Theoretical studies of Pb on Si(111) and Si(100), global search for
H-passivated Si nanowires, and construction of highly localized quasiatomic
minimal basis orbitals for Mo

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Tzu-Liang Chan

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Program of Study Committee:

Kai-Ming Ho, Major Professor

David A. Carter-Lewis

James W. Evans

Mark S. Gordon

Joerg Schmalian

Michael C. Tringides

Iowa State University

Ames, Iowa

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Graduate College
Iowa State University

This is to certify that the doctoral dissertation of
Tzu-Liang Chan
has met the dissertation requirements of Iowa State University

Major Professor

For the Major Program

DEDICATION

I would like to dedicate this thesis to my parents and Heep-Tung Shu, without whose support I would not have been able to complete this work.

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CHAPTER 1. Overview

Metal on semiconductor surfaces has been the topic of intense studies due to its technological applications. As nano-devices shrink in size, the conventional understanding of electronic devices are no longer applicable as quantum effects start to play an important role in the behavior of the devices. At the same time, when structures are approaching atomic scale, the precise fabrication by lithographic techniques, for example, are not even applicable. Very often, the fabrication of regular structures rely on self-assembly which is susceptible to fluctuations. Therefore, a deeper understanding to exploit the quantum behavior of nano-devices and precise control of building nano-structures are highly desired.

Si(100) and Si(111) surfaces are the most studied system because they are the Si surfaces with the lowest surface energy. Pb on Si(100) and Si(111) is often chosen as the prototype system for the study of metal/semiconductor interfaces because Pb is not reactive with Si thus forming a clean well-defined hetero-interface. A prominent problem for studying the physics of metal/semiconductor interfaces is that the interface structures are usually not known. While various experimental techniques can be employed to provide clues to the atomic geometries, definite conclusions usually cannot be drawn due to the intrinsic limitations of the experiments. For example, scanning-tunneling microscopy (STM) only probes the local electronic density of states in which a maximum in intensity does not necessarily correspond to atomic positions. Low-energy electron diffraction (LEED) and X-ray diffraction experiments provide results in the reciprocal space, which may elude a direct interpretation in the real space. A theoretical

investigation of plausible structures is very often necessary to supplement experimental studies.

Comparison between candidate structures can be made by calculating their surface energies. First-principles density functional calculations have proved to be very successful in accounting for the properties of many solid state systems, not only for bulk crystalline phases but also for structures involving surfaces or interfaces. In Chapter 2, a brief overview of the first-principles method will be presented. However, studying surface structures sometimes requires probing the huge phase space of possible atomic positions as well as calculations using large supercell due to long surface periodicity. It is therefore beneficial to employ a semi-empirical tight-binding approach to attack the problem which is otherwise unfeasible for first-principles calculations. While the gain in speed is actually by making a trade-off in accuracy, the tight-binding method is found to be an indispensable aid to explore plausible atomic geometries which can be later verified by separate first-principles calculations. Hence, the tight-binding method will also be introduced in Chapter 2. In certain applications, for example global search in structural phase space using a genetic algorithm, a huge number of structures is being generated and very quick energy evaluation is highly desired to differentiate between geometries. Hence, in Chapter 2, a classical empirical potential for semiconductors will be discussed briefly as well.

The study of the Pb/Si system began by investigating Pb on Si(111) at low coverage. By using first-principles calculations, the structures of Pb on Si(111) below a coverage of 1.3 ML are studied in Chapter 3. Different models suggested by experimental results or inspired by other metal/Si(111) systems are tested. STM images are simulated for the low energy candidate structures to compare with experiments. The results are in good agreement with the experiments, and complicated structural models with large periodicity, for example the hexagonal incommensurate phase and the devil's staircase linear phases, can be inferred based on our low energy structural motif.

