) are separated and sectioned by the same arbitrary plane oriented perpendicular to the surface. A new slab C is created by combining the part of A that lies to the left of the cutting plane and the part of slab B lying to the right of that plane. C is placed on a thicker slab, and the resulting structure is relaxed before considering its inclusion in the pool of candidate reconstructions.

4.3 Computational Methods

The study in Chapter 3 shows that the genetic algorithm would also be used for the surface systems. A specially designed genetic algorithm used to study the reconstruction surface will be described in this Chapter. Before describing the genetic algorithm, we pause to briefly discuss the computational details. The simulation cell has a single-face slab geometry with periodic boundary conditions applied in the plane of the surface, and no periodicity in the direction normal to it. The top atoms corresponding to a depth $d = 5 \text{ Å}$ (measured from the position of the highest atom) are shuffled via a set of genetic operations described below. In order to properly account for the surface stress, the atoms in a thicker zone of 15–20 Å are allowed to

relax to a local minimum of the potential energy after each genetic operation. In the present work, we first test the genetic algorithm for the case of Si(105) 2×1 ; the surface slab is made of four bulk unit cells of dimensions $a\sqrt{6.5} \times a \times a\sqrt{6.5}$ ($a = 5.431$ Å is the bulk lattice constant of Si), stacked two by two along the [010] and [105] directions. In terms of atomic interactions, we have used the highly-optimized empirical model developed by Lenosky *et al.* [52], which was found to have superior transferability to the diverse bonding environments present on high-index silicon surfaces [45].

The optimization procedure developed here is based on the idea of evolutionary approach in which the members of a generation (pool of models for the surface) mate with the goal of producing the best specimens, i.e. lowest energy reconstructions. "Generation zero" is a pool of p different structures obtained by randomizing the positions of the topmost atoms (thickness d), and by subsequently relaxing the simulation slabs through a conjugate-gradient procedure. The evolution from a generation to the next one takes place by mating, which is achieved by subjecting two randomly picked structures from the pool to a certain operation $\mathcal{O}:(A,B)\longrightarrow C$. Before defining this operation, we describe how the survival of the fittest is implemented. In each generation, a number of m mating operations are performed. The resulting m children are relaxed and considered for the possible inclusion in the pool based on their surface energy. If there exists at least one candidate in the pool that has a higher surface energy than that of the child considered, then the child structure is included in the pool. Upon inclusion of the child, the structure with the highest surface energy is discarded in order to preserve the total population p . As described, the genetic algorithm favors the crowding of the ecology with identical metastable configurations, which slows down the evolution towards the global minimum. To avoid the duplication of members, we retain a new structure only if its surface energy differs by more than δ when compared to the surface energy of any of the current members p of the pool. We also consider a criterion based on atomic displacements to account for the (theoretically possible) situation in which two structures have equal energy but different topologies: two models are considered structurally different if the relative displacement of at least one pair of corresponding atoms is greater

than ϵ . Relevant values for the parameters of the genetic algorithm are $10 \leq p \leq 40$, $m = 10$, $d = 5 \text{ \AA}$, $\delta = 10^{-5} \text{ meV/\AA}^2$, and $\epsilon = 0.2 \text{ \AA}$.

We now describe the mating operation illustrated in Fig. 4.1, which produces a child structure from two parent configurations as follows. The topmost parts of the parent models A and B (thickness d) are separated from the underlying bulk and sectioned by an arbitrary plane perpendicular to the surface. The child structure C is created by combining the part of A that lies to the left of the cutting plane and the part of slab B lying to the right of that plane: the assembly is placed on a thicker slab, and the resulting structure C is relaxed. We have found that the genetic algorithm mating operation is more efficient when the cutting plane is not constrained to pass through the center of the surface unit cell, and also when that plane is not too close to the cell boundaries. Therefore, we pick the cutting plane such that it passes through a random point situated within a rectangle centered inside the unit cell; numerical experimentation has shown that the algorithm performs very well if the area of that rectangle is about 80% of the area of the surface cell. Two versions of the genetic algorithm were developed. In the first version, the number of atoms n is kept the same for every member of the pool by automatically rejecting child structures that have different numbers of atoms from their parents (mutants). In the second version of the genetic algorithm, this restriction is not enforced, i.e. mutants are allowed to be part of the pool. As we shall see, the genetic algorithm is able to select the correct number of atoms for the low energy structures without any increase over the computational effort required for one single constant- n GA run.

4.4 Results and Discussion

4.4.1 Si(105) 2×1

The results for a Si(105) slab with 206 atoms (constant n) are summarized in Fig. 4.2(a), which shows the surface energy of the most stable member of a pool of $p = 30$ candidates as a function of the number of genetic operations. The lowest surface energy starts at a very high value because the members of early generations have random surface topologies.

We find that in less than 200 mating operations the most favorable structure in the pool is already reconstructed, i.e. each atom at the surface has at most one dangling (unsatisfied) bond. Furthermore, the density of dangling bonds (db) per unit area is the smallest possible for the Si(105) surface: the structure obtained is a double-step model termed DT [45] that has $4 \text{ db}/a^2\sqrt{6.5}$. The single-height rebonded structure SR [46–48] is retrieved in less than 400 mating operations. The SR model is in fact the global minimum for Si(105), as found recently in an exhaustive PTMC search [45]. We have verified this finding by performing constant- n GA runs for a set of consecutive numbers of atoms, $n = 206, 205, 204$, and 203 . These GA searches have retrieved all the models obtained in PTMC search [45] and also obtained some new models that is not found in PTMC search.

However, we take a further step in that we seamlessly integrate the search for the correct number of atoms within the search for the lowest-energy reconstruction: we achieve this by allowing energetically fit mutants to survive during the evolution, instead of restricting the number of atoms to be constant across the pool (use second version of mating operation). The results from a GA run with variable n are shown in Fig. 4.2(b), in comparison with an $n = 206$ run. We notice that the variable- n evolution displays a faster drop in the lowest surface energy, as well as in the average energy across the pool. For performance testing purposes, we started the variable- n run with all the candidates having an unfavorable number of particles, $n = 204$. Nevertheless, the most stable member in the pool predominantly selected a number of atoms that allows for the SR topology, i.e. $n = 198, 202$, and 206 as shown in Fig. 4.2(c). While we find no significant difference in the computational effort required by the two different evolutions, the variable- n and the constant- n ($n = 206$), the former is to be preferred: since the surface energy of a Si(105) slab is a periodic function of the number of atoms [45] with a period of $\Delta n = 4$, the variable- n run is ultimately four times faster than the sequential constant- n searches. The results from the sequential runs are summarized in Table 4.1, which shows the surface energies of twenty structures from runs with $n = 206, 205, 204$, and 203 .

4.4.2 Si(105) 2×2

Motivated by recent experimental work [53] that suggests the presence of a structure with large periodic length in the $[50\bar{1}]$ direction, we have also performed constant- n GA searches for configurations with larger surface unit cells ($2a\sqrt{6.5} \times 2a$), with n ranging from 405 to 412 atoms (double of 206 atoms and a period of $\Delta n = 8$). We found that the lowest energy model for Si(105) 2×2 is still SR model with the number of atoms $n = 412$ summarized in Table 4.1. To compare the efficiency between GA and PTMC, the results of GA run with $n = 406$ are illustrated in Fig. 4.3. A low-energy structure model of (105) 2×2 reconstruction of this size (termed DR2) was reported in earlier work by Ciobanu, Shenoy, Wang, and Ho [49], where it showed that step-edge rebonding lowers the surface energy below that of the proposed DU1 model [53]. Moreover, upon annealing, the DR2 model can evolve into three structures with lower surface energies, DR2 γ , DR2 β and DR2 α using PTMC method by Ciobanu and Predescu [45]. Using the GA technique described above, several structural models are found to be energetically more favorable than DR2 α shown in Fig. 4.3. For the number of atoms $n=406$, Fig. 4.4(a) and (b) shows the two structures obtained from GA which have lower energies than DR2 α obtained by PTMC method [45]. The results displayed in Fig. 4.3 indicate that the efficiency of the genetic algorithm improves upon increasing the number of candidates in the pool, from $p = 30$ to $p = 40$. In both cases, within couple thousands of the genetic operations, the evolution retrieves in the same lowest energy structure with $\gamma = 83.33 \text{ meV}/\text{\AA}^2$, which is lower than and nearly degenerate with DR2 α , as the surface energy difference is only $\sim 0.44 \text{ meV}/\text{\AA}^2$.