When a sufficient amount of Pb is deposited on Si(111), Pb islands can be formed. It is observed experimentally that the Pb islands grow in specific “magic” heights which are particularly stable. The stability of the Pb islands can be explained by the quantum size effect. The quantum size effect(QSE) is based on the simple model of a one-dimensional quantum well with the width of the well corresponding to the height of the Pb island. Enhanced stability corresponds to the height of the Pb islands that equals half-multiples of the Fermi wavelength of the confined electrons in the island. While this simple picture explains many gross features of the system, certain electronic properties cannot be accounted for. For example, the contrast of Moire pattern observed by STM on top of the islands is found to be independent of the tip bias. This contradicts the prediction of the quantum well model. Moire pattern is the beating due to the superposition of the Pb and Si lattices with slightly different periodicity. In the second section of Chapter 3, this problem is addressed by using tight-binding calculations due to the huge system size involved. It is found that there is geometric corrugation of the Pb film due to the influence of the Si substrate, thus modifying the electronic properties of the system.

While the uniformity of the heights of the Pb islands on Si(111) is intriguing, the kinetics involved in the formation of such islands remain a mystery. In order to control the formation of nano-structures, an understanding of the dynamical processes is as important as the energetics of the nano-structures. The third section of Chapter 3 addresses part of this problem by studying the diffusion barrier of Pb adatoms on top of the Pb islands using first-principles calculations. It is found that the diffusion barriers are also strongly affected by QSE, and exhibit bi-layer oscillation. This oscillation in turn manifests itself in the growth morphology of the Pb islands on Si(111) which is observed in STM experiments.

In Chapter 4, Pb and Sn on Si(100) will be studied. Previous studies of Si and Ge on Si(100) provided valuable experience for determining nano-structures. When Si, Ge, Sn or Pb atoms are deposited onto Si(100) at low coverage, dimers will be

observed in STM experiments. However, the composition of the observed dimer may not necessarily correspond to the deposited atoms because there can be intermixing between the deposited atoms and the Si substrate, and the composition of the dimer cannot be directly implied by STM experiments. It is found that the structure of a dimer on Si(100) can be deduced by studying their dynamical properties like rocking motion, rotation and diffusion of the dimer. Hence, this strategy is used to investigate the composition and the structure of Pb and Sn dimers and dimer chains on Si(100). A comparison of the energetics of models using pure metal dimers and mixed Pb-Si or Sn-Si dimers are made. In addition, rocking, rotation, and diffusion barriers and simulated STM images are calculated as well. All these measures lead to the conclusion that Pb and Sn, unlike Ge, do not intermix with Si to form mixed dimers if Si is not co-deposited with Pb or Sn. This is because the intermixing between Ge and Si is facilitated by exchanging atoms between the Ge dimers and the Si substrate, but such exchange mechanism is not favorable for Pb and Sn dimers leading to a kinetic barrier for the formation of Pb-Si and Sn-Si dimers. However mixed Pb-Si and Sn-Si dimers can in fact be engineered if Si is co-deposited onto Si(100) thus avoiding the kinetic barrier due to the exchange process.

In Chapter 5, a construction of a minimal basis set of highly localized quasiatomic orbitals (QUAMBOs) for Mo in the bcc crystal structure will be described. The construction uses the fully converged first-principles eigenstates as input. The orbitals are constructed such that they look similar to the free-atomic orbitals, but are able to deform in order to adapt to the bonding environment of the system, hence the orbitals as a minimal basis set can reproduce all the occupied eigenstates of the system. The QUAMBOs can be used in the *a posteriori* analysis of the self-consistent eigenstates from first-principles large-basis-set calculations to obtain interpretations based on the concept of atoms and chemical bonding, which is otherwise hard to make using the conventional reciprocal space formulation for a periodic system, for example Mulliken population and

bond order index analysis. QUAMBOs are superior to Wannier functions because localized orbitals can be obtained for both insulating and metallic systems. Previous work has been done on constructing QUAMBOs for crystalline Si and Al in diamond and fcc structures. In this chapter, it is explicitly demonstrated that QUAMBOs can also be constructed for transition metals with localized d-electrons as well.