It is noteworthy that, within the current computational resources, the variable- n genetic algorithm performs quite well even when the number of atoms is doubled. We have also run a variable- n calculation with all the structures in the pool having a number of atoms ($n=406$) which does not correspond to the optimal configuration ($n = 412$): this simulation still retrieves the SR model, which is the global minimum of $n=412$ (double of 206), within about 10,000 genetic operations. Since the GA search have been performed with an empirical

potential, the energy order using an empirical potential will not be the same with that using first-principles calculations. It is necessary to examine those models with the first-principles calculations. Such an issue will be addressed and clearly shown in the next chapter.

4.5 Conclusion

We have shown that the reconstruction of semiconductor surfaces can be determined via a genetic algorithm. This procedure can be used to generate a database of model configurations for any given high-index surface, models that can be subsequently relaxed using electronic structure methods and compared with available experimental data. The process of systematically building a set of models for a given surface drastically reduces the probability of missing the actual physical reconstruction, which imminently appears when heuristic approaches are used [40, 51]. The genetic algorithm presented here can naturally select the number of atoms required for the topology of the most stable reconstruction, as well as the lowest-energy bonding configuration for that number of atoms. Future work will be focused on other high-index silicon and germanium surfaces [39, 54, 55]. We will show a systematic study of Si(1114) in the next Chapter combining GA search and first-principles calculations.

4.6 Acknowledgement

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Figure 4.2 (a) Surface energy γ of the most stable Si(105) candidate from a pool of $p = 30$ structures (206-atom slabs with dimensions $a\sqrt{6.5} \times 2a$), plotted as a function of the number of mating operations. The insets show top views (i.e. along the $[\bar{1}05]$ direction) of the DT and SR models; atoms are rainbow-colored according to their coordinate along the $[105]$ direction (red being the highest), and the rectangles show the surface unit cells. (b) Comparison between runs with variable number ($198 \leq n \leq 210$) of atoms (red lines) and constant n , $n = 206$ (black lines). The lowest (average) surface energies are shown as solid (dashed) lines. (c) The variation of the number of atoms.

Figure 4.3 Lowest surface energy γ for pools of $p = 30$ and $p = 40$ Si(105) candidate models. The simulation slab has a periodic cell of $2a\sqrt{6.5} \times 2a$ and contains $n = 406$ atoms, of which the highest-lying 70 atoms are subject to mating operations. As seen in the inset, the procedure finds two structures ((a) and (b)), that are slightly more stable than the DR2 α model obtained using PTMC method [45]; these configurations are shown in Fig. 4.4, along with DR2 α .

Figure 4.4 Low-energy structures of the $2a\sqrt{6.5} \times 2a$, 406-atom surface unit cells (rectangles) for Si(105). The surface energies γ are indicated next to the corresponding model labels. Atoms are rainbow-colored according to their height, as described in Fig. 4.2.

n	Surface energy (meV/Å ²)	Label from Refs. [45, 49]
206	82.20	SR
	85.12	DT
	88.12	DU1
	88.28	
	88.35	SU
205	86.73	DY1
	88.59	DY2
	88.61	
	88.70	
204	88.97	
	84.90	DX1
	86.04	DX2
	88.98	
	89.11	
203	89.78	
	86.52	DR1
	87.74	
	89.49	
	90.50	
412	90.54	
	82.20	SR
	82.82	
	82.94	
	83.70	
406	84.12	
	83.33	
	83.68	
	83.77	DR2 α
	83.82	
	84.99	

Table 4.1 Surface energies of 20 different Si(105) 2×1 and 10 different Si(105) 2×2 reconstructions obtained by the genetic algorithm (GA), calculated using the HOEP interatomic potential [52]. The structures are grouped according to the number of atoms n in the simulation cell.

CHAPTER 5 STRUCTURE OF SILICON (114) DETERMINED BY A GENETIC ALGORITHM

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5.1 Abstract

In this chapter we report the results of global structural optimization of the Si(114) surface, which is a stable high-index orientation of silicon. We use the genetic algorithm recently developed for the determination of surface reconstructions. The procedure, coupled with the use of a highly-optimized interatomic potential for silicon, lead to finding a set of possible models for Si(114), whose energies are recalculated with density functional methods. The most stable structure obtained here without experimental input coincides with the structure determined from scanning tunneling microscopy experiments and density functional calculations by Erwin, Baski and Whitman [Phys. Rev. Lett. 77, 687 (1996)].

5.2 Introduction

Treating the reconstruction of semiconductor surfaces as a problem of global optimization, we have developed and shown the genetic algorithm for structural determination in chapter 4 [26]. As described in previous chapter, the use of such method can help avoid situations in which the actual physical reconstruction of a high-index surface is not part of the set

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of heuristic models that are considered for computation of surface energies and comparison with experimental data. Given that there are examples of semiconductor surfaces [40, 51] for which the initially proposed models did not withstand further scientific scrutiny from different research groups, it appears worthwhile to perform searches for the structure of some other stable high-index surface orientations of silicon. One such surface is Si(114), reported to be as stable as the well studied low-index surfaces Si(001) and Si(111) [57]: given this stability of Si(114), it is somewhat surprising that this surface has not attracted more interest, at least from a technological perspective. There are few studies of Si(114) to date, which include the pioneering study reporting on the atomic configuration [57], and two recent works reporting on the electronic structure of this surface [61].

Based on scanning tunnelling microscope (STM) images combined with density functional calculations, two atomic models $[(2 \times 1)$ and $c(2 \times 2)]$, were proposed for the Si(114) orientation [57]. These models have very similar bonding topology, differing only in terms of dimerization pattern of their surface. The surface energies of the two models are also similar, as both can be found on sufficiently large areas of the scanned samples [57]. To best of our knowledge, so far the study by Erwin *et al.* [57] represents the *only* proposal for the structure of Si(114). The purpose of this chapter is to present several other model candidates for the structure of Si(114), models that are likely to be experimentally observed on this surface. Addressing the problem of atomic structure from a different perspective than the previous reports [57, 61], we perform searches for the global minimum configuration of this surface. As we shall see, the lowest energy configuration (at zero Kelvin) obtained here from purely theoretical means is consistent with the original proposal [57]; however, the global search methods provide several other structural models with low surface energy, which could be relevant in various experimental conditions. The remainder of this chapter is organized as follows. Chapter 5.3 presents the brief review of simulation cell and the genetic algorithm for structural determination. The results of the structural optimization for Si(114) surface are presented and discussed in Chapter 5.4 and 5.5, as well as our conclusions are outlined in the last section of this chapter.

5.3 Methods

5.3.1 Simulation Cell

The reconstructions of semiconductor surfaces are determined not only by the efficient bonding of the surface atoms, but also by the stress created in the process [40]. Therefore, we retain a large number of subsurface atoms when performing a global search for the lowest energy configuration: this way the surface stress is intrinsically considered when reconstructions are sorted out. The number of local minima of the potential energy is also large, as it scales roughly exponentially [58, 59] with the number of atoms involved in the reconstruction; by itself, such scaling requires the use of fast stochastic search methods. Before outlining the procedure, we discuss briefly the computational cell and the empirical potential used.

Similar to the cell used for Si(105) in Chapter 4, the simulation cell (of dimensions $3a \times a\sqrt{2}$ in the plane of the surface) has a single-face slab geometry with periodic boundary conditions applied in the plane of the surface, and no periodicity in the direction normal to it. The “hot” atoms from the top part of the slab (10–15 Å thick) are allowed to move, while the bottom layers of atoms are kept fixed to simulate the underlying bulk crystal. The area of the simulation cell and the number of atoms in the cell are kept fixed during each simulation. Under these conditions, the problem of finding the most stable reconstruction reduces to the global minimization of the total potential energy $V(\mathbf{x})$ of the atoms in the simulation cell (here $\mathbf{x}$ denotes the set of atomic positions). In terms of atomic interactions, we are constrained to use empirical potentials because the highly accurate first-principles or tight-binding methods are prohibitive as far as the search itself is concerned. Since this work is aimed at finding the *lowest* energy reconstructions for arbitrary surfaces, the choice of the empirical potential is important. After numerical experimentation with several empirical models, we chose to use the highly optimized empirical potential (HOEP) recently developed by Lenosky *et al.* [52]. HOEP is fitted to a large database of first-principles calculations using the force-matching method, and provides a good description of the energetics of all atomic coordinations up to $Z = 12$.

5.3.2 Genetic Algorithm

Detailed implementations of a genetic procedure have been described in chapter 4. We will directly go into the results of global structural optimization using a genetic algorithm with a highly optimized empirical potential (HOEP).

As mentioned in previous chapter, two versions of the algorithm used for surface systems have been developed. In the first version, the number of atoms n is kept the same for every member of the pool by automatically rejecting child structures that have different numbers of atoms from their parents (mutants). In the second version of the algorithm, this restriction is not enforced, i.e. mutants are allowed to be part of the pool: in this case, the procedure is able to select the correct number of atoms for the ground state reconstruction without any increase over the computational effort required for one single constant- n run.

First, we repeat the genetic algorithm for different values of n ranging from 208 to 220, and look for a periodic behavior of the lowest surface energy as a function of n . For the case of Si(114), this periodicity occurs at intervals of $\Delta n = 4$, as shown in Fig. 5.1. Therefore, the (correct) number of atoms n at which the lowest surface energy is attained is $n = 216$, up to an integer multiple of Δn . As we shall show in the next, the repetition of the simulation for different values of n in the simulation cell can be avoided within the second version of the genetic algorithm approach. The results of a variable- n run are shown in Fig. 5.2(a) which shows how the lowest energy and the average energy from a pool of $p = 30$ structures decreases as the genetic algorithm run proceeds. The plot in Fig. 5.2(a) displays typical features of the evolutionary approach: the most unfavorable structures are eliminated from the pool rather fast (initial steep transient region of the graphs) and a longer time is taken for the algorithm to retrieve the most stable configuration. The lowest energy structure is retrieved in less than 500 mating operations. The correct number of atoms [refer to Fig. 5.2(b)] is retrieved much faster, within approximately 100 operations. It is noteworthy that even during the transient period, the lowest-energy member of the pool spends most of its evolution in a state with a number of atoms ($n = 212$) that is compatible with the global minimum structure.

Figure 5.1 Surface energy of the global minimum structure showing a periodic behavior as a function of n , with a period of $\Delta n = 4$; this finding helps narrowing down the set of values for n that need to be considered for determining the Si(114) reconstructions that have a $3a \times a\sqrt{2}$ periodic cell.

The genetic algorithms (GA) presented briefly in this section is able to retrieve a set of possible candidates for the lowest energy surface structure. The genetic algorithm not only finds the same lowest energy structures for each value of the total number of atoms n , but also most of the other low-energy reconstructions – a finding that builds confidence in the quality of the configuration sampling performed here. Since the atomic interactions are modelled by an empirical potential [52], it is desirable to check the relative stability of different model structures using higher-level calculations based on density functional theory; the details of these calculations are presented next.

5.3.3 Density Functional Calculations

Using the methodologies described above, we build a database of model structures that are sorted according to the surface energy given by the HOEP [52] interaction model. Since the empirical potentials may not give a reliable energetic ordering when a large number of structures are considered, we recalculate the surface energies of the models in the database

Figure 5.2 (a) Evolution of the lowest surface energy (solid line) and the average energy (dash line) for a pool of $p = 30$ structures during a genetic algorithm (GA) run with variable n ($210 \leq n \leq 222$). (b) Evolution of the number of atoms n that corresponds to the model with the lowest energy from the pool, during the same GA run. Note that the lowest energy structure of the pool spends most of its evolution in states with numbers of atoms that are compatible with the global minimum, i.e. $n = 212$ and $n = 216$.

at the level of density functional theory. The calculations were performed with the plane-wave based PWscf package [33], using the Perdew-Zunger [35] exchange-correlation energy. The slab geometry and the computational parameters are similar to the ones proposed by Erwin *et al.* [57]; given the increase in computational speed over the last eight years, we used thicker slabs and a different sampling of the Brillouin zone. The cutoff for the plane-wave energy was set to 12 Ry, and the irreducible Brillouin zone was sampled with 4 k -points. The equilibrium bulk lattice constant was determined to be $a = 5.41$ Å, which was used for all the surface calculations in this work. The simulation cell has the single-face slab geometry, with 24 layers of Si, and a vacuum thickness of 12 Å. The bottom three layers are kept fixed in order to simulate the underlying bulk geometry, and the lowest layer is passivated with hydrogen. The remaining Si layers are allowed to relax until the forces become smaller than 0.025 eV/Å.

The surface energy γ for each reconstruction is determined indirectly, by first considering the surface energy γ_0 of an unrelaxed bulk truncated slab, then by calculating the difference $\Delta\gamma = \gamma - \gamma_0$ between the surface energy of the actual reconstruction and the surface energy of bulk truncated slab that has the bottom three layers fixed and hydrogenated. The energy of the bulk truncated surface, as computed from a two-faced slab with 24 layers, was found to be $\gamma_0 = 143$ meV/Å². This indirect procedure for calculating the surface energies at the DFT level was outlined, for instance, in Ref. [56].

5.4 Results

At the end of the global search procedures, we obtain a set of model structures which we sort by the number of atoms in the simulation cell and by their surface energy. Since the empirical potentials may not be fully transferable to different surface environments, we study not only the global minima given by the model for different values of n , but also most of the local minima that are within 15 meV/Å² from the lowest energy configurations. After the global optimizations, the structures obtained are also relaxed by density functional theory

(DFT) methods as described in Sec. 5.3.3. The results are summarized in Table 5.1, which will be discussed next.

Table 1 lists the density of dangling bonds (db per area), as well as the surface energies of several different models calculated using the HOEP potential and DFT. The configurations have been listed in increasing order of the surface energies computed with HOEP, as this is the actual outcome of the global optimum searches. For reasons of space, we limit the number of structures in the Table 5.1 to at most six for each value of the relevant numbers of atoms in the simulation cell. However, when performing DFT relaxations we consider more structures than the ones shown in the table because we expect changes in their energetic ordering at the DFT level. The inclusion of a larger number of structures helps avoid excessive reliance on the empirical potential [52], which is mainly used a fast way to provide physically relevant reconstructions (i.e. where each atom at the surface has at most one dangling bond).

Table 5.1 and Fig. 5.1(b) suggest that the most unfavorable number of atoms in the simulation cell is $n = 215$, both at the level of HOEP and at the level of DFT. Therefore, it is justifiable to focus our attention on the other three values of n ($n = 216, 214$ and 213), which yield considerably lower surface energies. For each of these numbers of atoms, we present four low energy structures (as given by DFT), which are shown in Figs. 5.3–5.5. These structures are not necessarily the same as those enumerated in Table 5.1, as they are chosen based on their DFT surface energies. Since the global optimization has not been performed at the DFT level, the reader could argue that the lowest energy structure obtained after the sorting of the DFT-relaxed models may not be the DFT global minimum. While we found that a *thorough* sampling for systems with ~ 200 atoms is impractical at the DFT level, we have performed DFT relaxations for most of the local minima given by HOEP. Therefore, given the rather large set of structural candidates with different topological features considered here, the possibility of missing the actual reconstruction for Si(114) is much diminished in comparison with heuristic approaches.