Lastly in Chapter 6, the use of a genetic algorithm to perform a global search of H-passivated Si nanowires will be presented. Si nanowires, possibly doped, can act as nanoscale devices or as interconnects. Si nanowires fabricated in experiments are mostly passivated by oxide or hydrogen, and nanowires with various diameters (as small as 1.3 nm) and different axis orientations can be made. However, theoretical prediction of the structure of Si nanowires are still at a beginning stage, and attempts being made are mostly based on manual construction without exploring the vast configurational space. Hence, we designed an efficient optimization procedure based on a genetic algorithm (GA) to investigate the structures of H-passivated Si nanowires with the axes along the $\langle 110 \rangle$ direction, which are the smallest diameter nanowires fabricated in experiments. The GA is coupled to a Si-H empirical potential which facilitates fast exploration of the configurational space, followed by structural refinements at the density functional theory level. We found that the structures of H-passivated Si nanowires are bulk-like down to sub-nanometer wire dimensions. In addition, we recognized several structural motifs of “magic” nanowires with chain-like and hexagonal-shaped cross sections. The first type of magic nanowires has not been experimentally observed yet due to its small diameter, but our model for Si nanowires with hexagonal cross section has consistent dimensions and simulated STM images with the smallest ones observed experimentally.

CHAPTER 2. Calculation methods

2.1 First-principles method

My first-principles calculations are based on density functional theory developed by Hohenberg and Kohn in 1964[1]. They proved that the total energy of an electronic system is a functional of the electron density, and the ground state energy of the system can be obtained by minimizing the energy functional, with the corresponding electron density distribution being the electron density at the ground state. In 1965, Kohn and Sham showed that it is possible to approximate the many-electron energy functional by an equivalent set of one-electron equations with an appropriate choice of the exchange-correlation potential to model the many-electron interaction, and the set of equations can be solved self-consistently. Under this approach, the total energy can be written as

$$E[\rho] = E_{KE} + E_H + E_{XC} + E_{ion-e} + E_{ion-ion}, \quad (2.1)$$

where E_{KE} is the kinetic energy, E_H is the Hartree electron-electron energy, E_{XC} is the exchange-correlation energy, E_{ion-e} is the ion-electron interaction energy, and $E_{ion-ion}$ is the ion-ion interaction energy. $\rho = 2 \sum_i |\phi_i|^2$ is the sum of all the one-electron densities. The kinetic energy E_{KE} is taken to be the sum of the one-electron kinetic energy integrals:

$$E_{KE} = \sum_i \langle \phi_i | -\nabla^2 | \phi_i \rangle, \quad (2.2)$$

and

$$E_H = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}. \quad (2.3)$$

The E_{XC} can be expressed as

$$E_{XC} = \int \epsilon_{XC}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad (2.4)$$

under local density approximation(LDA), in which $\epsilon_{XC}(\mathbf{r})$ is the exchange-correlation energy per electron at $\mathbf{r}$ and is approximated by using a homogeneous electron gas with the same density as $\rho(\mathbf{r})$. The generalized gradient approximation(GGA) can be used which takes into account the gradient of the electron density in addition to the local electron density.

The minimization of the total energy under the constraint that the ϕ_i 's are normalized gives rise to a set of Kohn-Sham equations that have to be solved self-consistently:

$$\left(-\frac{1}{2}\nabla^2 + V_H + V_{XC} + V_{ion-e}\right)\phi_i = \epsilon_i\phi_i \quad (2.5)$$

$$\left(-\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{XC}[\rho(\mathbf{r})]}{\rho(\mathbf{r})} + V_{ion-e}\right)\phi_i = \epsilon_i\phi_i, \quad (2.6)$$

where V_H , V_{XC} , and V_{ion-e} are the Hartree, exchange-correlation and the ionic potential respectively. Under the local density approximation, $V_{XC} = \frac{\partial \epsilon_{XC}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})}$. The self-consistent Kohn-Sham equations are usually solved by expanding the wavefunctions ϕ_i into plane waves. However, the wavefunctions close to the core region of the ions are oscillating rapidly due to the requirement of orthogonality to the core-state wavefunctions, resulting in a large plane wave set needed to expand the wavefunctions. Since most of the electronic or chemical properties of a system can be described adequately by the valance electrons, removal of the oscillations in the core region without disrupting the electronic properties of the system will be desired. Hence, the ionic potential V_{ion-e} is usually replaced by a pseudopotential constructed such that the scattering properties of the original ionic potential are reproduced as closely as possible in the energy range of interest while the oscillations of the wavefunction in the core region are removed.