We will now describe in turn the surface models corresponding to $n = 216, 214$ and 213 . After the DFT relaxation, the lowest energy model that we found has turned out to be the

n	Bond counting ($db/3a^2\sqrt{2}$)	HOEP (meV/Å ²)	DFT (meV/Å ²)
216	8	81.66	89.48
	8	83.16	90.34
	8	83.31	91.29
	8	83.39	88.77
	8	83.64	94.68
	8	84.42	92.16
215	8	91.61	97.53
	8	91.82	95.30
	8	92.00	94.20
	11	92.46	98.73
214	6	86.95	95.17
	10	87.32	99.58
	10	87.39	98.47
	10	87.49	93.88
	10	88.26	95.18
213	4	89.46	90.43
	6	89.76	94.01
	4	90.07	90.85
	6	91.73	94.66
	7	93.99	90.48

Table 5.1 Surface energies of different reconstructions for the Si(114) surface, sorted by the number of atoms n in the $3a \times a\sqrt{2}$ periodic cell. The second column shows the number of dangling bonds (counted for structures relaxed with HOEP) per unit area. The last two columns list the surface energies given by the HOEP interaction model [52] and by density functional calculations (DFT) [33] with the parameters described in text.

same as the one proposed by Erwin and coworkers [57], perhaps with the exception of different relative tilting of the surface bonds. The model is shown in Fig. 5.3(a), and it is characterized by the presence of dimers, rebonded atoms and tetramers occurring in this order along the (positive) $[22\bar{1}]$ direction. These features have been well studied [57, 61], and we shall not insist on them here. The surface energy of the most stable model for Si(114)- (2×1) reconstruction is $\gamma = 88.77 \text{ meV}/\text{\AA}^2$. Although this surface energy is somewhat different from the previously reported value of $85 \text{ meV}/\text{\AA}^2$ [57], the discrepancy between these absolute values can be attributed to the somewhat different computational parameters (slab thickness, number of k -points) and/or different pseudopotentials.

It is notable that a different succession of the above-mentioned atomic scale features is also characterized by a low surface energy: specifically, dimers, tetramers and rebonded atoms (in this order along $[22\bar{1}]$), as shown in Fig. 5.3(c), give a surface energy which is only $\sim 2 \text{ meV}/\text{\AA}^2$ higher than that of the Erwin *et al.* model shown in 5.3(a). This surface energy gap is apparently large enough to allow for another configuration [see Fig. 5.3(b)] with a surface energy that lies between the values corresponding to the first two models described above. As shown in Fig. 5.3(b), this new model has two consecutive dimer rows followed by a row of rebonded atoms, and arrangement that gives rise to surface corrugations of 0.4–0.5 nm. Remarkably, this corrugated model [Fig. 5.3(b)] is almost degenerate with the planar, (2×1) structure shown in Fig. 5.3(a). The last panel of Fig. 5.3 shows another planar model of Si(114), made of dimers, rebonded atoms and inverted tetramers, with the latter topological feature distinguishable as a seven-member ring when viewed along the $[110]$ direction.

Dimers, rebonded atoms and tetramers also occur on low-energy structural models with $n = 214$, as shown in Fig. 5.4. The most favorable structure with $n = 214$ that we found [depicted in Fig. 5.4(a)] has a 5-coordinated subsurface atom and a 4-coordinated surface atom per unit cell. These topological features are determined by the bonding of a subsurface atom with one of the atoms of a tilted surface dimer; the corresponding surface energy is $90.09 \text{ meV}/\text{\AA}^2$. Other structures with $n = 214$ atoms [examples shown in Fig. 5.4(b)–(d)] generally have higher energies than models with $n = 216$, (refer to Table 5.1) most likely

because the two missing atoms lead to pronounced strains in the surface bonds.

The analysis of simulation slabs with $n = 213$ atoms reveals novel atomic scale features. Energetically favorable configurations with $n = 213$ [5.5(a) and (c)] show a 5-atom ring on the surface stabilized by a subsurface interstitial, a structural complex that was first encountered in the case of Si(113) surface [56]. Structures in Figs. 5.5(a) and (c) differ in terms of the succession of the topological features along the $[22\bar{1}]$ direction, i.e. dimers, 5-member rings, rebonded atoms [5.5(a)] as opposed to dimers, rebonded atoms and 5-member rings [5.5(c)]. The model in Fig. 5.5(a) is degenerate with the one shown in 5.5(b), as their relative surface energy is much smaller than the $1\text{--}2\text{ meV}/\text{\AA}^2$ expected accuracy of the relative surface energies determined here. The reconstruction 5.5(b) is very similar to the lowest energy structure in Fig. 5.3(a) (achievable with $n = 212$): the only different feature is the extra atom lying in between two rebonded atoms and sticking out of the surface [refer to Fig. 5.5(b)]. Likewise, the model in Fig. 5.5(d) can be obtained from structure 5.3(b) by adding one atom per unit cell in such a way that it bridges the two atoms of a dimer on one side, and rebonds on the other side.

The simulated filled-state STM images of the two lowest energy models shown in Fig. 5.3(a) and Fig. 5.3(b) are calculated for Si(114)-(2 $\times$ 1) at the sample bias of -1.5V. The simulated images are shown in Fig. 5.6.

5.5 Discussion

The data in Table 5.1 shows clearly that the density of dangling bonds at the Si(114) surface is, in fact uncorrelated with the surface energy. The lowest number of dbs per area reported here is 4, and it corresponds to $n = 213$ and $\gamma = 90.43\text{ meV}/\text{\AA}^2$ at the DFT level. The optimum structure [5.3(a)], however, has twice as many dangling bonds but the surface energy is smaller, $88.77\text{ meV}/\text{\AA}^2$. Furthermore, for the same number of atoms in the supercell ($n = 216$) and the same dangling bond density ($8db/3a^2\sqrt{2}$), the different reconstructions obtained via global searches span an energy interval of at least $5\text{ meV}/\text{\AA}^2$. These findings

Figure 5.3 Structural models (top and side views) of Si(114)-(2 $\times$ 1), with $n = 216$ atoms per unit cell after relaxation with density functional methods [33]. The surface energy γ computed from first-principles is indicated for each structure, along with the corresponding value (in parentheses) obtained using the empirical potential [52]. The darker shade marks the undercoordinated atoms.

Figure 5.4 Structural models (top and side views) of Si(114)-(2 $\times$ 1), with $n = 214$ atoms per unit cell after relaxation with density functional methods [33]. The surface energy γ computed from first-principles is indicated for each structure, along with the corresponding value (in parentheses) obtained using the empirical potential [52]. The darker shade marks the undercoordinated atoms, while the overcoordinated atoms are shown in white.

Figure 5.5 Structural models (top and side views) of Si(114)-(2 $\times$ 1), with $n = 213$ atoms per unit cell after relaxation with density functional methods [33]. The surface energy γ computed from first-principles is indicated for each structure, along with the corresponding value (in parentheses) obtained using the empirical potential [52]. The darker shade marks the undercoordinated atoms, while the white atoms are either four-coordinated or overcoordinated.

Figure 5.6 The simulated filled-state STM images of the two lowest energy models in Fig. 5.3(a) and Fig. 5.3(b) for Si(114)-(2 $\times$ 1) at the sample bias of -1.5V.

constitute a clear example that the number of dangling bonds can not be used as a criterion for selecting model reconstructions for Si(114); we expect this conclusion to hold for many other high-index semiconductor surfaces as well.

The HOEP surface energy and the DFT surface energy also show very little correlation, indicating that the transferability of the interaction model [52] for Si(114) is not as good as, for instance, in the case of Si(001) and Si(105) [45]. The most that can be asked from this model potential [52] is that the observed reconstruction [57] is amongst the lower lying energetic configurations –which, in this case it is. We have also tested the transferability of HOEP for the case of Si(113), and found that, although the ad-atom interstitial models [56] are not the most stable structures, they are still retrieved by HOEP as local minima of the surface energy. We found that the low-index (but much more complex) Si(111) 7 $\times$ 7 reconstruction is also a local minimum of the HOEP interaction model, albeit with a very high surface energy. Other tests indicated that, while the transferability of HOEP to the Si(114) orientation is marginal in terms of sorting structural models by their surface energy, this potential [52] performs much better than the more popular interaction models [60, 63],

which sometimes do not retrieve the correct reconstructions even as local minima. Therefore, HOEP is very useful as a way to find different local minimum configurations for further optimization at the level of electronic structure calculations.

A practical issue that arises when carrying out the global searches for surface reconstructions is the two-dimensional periodicity of the computational slab. In general, if a periodic surface pattern has been observed, then the lengths and directions of the surface unit vectors may be determined accurately through experimental means (e.g., STM or LEED analysis): in those cases, the periodic vectors of the simulation slab should simply be chosen the same as the ones found in experiments. When the surface does not have two-dimensional periodicity, or when experimental data is difficult to analyze, then one should systematically test computational cells with periodic vectors that are integer multiples of the unit vectors of the bulk truncated surface, which are easily computed from knowledge of crystal structure and surface orientation. There is no preset criterion as to when the incremental testing of the size of the surface cell should be stopped –other than the limitation imposed by finite computational resources; nevertheless, this approach gives a systematic way of ranking the surface energies of slabs of different areas, and eventually finding the global minimum surface structure.

Motivated by a previous finding that larger unit cells can lead to models with very low surface energies (see, for instance the example of Si(105) [26, 45]), we have also performed global minimum search using GA for slabs of dimensions $6a \times a\sqrt{2}$, which correspond to a doubling of the unit cell in the $[22\bar{1}]$ direction. The ground state structure at the HOEP level found in this case is still the corrugated model 5.3(b) with a surface energy of $\gamma = 81.66$ meV/Å². As a low-lying configuration we again retrieve the original model [57] with $\gamma = 83.39$ meV/Å². Furthermore, we also find a several models that have surface energy in between the two values, characterized by the presence of different $3a \times a\sqrt{2}$ structures in the two halves of the $6a \times a\sqrt{2}$ simulation cell. This finding suggests that $[1\bar{1}0]$ -oriented boundaries between different $3a \times a\sqrt{2}$ models on Si(114) are not energetically very costly: this is consistent with the experimental reports of Erwin *et al.*, who indeed found (2×1) and $c(2 \times 2)$ structures next

to one another [57].

5.6 Conclusion

In conclusion, we have obtained and classified structural candidates for the Si(114) surface reconstructions using global optimization methods and density functional calculations. We have used the genetic algorithm [26] in conjunction with the latest empirical potential for silicon [52], which has a better transferability in comparison with more popular potentials [60, 63]. We have built a large database of structures (reported, in part, in Table 5.1) which were further optimized at the DFT level. The lowest energy structure that we found (Fig. 5.3(a)) after the DFT relaxation is the same as the one originally reported for Si(114)-(2 × 1) in [57].

In addition, we have discovered several other types of structures (refer to Figs. 5.3(b), 5.3(c) and 5.4(a) and 5.5(a)) that are separated (energetically) by 1–2 meV/Å² from the lowest energy model [57]. Given that the relative surface energies at the DFT level have an error of ±1 meV/Å², and that the experiments of Erwin *et al.* [57] already identified two reconstructions ([(2×1) and *c*(2×2)] whose surface energies are within 1–2 meV/Å² from one another, it is conceivable that some of the models in Figs. 5.3–5.5 could also be found on the Si(114) surface. This prediction could be tested, e.g., by high-resolution transmission electron microscopy experiments such as the ones reported recently for the Si(5512) surface [64]. Low-energy electron diffraction experiments, as well as more STM measurements could also shed light on whether there exist other structural models on a clean Si(114) surface than initially reported model [57].

5.7 Acknowledgment

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algorithm runs were performed at the National Energy Research Supercomputing Center (NERSC) in Berkeley, California. We gratefully acknowledge the use of the EMSL computational resources at the Pacific Northwest National Laboratory, where the density functional calculations were completed. The Monte Carlo simulations were done at the Center of Advanced Scientific Computation and Visualization (CASCV) at Brown University; we thank Professor J. D. Doll for generously allowing us to use his computational facilities at CASCV.

CHAPTER 6 STRUCTURE OF SILVER-INDUCED SILICON (111) RECONSTRUCTIONS

A paper to be submitted

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6.1 Introduction

The growth of metals on Si(111) surface has been the focus of many studies over the past several decades. One of the prototypical metal-semiconductor interfaces is the silver-silicon interface. Limited reaction or intermixing between two species reduces the complexity of interface structures between Ag and Si. However, there are several aspects of the Ag/Si(111) system that have remained unresolved. The detailed phase diagram presented by Wan *et al.* [65] shows that Si(111) surface under submonolayer Ag coverage the Si(111) surface exhibits $\sqrt{3} \times \sqrt{3}$, 3×1 and 5×2 phases. The atomic arrangements of $\sqrt{3} \times \sqrt{3}$ and 3×1 phases have been well studied [66–79], whereas there is no follow-up study after the first report of 5×2 phase presented by Wan *et al.* [65]. On the other hand, 5×1 and 5×2 phases of the Au/Si(111) system have attracted more attention due to the unique band dispersion along the Au chained direction and metallic-semiconductor transition [80–97]. So far, for the Ag/Si(111) system, it is widely accepted that the structure of the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ phase can be explained by the honeycomb-chained triangle (HCT) model which is supported by a number of experimental and theoretical results, while the structure of the Ag/Si(111) 3×1 phase can be explained by the honeycomb chained (HCC) model at Ag coverage of $1/3$ ML.

Treating the reconstruction of semiconductor surfaces as a problem of global optimization, the recently developed genetic algorithm for structural determination of the clean silicon high index surfaces as presented in Chapter 4 and 5 can be applied to find the lowest energy structure for Ag/Si(111).

In this chapter, the global structural optimizations of the Ag-induced Si(111) reconstructions were performed, which involve two types of elements in the reconstructed layers. The genetic algorithm (GA) coupled with environment-dependent Si and Ag tight-binding (TB) potentials [6, 101] were performed for $\sqrt{3} \times \sqrt{3}$ and 3×1 phases of the Ag/Si(111) system. The low energy structural candidates selected from the GA search were further optimized using first-principles total energy calculations. Since considerable efforts have been made in the structural and electronic analysis of the Ag induced $\sqrt{3} \times \sqrt{3}$ and 3×1 phases, it is crucial to test the genetic algorithm and the TB potentials on these two phases before studying the more complex 5×2 phase. The extensive calculations showed that the previous proposed structural models, the honeycomb chain-channel (HCC) model and the Honeycomb Trimer (HCT) models, are indeed the lowest energy models for the 3×1 and $\sqrt{3} \times \sqrt{3}$ phases, respectively, in both tight-binding and first-principles calculations. Moreover, a novel structural model has been found to have lower surface energy than the double honeycomb chained (DHC) model for both Ag/Si(111) and Au/Si(111) 5×2 phases.

This chapter is arranged as follows: In Chapter 6.2, the computational methods will be discussed. Results are presented in Chapter. 6.3. Discussion and recommendation for future research are presented in Chapter 6.4. The conclusion will be draw in Chapter 6.5.

6.2 Methods

The bulk truncated Si(111) surface is illustrated in Fig. 6.1. The surface unit cells of $\sqrt{3} \times \sqrt{3}$, 3×1 , and (5×2) phases are outlined from top to bottom in Fig. 6.1. Two bulk truncated (111)- 5×1 unit cells stacked along $[\bar{1}10]$ are indicated as well. The simulation cell has a slab geometry with periodic boundary conditions applied in the plane of the surface,

and no periodicity in the direction normal to it. In the present work, the genetic algorithm were performed for the cases of $\sqrt{3} \times \sqrt{3}$, 3×1 and 5×1 (5×2) phases, since these phases are in STM experiment [65]. The simulation cells for tight-binding calculations contains totally four bilayers. Since naturally the intermixing between silver and silicon is limited to the top bilayer, the top bilayer atoms corresponding to a depth of $d = 3.14 \text{ \AA}$ (measured from the position of the highest atom of a ideal bilayer) are shuffled via a set of genetic operations. In order to properly account for the surface stress, atoms in a thicker zone of second and third bilayers are allowed to relax to a local minimum of the potential energy after each genetic operation, while the bottom bilayer is kept fixed. In terms of atomic interactions, tight-binding potentials [6, 101] are used. These potentials have superior transferability in the diverse bonding environments present on silicon surfaces [6, 101]. The detailed formalism of Ag and Si tight-binding potentials is presented in the Appendix.