After the self-consistent Kohn-Sham wavefunctions are obtained, the force $\mathbf{F}_I$ on an

ion at position $\mathbf{R}_I$ can be calculated using the Hellmann-Feynman theorem:

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I}. \quad (2.7)$$

The ions are treated adiabatically and the electrons are assumed to respond instantaneously to the motion of the ions due to the large difference in mass between the electrons and ions, this is the Born-Oppenheimer approximation.

2.2 Tight-binding semi-empirical method

The Kohn-Sham equations in Eq. (2.6) can also be solved by expanding the wavefunctions ϕ_i by atomic orbitals $|I\mu\rangle$ in which I labels the atom and μ labels the angular momentum of the orbital:

$$|\phi_i\rangle = \sum_{I,\mu} c_{I\mu}^i |I\mu\rangle, \quad (2.8)$$

resulting in

$$\sum_{I,\mu} H_{I'\mu',I\mu} c_{I\mu}^i = \epsilon_i \sum_{I,\mu} S_{I'\mu',I\mu} c_{I\mu}^i. \quad (2.9)$$

The Hamiltonian matrix is $H_{I'\mu',I\mu} = \langle I'\mu' | -\nabla^2 + V_{eff} | I\mu \rangle$ where $V_{eff} = V_H + V_{XC} + V_{ion-e}$ is an effective potential encountered by the electrons, and $S_{I'\mu',I\mu} = \langle I'\mu' | I\mu \rangle$ is the overlap matrix because $|I\mu\rangle$ is not an orthogonal basis set in general. Tight-binding approximation can be made on the matrix elements of the Hamiltonian by setting $H_{I'\mu',I\mu} = 0$ if the distance between atoms I and I' is larger than a chosen cutoff radius.

The total energy can be expressed as a sum of the eigen-energies ϵ_i , but this will overcount the effects of the electron-electron Hartree energies and exchange-correlation energy. By accounting for this double counting, it can be shown that

$$E = \sum_i f_i \epsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + \int \rho(\mathbf{r})(\epsilon_{XC}[\rho] - V_{XC}[\rho]) d\mathbf{r} + E_{ion-ion}, \quad (2.10)$$

where f_i is the occupancy of the eigenstate ϕ_i . Hence, the total energy can be written as a sum of two terms

$$E = E_{bs} + E_{rep}, \quad (2.11)$$

in which E_{bs} is the band structure energy (first term in Eq. (2.10)) and E_{rep} is the repulsive part which accounts for the double counting in the electron-electron interaction (second and third term) and also includes the ion-ion interaction. By parametrizing the tight-binding Hamiltonian and the repulsive term E_{rep} , total-energy electronic calculations can then be performed. A two-center approximation is usually applied to both the tight-binding Hamiltonian $H_{I'\mu', I\mu}$ and the repulsive energy E_{rep} [2]. However, the approximation is only appropriate for electrons well localized in strong covalent bonds, and cannot adequately describe delocalized electrons in metallic system. Recently, an environment-dependent tight-binding scheme[3] was developed that goes beyond the two-center approximation by taking into account the bonding environment in the parameterization of the tight-binding Hamiltonian and the repulsive energy, therefore improving the transferability of the potential.

2.3 Empirical potential for semiconductors

A very popular empirical potential for semiconductors (for example C, Si and Ge) is the Tersoff potential[4]. It is written as a pairwise sum of interaction energy between atom i and j with a Morse-like form:

$$E = \frac{1}{2} \sum_{i,j \neq i} f_c(r_{ij}) (A \exp(-\lambda_1 r_{ij}) - B_{ij} \exp(-\lambda_2 r_{ij})). \quad (2.12)$$

f_c is a cut-off function in which the interaction between two atoms is zero beyond certain chosen cut-off distance. The first term in Eq. (2.12) is repulsive, which represents repulsion due to the Pauli principle or orthogonalization, and the second term is the attractive part due to bonding. The parameter B_{ij} depends on the environment around

the atoms i and j , for example bond length, bond angles and bond order. Although the Tersoff potential form is pairwise, it is in fact implicitly beyond two-body through the parameters, and hence it can be fitted to describe open structures like semiconductor crystal. The parametrization can be extended to include multi-component systems in which the parameters A and B_{ij} not only depend on the coordinates of the atoms, but also on the types of atoms.