The development of the genetic algorithm (GA) for surface structure determination was motivated by its successful application for structural optimization of atomic clusters [1, 25]. It has been shown that the newly developed GA is a suitable tool for high-index surface systems in Chapter 4 and Chapter 5 as well as for the study of the Si magic clusters on a Si(111) 7×7 surface in Chapter 3 [26, 27]. Because the optimization procedure has been described in Chapter 4 and Chapter 5, the details will not be described again here.

The difference between previous chapters and this chapter is that the mating operation involves two types of elements here. Similar to the mating operation described in chapter 4, the number of atoms n_a and n_b for each type are kept the same for every member of the pool by automatically rejecting child structures that have different numbers of atoms from their parents. The GA searches are implemented for different coverages of each type of element, corresponding to different numbers of atoms n_a and n_b in each simulation.

Since the tight-binding potentials would not give a exact energetic ordering when a large number of structures are considered, the surface energies of the models obtained from the genetic algorithm were further calculated at the level of density functional theory (DFT) [2]. The calculations in the present work were done within the generalized gradient approximation

Figure 6.1 Top and side views of a unreconstructed Si(111) 7×7 surface. The unit cells of $\sqrt{3} \times \sqrt{3}$, 3×1 , and 5×2 are outlined at top, middle and bottom, respectively. The Si atoms in top two layers are colored gold and blue, respectively; the Si atoms in the second bilayer is colored white.

(GGA) to density functional theory using projector-augmented-wave potentials (PAW) [98], as implemented in VASP [29]. The kinetic energy cutoff is set to be 250 eV (18.37 Ry) and sampling (7×7) , (3×9) , and (2×4) of the surface Brillouin zone were used for $\sqrt{3} \times \sqrt{3}$, 3×1 , and 5×2 , respectively. The Si(111) surface in the DFT calculations is modeled by a periodically repeating slab of up to six layers of Si including the reconstructed surface layer and a vacuum space of 12 Å. The bottom Si bilayer was passivated by hydrogen and held fixed to simulate the bulk environment, while all other atoms above it are allowed to relax until the forces are less than 0.025 eV/Å. Theoretical bulk lattice constant of 5.465 Å was used in the surface calculations.

The surface energy γ for each surface reconstruction is calculated as follows. First, the surface energy γ_0 of a slab which is bulk truncated on both sides is calculated as follow.

$$\gamma_0 = \frac{1}{2}(E_t - N_{Si} \times E_{Si-bulk}) \quad (6.1)$$

The bulk truncated Si(111) of 6 bilayers has surface energy $\gamma_0 = 106.51$ meV/Å². Next, surface energy difference $\Delta\gamma$ was calculated with respect to a reference slab of total energy, E_{sub} , which was bulk truncated on one side and terminated with H on the other side. $\Delta\gamma$ is expressed as

$$\Delta\gamma = (E_t - E_{sub} - \Delta N_{Si} \times E_{Si-bulk} - \Delta N_{Ag} \times E_{Ag-bulk})/A, \quad (6.2)$$

where E_t is the total energy of a considered structural model with the same substrate as in the reference slab. ΔN_{Si} (ΔN_{Ag}) is the difference in number of Si (Ag) atoms relative to the reference slab and $E_{Si-bulk}$ ($E_{Ag-bulk}$) is the bulk energy of Si diamond structure (Ag fcc structure). The surface energy γ is determined as $\gamma_0 + \Delta\gamma$. The reference slab for our DFT calculations is a hydrogen-passivated two-bilayer substrate. The total energies of the structural models are calculated using the hydrogen-passivated three-bilayer substrate including the reconstructed layer.

6.3 Results and Discussion

6.3.1 Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ phase

Since 8 structural models of $\sqrt{3} \times \sqrt{3}$ phase were included in the fitting of the Ag-Si TB potentials (also see Appendix), the structural optimizations of the $\sqrt{3} \times \sqrt{3}$ phase were performed first. Selected structural models obtained from GA search at various Ag and Si coverages are further optimized using first-principles calculations. The surface energies of selected models are plotted in Fig. 6.2. The results show that Si-Ag tight-binding potentials can basically reproduce the results of DFT calculations except for a few structure where Ag atoms are found underneath the Si surface layer and hence have higher coordination than the Ag atoms on the surface. Most importantly, the lowest energy model using TB calculations remains the lowest using DFT calculations. The GA search retrieved the same lowest energy structures. The lowest energy structure corresponds to Ag coverage of 1 ML Ag and Si coverage of 1 ML. The lowest energy structural model of such a coverage is identified as the honeycomb trimer (HCT) model. Since the HCT model has also been well-studied elsewhere [72–79], further electronic analysis will not be performed here.

6.3.2 Ag/Si(111) 3×1 phase

Since the 3×1 phase has also been well-studied, structural optimizations of the 3×1 phase were performed at Ag coverage of $1/3$ ML and at various Si coverages. The Ag coverage of $1/3$ ML is chosen according to the well-accepted honeycomb chain-channel (HCC) model [66–71]. Selected structural models at each Si coverage are further optimized using first-principles calculations. The surface energies of selected structural models versus Si coverage are plotted in Fig. 6.3(a). The plot shows that the surface energies calculated using tight-binding potential are in good agreement with those calculated using first-principle method except for two structures at Si coverage of 1 ML which Ag atoms are found underneath the Si surface layer. In order to clarify the plot in Fig. 6.3(a), only the lowest surface energies versus Si coverage are plotted in Fig. 6.3(b). The plot shows that the lowest energy model

Figure 6.2 Surface energies of selected models using first-principles and tight-binding calculations for the $\sqrt{3} \times \sqrt{3}$ phase. The big Xs are the models involving Ag-Si TB potential fitting.

corresponds to Ag coverage of $1/3$ ML and Si coverage of $4/3$ ML. The structural model at this coverage is identified as the honeycomb chained (HCC) model, as well as several low energy models at this coverage are illustrated in Fig. 6.4. Fig. 6.4(a), (b), (c), and (d) are models with the honeycomb chained (HCC) feature with Ag atoms at different positions. Fig. 6.4(e) is another model obtained from our GA search. Since the HCC model for the 3×1 phase has been well studied elsewhere [66–71], further electronic analysis of HCC model will not be performed here.

6.3.3 Ag/Si(111) 5×1 phase

As the surface area of the reconstruction increases, the number of the combinations of Ag and Si coverage increases in the order of $O(N^2)$. For the 5×2 phase of Ag/Si(111) system, there is no model proposed after the first report of the phase diagram [65]. However, the Au/Si(111) surface also exhibits 5×2 and 5×1 phases. The Au coverage has been determined precisely to be $2/5$ ML experimentally. There are numerous studies of Au/Si(111) 5×2 and 5×1 phases at this Au coverage. Among them, the double honeycomb chained (DHC) model is

Figure 6.3 Top: Surface energies of selected models using first-principles and tight-binding calculations versus Si coverage for the 3×1 phase at Ag coverage of $1/3$ ML. Bottom: The lowest surface energies using first-principles calculations versus Si coverage for the 3×1 phase at Ag coverage of $1/3$ ML. The plot shows that the reconstruction with lowest surface energy is at Si coverage of $4/3$ ML.

Figure 6.4 The low energy structural models of Ag/Si(111) 3×1 phase at Ag coverage of $1/3 \text{ ML}$ and Si coverage of $4/3 \text{ ML}$. (a) and (b) are models of mirror symmetry, while (c) and (d) are models of mirror symmetry. They are all honeycomb chained (HCC) models with the Ag atoms at different positions. (e) is another models of this coverage. The Ag atoms are colored blue. The Si atoms in the reconstructed layer are colored gold, while the Si atoms in the substrate are colored white. The surface energies in the figure are done using DFT calculations with the two-bilayer substrate. Only one bilayer is shown in the figure.