CHAPTER 3. Pb on Si(111)

3.1 Structures and Stabilities of Pb/Si(111) at low coverage

3.1.1 Introduction

Ordering of two dimensional epitaxial overlayer on a substrate is an interesting problem in physics[4, 5, 6, 7]. One of the prototype system for studying this type of problem is Pb/Si(111). It is known that Pb is not reactive with Si and they are mutually insoluble[8, 9, 10]. Pb/Si(111) can form a well-defined interface which is ideal for studying two dimensional behavior. Both Pb and Si are group IV elements but their lattice constants are incommensurate. It is of great interest to understand what the resultant overlayer structure will be for different coverage of Pb on Si(111).

Experimentally, it turns out that the phase diagram of Pb/Si(111) is complicated which depends on coverage, temperature and annealing history[10, 11, 12], and Fig. 3.1 shows the different phases proposed by experiments between 1/6 and 4/3 ML coverage. For a Pb coverage of 1/6ML, experiments observed the so-called mosaic phase(or γ -phase), in which Pb and Si adsorb on T4 sites with equal proportion[13, 14]. As coverage increases, the adsorbed Si atoms at the T4 sites are gradually replaced by Pb atoms until all the Si atoms are replaced[15]. This is the β -phase which has a coverage of 1/3ML. The β -phase has $\sqrt{3} \times \sqrt{3}$ symmetry with Pb atoms adsorbed on the T4 sites. Upon cooling below room temperature at 1/3ML coverage, a (3 $\times$ 3) phase is observed[12, 16]. The exact nature of the transition from $\sqrt{3} \times \sqrt{3}\beta$ phase to (3 $\times$ 3) is not clear, but it

may be related to charge density wave instability[17, 18, 19, 20]. At $2/3\text{ML}$, Le Lay et al. observed a stable phase and the proposed structure has a $\sqrt{3} \times \sqrt{3}$ symmetry with two Pb atoms adsorbed at T4 sites[10]. Since then, no other groups reported this particular phase at this coverage. At 1ML , domains composed of $\sqrt{3} \times \sqrt{3}$ unit cells are observed[21, 22]. STM experiments observed alternating domains of trimers with quasi- (1×1) region in between[21]. Two types of trimer domain are observed. The trimers are composed of three Pb atoms at T1 sites displaced either towards H3 site or T4 site. At high temperature, a commensurate-incommensurate(CI) transition from trimer domains to (1×1) phase is observed. For coverage between 1 and $4/3\text{ML}$, hexagonal incommensurate phase(HIC) and striped incommensurate phase(SIC) are observed[11, 12]. They are also known as α -phase. The exact structure of the α -phase is not well understood. Upon cooling of the α -phase, a low temperature phase with $\sqrt{3} \times \sqrt{7}$ symmetry is observed[12, 15, 16, 23]. Except for the $1/6\text{ML}$ mosaic phase and $1/3\text{ML}$ β -phase, there are controversies on the exact coverage and the corresponding structures of the other phases.

The purpose of this section is to explore the various proposed structural models and other plausible models for Pb coverage between $1/6\text{ML}$ to $4/3\text{ML}$ using first-principles calculations in order to determine the energetically stable Pb coverage and the corresponding energetically favorable geometries. This section is divided into five parts. Section 3.1.2 describes the theoretical tools and settings that our calculations are based on. Section 3.1.3 describes the structures that we have calculated together with simulated STM images for certain structures. In Section 3.1.4, energetics of the structures mentioned in Section 3.1.3 will be discussed, and our results will be compared with experiments. Section 3.1.5 is the conclusion.

Figure 3.1 Proposed phases of Pb/Si(111) by experiments for coverage between 1/6 and 4/3 ML.