Figure 6.5 Surface energies versus Si coverage for the 5×1 phase at Ag coverage of $2/5$ ML. The hollow circles are the DHC models for the 5×1 phase. The plot shows that the reconstruction with lowest surface energy is at Si coverage of $7/5$ ML.

the lowest energy model for 5×1 and 5×2 in the literature [93, 94, 96]. DHC model of the 5×2 phase can be obtained by removing one atoms every two 5×1 cells. Structural optimizations of 5×1 phase at Ag coverage of $2/5$ ML were performed at various Si coverages. Selected structural models are further optimized using first-principles calculations. The lowest surface energies versus Si coverage as well as the DHC model are plotted in Fig. 6.5 at Ag coverage of $2/5$ ML. The plot shows that the lowest energy group is at Si coverage of $7/5$ ML. The structure model obtained at this coverage is found to have lower surface energy than DHC model by $5 \text{ meV}/\text{\AA}^2$. The selected low energy models from our search and the DHC model are shown in Fig. 6.6.

6.3.4 Ag/Si(111) 5×2 phase

Knowing that the DHC model of 5×2 phase removes the bridged Si atom from bridged DHC model every two 5×1 cells, several structural models of 5×2 phase were created from other 5×1 search and optimized using first-principles calculations. One model of 5×2 phase

Figure 6.6 The low energy structural models for Ag/Si(111) 5×1 phase at Ag coverage of $2/5$ ML and Si coverage of $7/5$ ML. (a) is obtained from GA search. (b) is the DHC model. (c) and (d) are other low energy models from GA search. The Ag atoms are colored blue. The Si atoms in the reconstructed layer are colored gold, while the Si atoms in the substrate are colored white. The surface energies in the figure are done using DFT calculations with the two-bilayer substrate. Only one bilayer is shown in the figure.

is found to have lower surface energy than the DHC model by 5 meV/Å². The structural models of 5×2 phase as well as the DHC model 5×2 are shown in Fig. 6.7. The simulated STM image of new model and DHC model are calculated and shown in Fig. 6.8(a) and (b) at the sample bias of -1.0V.

6.3.5 Au/Si(111) 5×2 phase

Since all the structural models of Ag/Si(111) system are at Ag coverage 2/5 ML, all the considered models could also be optimized for Au/Si(111) system. The lowest energy model obtained from GA also has lower surface energy than the DHC model for Au/Si(111) 5×2 phase by 0.5 meV/Å². The simulated STM image of new model and DHC model are calculated and shown in Fig. 6.8(c) and (d) at the sample bias of -1.0V.

6.4 Recommendation for Future Research

The simulated STM images of the novel model and DHC model for Ag/Si(111) 5×2 do not match the experimental STM image [65]. There are two issues here. First, the resolution of STM images need to be improved and the Ag coverage need to be controlled precisely in experiments. The experimental STM image might not be taken at Ag coverage of 2/5 ML. Second, the exact Ag coverage is unknown. In order to verify the new model of the Ag/Si(111) 5×2 phase, it is also necessary to perform the structural optimizations of the 5×2 phase at other Ag coverage.

Beyond the Ag/Si(111) system, there are several future research topics. Metal-induced reconstruction is not only on low index (111) surface but also on high index surfaces, (557) and (337)/(225)/(5512), as well. Accurate TB potentials are highly desired in order to pursue this study.

6.5 Conclusion

Global structural optimizations of $\sqrt{3} \times \sqrt{3}$, 3×1 , and 5×1 phases were performed at certain Ag coverages. The lowest energy models for $\sqrt{3} \times \sqrt{3}$ and 3×1 phases have been determined successfully at Ag coverage of 1 ML and $1/3$ ML, respectively. For 5×1 and 5×2 phases, a novel structural model is obtained at Ag coverage of $2/5$ ML which has lower surface energy than the proposed DHC model both for Ag/Si(111) and Au/Si(111) 5×1 and 5×2 phases.

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Figure 6.7 The low energy structural models for Ag/Si(111) 5×2 phase at Ag coverage of $2/5$ ML and Si coverage of $6.5/5$ ML. (a) is obtained from GA search. (b) is the DHC model. (c) and (d) are other low energy models from GA search. The Ag atoms are colored blue. The Si atoms in the reconstructed layer are colored gold, while the Si atoms in the substrate are colored white. The surface energies in the figure are done using DFT calculations with the two-bilayer substrate. Only one bilayer is shown in the figure.

Figure 6.8 (a) and (b) are the simulated STM images of new model and the DHC model for Ag/Si(111) 5×2 phases, respectively. (c) and (d) are the simulated STM images of new model and the DHC model for Au/Si(111) 5×2 , respectively. All the filled state STM images are simulated at the sample bias of -1.0V.

APPENDIX ENVIRONMENT-DEPENDENT TIGHT-BINDING POTENTIAL MODELS

1 Fundamentals of Tight-Binding Potential Models

The expression for the binding energy of a system with M atoms and N valence electrons in tight-binding molecular dynamics is given by

$$E_{binding} = E_{bs} + E_{rep} - E_0. \quad (\text{A.1})$$

The first term on the right hand side of Eq. (A.1) is the band structure energy which is equal to the sum of the one-electron eigenvalues ε_i of the occupied states given by a tight-binding Hamiltonian H_{TB} ,

$$E_{bs} = \sum_i f_i \varepsilon_i \quad (\text{A.2})$$

where f_i is the electron occupation (Fermi-Dirac) function and $\sum_i f_i = N$.

The second term on the right hand side of Eq. (A.1) is a repulsive energy usually expressed as a sum of short-ranged pairwise interactions

$$E_{rep} = \frac{1}{2} \sum_{i,j} \phi(r_{i,j}) \quad (\text{A.3})$$

or a functional of sum of pairwise interactions

$$E_{rep} = \sum_i F_i \left(\sum_j \phi(r_{i,j}) \right) \quad (\text{A.4})$$

where F is a function which for example can be a 4th order polynomial [99].

The last term E_0 in Eq. (A.1) is a constant which represents the sum of the energies of the individual atoms.

2 Environment-Dependent Tight-Binding Potential Models

In the environment-dependent tight-binding potential model of Wang *et al.*, the minimal basis set is taken to be orthogonal. The effects of Löwdin orthogonality, three-center interactions and the variation of the local basis set with environment are taken into account empirically by renormalizing the interaction strength between atom pairs according to the surrounding atomic configurations. The TB hopping parameters and the repulsive interaction between atoms i and j depend on the environments of atoms i and j through two scaling functions [100]. The first one is a screening function that is designed to weaken the interactions between two atoms when there are intervening atoms between them. Another is a bond-length scaling function which scales the interatomic distance (hence the interaction strength) between the two atoms according to their effective coordination numbers. Longer effective bond lengths are assumed for higher coordinated atoms.

Specifically, the hopping parameters and the pairwise repulsive potential for silicon and carbon are expressed as

$$h(r_{ij}) = \alpha_1 R_{ij}^{-\alpha_2} \exp[-\alpha_3 R_{ij}^{\alpha_4}] (1 - S_{ij}) \quad (\text{A.5})$$

In this expression, $h(r_{ij})$ denotes the possible types of interatomic hopping parameters $h_{ss\sigma}$, $h_{sp\sigma}$, $h_{pp\sigma}$, $h_{pp\pi}$ and pairwise repulsive potential $\phi(r_{ij})$ between atoms i and j . r_{ij} is the real distance and R_{ij} is a scaled distance between atoms i and j . S_{ij} is a screening function. The parameters α_1 , α_2 , α_3 , α_4 , and parameters for the bond-length scaling function R_{ij} and the screening function S_{ij} can be different for different hopping parameters and the pairwise repulsive potential. Note that expression Eq. (A.5) will reduce to the traditional two-center form if we set $R_{ij} = r_{ij}$ and $S_{ij}=0$.