3.1.2 Calculation Method

Our first-principles calculations are based on density functional theory (DFT) under local density approximations (LDA)[1]. Pseudopotential and plane wave basis are being used. The Ceperley-Alder functional[24] parametrized by Perdew and Zunger[25] is used for the exchange-correlation energy functional. The kinetic energy cutoff is set to be 12 Ryd. The Si(111) surface is modeled by a periodically repeating slab which consists of 6 layers of Si passivated by H at the bottom and a vacuum space of at least 12Å. The bottom double layer of Si atoms is kept fixed to simulate the bulk environment, while all other atoms are allowed to relax until the forces are less than 0.025 eV/Å. A set of 48 special k points are chosen to sample the irreducible Brillouin zone of (1×1) unit cell. For unit cells other than (1×1), equivalent k points have been used.

3.1.3 Optimized Structures

3.1.3.1 Structure of the mosaic phase at 1/6 ML

The 1/6ML mosaic phase is modeled by a $2\sqrt{3} \times 2\sqrt{3}$ unit cell. The adsorbed atoms are located at T4 sites in which half of them is Pb and the other half is Si, as shown in Fig. 3.2. Our calculations show that this is a stable structure. Pb adatoms are higher than Si adatoms resulting in a corrugation of 0.87Å. The Pb-Si bond length is 2.82Å, and the bond length between the Si adatom and Si substrate atom is 2.44Å as shown in the figure. It should be noted that the Si adatoms are very close to the substrate, such that the Si atoms in the substrate directly below the adatoms are being pushed downwards relative to the other Si atoms in the same layer.

Figure 3.2 (a) The top view and (b) side view of 1/6 ML mosaic phase in a $2\sqrt{3} \times 2\sqrt{3}$ unit cell. Pb(Si) adatoms are black(light gray). Si atoms in the first(second and below) layer of the Si substrate are white(gray). Only the first two layers of the Si substrate are shown for the top view with the Pb and Si adatoms represented by larger spheres. For the side view, top four layers of the Si substrate are shown. The (1×1) unit cell is indicated by a dotted line, and a dashed line for $\sqrt{3} \times \sqrt{3}$ unit cell. The top view and the side view are not in the same scale.

Simulated STM images[26] of this structure are shown in Fig. 3.3. The STM tip is assumed to position at a height of 2Å above the highest atom in the structure. This assumption will be used for the other simulated STM images. Although Pb adatoms are higher than Si adatoms geometrically by 0.87Å, the apparent height between them

depends on the applied bias voltage. For negative bias voltages, there are only bright spots corresponding to Pb atoms. This is true for various bias voltages that have been tested between -0.5V to -2V. Filled states images for -1V and -2V are shown in Fig. 3.3(a) and (b) respectively. The situation is different for positive bias voltages. For an empty state image with a bias of 0.5 V(Fig. 3.3(c)), both Pb and Si atoms can be seen, although the spots corresponding to Si atoms are weaker. For voltages above 0.5 V(Fig. 3.3(d)), Pb adatoms are much brighter than Si. Dependence of apparent height difference between Si and Pb on sample bias was studied in Ref. [13] experimentally. For negative bias voltages, Ref. [13] has the same observation as our calculations. For positive bias voltages, the experiment observed the same apparent height for Pb and Si adatoms at 1.0V. Pb adatoms look brighter than the Si for larger bias voltages. Although the precise bias voltages where Pb looks brighter than Si from the experiment is different from our calculation results, both the experiment and our calculations agree that there are changes on the apparent height between Pb and Si adatoms for positive bias voltages, but not for the negative case.