The screening function S_{ij} is expressed as a hyperbolic tangent (tanh) function (i.e., $S_{ij} = \tanh(\xi_{ij})$) with argument ξ_{ij} given by

$$\xi_{ij} = \beta_1 \sum_l \exp[-\beta_2 (\frac{r_{il} + r_{jl}}{r_{ij}})^{\beta_3}] \quad (\text{A.6})$$

where β_1 , β_2 , and β_3 are adjustable parameters. Maximum screening effect occurs when the atom l is situated close to the line connecting the atoms i and j (i.e., $r_{il} + r_{lj}$ is minimum). This approach allows us to distinguish between first and further neighbor interactions without explicit specification. This is well-suited for molecular dynamics simulations where it is difficult to define exactly which atoms are first neighbors and which are second neighbors.

The bond-length scaling function scales the distance between two atoms according to their effective coordination numbers. Longer effective bond lengths are assumed for higher coordinated atom pairs, leading to reduced interactions per atom pair for larger-coordinated structures. The scaling between the real and effective interatomic distance is given by

$$R_{ij} = r_{ij}(1 + \delta_1\Delta + \delta_2\Delta^2 + \delta_3\Delta^3) \quad (\text{A.7})$$

where $\Delta = \frac{1}{2}[(\frac{n_i - n_0}{n_0}) + (\frac{n_j - n_0}{n_0})]$ is the fractional coordination number relative to the coordination number of the diamond structure n_0 , averaged between atoms i and j . The coordination number can be modeled by a smooth function, $n_i = \sum_j (1 - S_{ij})$ with a proper choice of parameters for S_{ij} which has the form of the screening function described above.

Besides the hopping parameters, the diagonal matrix elements are also dependent on the bonding environments. The expression for the diagonal matrix elements is

$$e_{\lambda,i} = e_{\lambda,0} + \sum_j \Delta e_{\lambda}(r_{ij}) \quad (\text{A.8})$$

where $\Delta e_{\lambda}(r_{ij})$ takes the same expression as Eq. (A.5), λ denotes the two types of orbitals (s or p). $e_{s,0}$ and $e_{p,0}$ are the on site energies of a free atom.

Finally, the repulsive energy term is expressed in a functional of the sum of pairwise interactions as defined in Eq. (A.4) in the previous section.

The parameters in the model are determined by fitting to the self-consistent first-principles density functional calculations results of electronic band structures and the cohesive energy versus volume curves of several crystalline structures of different coordination numbers.

For a silicon system, such crystalline structures include diamond, graphite, β -tin, simple cubic, bcc, and fcc structures. In addition, some elastic constants and vibration frequencies of

the lowest-energy structures are also included in the fitting in order to ensure that the model gives good description of elastic and vibrational properties in addition to electronic structures and binding energies. The parameters of the EDTB Si potential are listed in Table A.1 and Table A.2. The parameters for calculating the coordination number of Si are $\beta_1 = 2.0$, $\beta_2 = 0.02895$, $\beta_3 = 7.96284$. The cutoff distance for the interaction is $r_{ij} = 5.2 \text{ \AA}$.

Liu *et al.* [101] have extended the EDTB model to silver-silicon system. In their approach, the expression for the binding energy of a system is also given by Eq. (A.1). The same set of parameters used for band structure energy E_{bs} of pure silicon system are used for the silver-silicon system. The number of valence electron for silver atoms is set to be 1, whereas the number of valence electrons for silicon atoms is kept to be 4.

Finally, the repulsive energy term is expressed in a functional of sum of pairwise interactions as

$$E_{rep} = \sum_{i \in \alpha} F_i^\alpha(x_{i \in \alpha}) \quad \alpha \in Si, Ag, \quad (A.9)$$

where $x_{i \in \alpha}$ is the sum of pairwise repulsive potential on atom i which is expressed as

$$x_{i \in \alpha} = \sum_{j \in \alpha} \phi_{\alpha-\alpha}(r_{ij}) + \kappa_\alpha \sum_{j \in \beta} \phi_{\alpha-\beta}(r_{ij}) \quad \alpha, \beta \in Si, Ag \quad \beta \neq \alpha, \quad (A.10)$$

where $\kappa_\alpha = 1.33$, if $\alpha \in Si$ and $\kappa_\alpha = 1.00$, if $\alpha \in Ag$. The parameters of ϕ_{Si-Si} are the same as those for pure Si system which have been listed in Table A.1. The coefficients of the polynomial function F_i^{Si} is also taken from pure Si system which are listed in Table A.2.

The parameters of ϕ_{Ag-Ag} , ϕ_{Ag-Si} , and the coefficients of polynomial function for F_i^{Ag} listed in Table A.3 and A.4 are fitted to the cohesive energy versus volume curve of silver in the fcc structure and energy vs. Si-Ag bond distance curve of the tetrahedral $SiAg_4$ structure. These parameters and coefficients are further adjusted by fitting to the energy order of 8 selected models for Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ phase [75].

	α_1	α_2	α_3	α_4	β_1	β_2	β_3
$h_{ss\sigma}$	-5.9974	0.4612	0.1040	2.3000	4.4864	0.1213	6.0817
$h_{sp\sigma}$	3.4834	0.0082	0.1146	1.8042	2.4750	0.1213	6.0817
$h_{pp\sigma}$	11.1023	0.7984	0.1800	1.4500	1.1360	0.1213	6.0817
$h_{pp\pi}$	-3.6014	1.3400	0.0500	2.2220	0.1000	0.1213	6.0817
ϕ	126.640	5.3600	0.7641	0.4536	37.00	0.56995	19.30
$\Delta e_s, \Delta e_p$	0.2830	0.1601	0.050686	2.1293	7.3076	0.07967	7.1364
	δ_1	δ_2	δ_3				
$h_{ss\sigma}$	0.0891	0.0494	-0.0252				
$h_{sp\sigma}$	0.1735	0.0494	-0.0252				
$h_{pp\sigma}$	0.0609	0.0494	-0.0252				
$h_{pp\pi}$	0.4671	0.0494	-0.0252				
ϕ	0.082661	-0.023572	0.006036				
$\Delta e_s, \Delta e_p$	0.7338	-0.03953	-0.062172				

Table A.1 The parameters obtained from the fitting for the EDTB model of Si [6]. The α_1 is in the unit of eV. Other parameters are dimensionless.

	$c_0(eV)$	c_1	$c_2(eV^{-1})$	$c_3(eV^{-2})$	$c_4(eV^{-3})$
$x \geq 0.7$	-0.739×10^{-6}	0.96411	0.68061	-0.20893	0.02183
$x < 0.7$	-1.8664	6.3841	-3.3888	0.0	0.0

Table A.2 The coefficients of the polynomial function $f(x)$ for the EDTB potential of Si.

	α_1	α_2	α_3	α_4	β_1	β_2	β_3
ϕ_{Ag-Si}	89.3393	-4.68788	0.65683	0.87105	8.59	10.3793	11.269
ϕ_{Ag-Ag}	1085.1335	-7.46285	0.31731	1.38884	8.59	10.3793	11.269
	δ_1	δ_2	δ_3				
ϕ_{Ag-Si}	0.00	0.00	0.00				
ϕ_{Ag-Ag}	0.00	0.00	0.00				

Table A.3 The parameters used in the Ag-Si system. The parameters of the repulsive energy for Ag-Ag and Si-Ag are fitted and adjusted by Dr. Bei Liu. The α_1 is in the unit of eV. Other parameters are dimensionless.

	$c_0(eV)$	c_1	$c_2(eV^{-1})$	$c_3(eV^{-2})$	$c_4(eV^{-3})$
$x \geq 1.5$	-2.0445	0.7849	0.00	0.00	0.00
$0.2 \leq x < 1.5$	-3.6683	4.55378	-6.0909	5.02057	-1.4359
$x < 0.2$	-3.8553	23.249	-473.32	0.00	0.00

Table A.4 The coefficients of the polynomial function $f(x)$ for the EDTB potential of Ag.

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