3.1.3.2 Structures of $\sqrt{3} \times \sqrt{3}$ phase at 1/3 ML

Three geometries based on $\sqrt{3} \times \sqrt{3}$ unit cell are tested for the Pb coverage of 1/3 ML. They correspond to Pb atom placed at the T1, H3, or T4 site respectively, as shown in Fig. 3.4. Our calculations show that these three structures are all energetically stable, but the T4 structure is most energetically favorable among the three. As one can see from Fig. 3.4(d), in the T4 structure the dangling bonds of the top Si layer of the substrate are all saturated by Pb adatoms. The Pb-Si bond length is 2.80Å. The second layer of the Si substrate is 0.62Å below the first layer, which is the same as a relaxed Si(111) substrate, but it is not flat. Those Si atoms which are directly below the T4 Pb adatoms are being pushed downwards by 0.46Å relative to the other Si atoms in the second layer, and their distances to the Pb adatoms directly above is 2.93Å. Simulated

Figure 3.3 Simulated STM images of the $1/6$ ML mosaic phase with a bias voltage of (a) -1.0 V, (b) -2.0 V, (c) 0.5 V, and (d) 1.0 V. The dashed lines indicate the same $\sqrt{3} \times \sqrt{3}$ unit cells as in Fig. 3.2(a).

STM images of this structure are shown in Fig. 3.5. For both the empty states and occupied states images, there are bright spots corresponding to the T4 Pb atoms.

Since it is experimentally observed that there is a transition from the β -phase to a (3×3) phase upon lowering the temperature, the stability of the T4 structure is studied by using a (3×3) unit cell as shown in the inset of Fig. 3.6. The stability of the T4 model is tested with respect to a surface phonon distortion with (3×3) symmetry. One of the Pb adatom is picked, which is labeled A in the inset, with its height fixed, and all the other atoms are free to relax. This is repeated with different height of the chosen Pb adatom, and the result is shown in the plot of Fig. 3.6. If this surface phonon mode is soft, there will be a spontaneous distortion of the originally flat Pb overlayer. Our calculations show that the minimum in energy corresponds to a flat Pb layer. Simulated

Figure 3.4 (a) T1 model, (b) H3 model, (c) T4 model, and (d) side view of the T4 model for the 1/3 ML β -phase. The top view and the side view are not in the same scale. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

STM images for the T4 model with a (3×3) unit cell are also calculated. all the bright spots are found to have the same brightness, which look exactly the same as in Fig. 3.5. Even though a (3×3) unit cell is being used in the calculation, all results simply reduced to $\sqrt{3} \times \sqrt{3}$ symmetry both structurally and electronically.

3.1.3.3 Structures Models at 2/3 ML

For a Pb coverage of 2/3 ML, our structural models consist of two Pb adatoms in a $\sqrt{3} \times \sqrt{3}$ unit cell. Each Pb adatom can be put on T1, T4, or H3 sites. Different ways of putting the two Pb adatoms on the three sites give six initial geometries. Upon relaxation, we found that when the two Pb atoms are placed at different sites, they will go off-site and dimerize with the other Pb atom. In particular, when Pb adatoms are located at T1 and T4 sites, the T4 Pb adatom will go to the bridge site. The Pb dimer

Figure 3.5 Simulated STM images of the $1/3$ ML β -phase with a bias voltage of (a) 1.0 V, and (b) -1.0 V. The dashed lines indicate the same $\sqrt{3} \times \sqrt{3}$ unit cells as in Fig. 3.4(c).

has a bond length of $3.19\text{\AA}$. When Pb adatoms are located at T1 and H3 sites, the H3 Pb adatom will also go to the bridge site to give the exact same structure as the previous case. When the Pb adatoms are put at T4 and H3 sites, they will form a dimer with a length of $3.22\text{\AA}$. Since two of the initial structures give the same final result, five stable structures are obtained as illustrated in Fig. 3.7. They are named according to where the Pb adatoms are located.

3.1.3.4 Structure Models at 1 ML

The simplest models for 1 ML are structures based on (1×1) unit cells. Three structures are tested, in which a Pb adatom is placed at T1, T4, or H3 site respectively. The T1 is the most energetically stable structure among the three[27]. In this T1 model, the dangling bonds of the Si atoms in the first layer of the substrate are all saturated by Pb adatoms, with Pb-Si bond length equals to $2.66\text{\AA}$. The vertical distance between the first and second Si layers is $0.81\text{\AA}$, which is bigger than $0.78\text{\AA}$ for an unrelaxed Si(111) substrate.

The trimer models based on $\sqrt{3} \times \sqrt{3}$ unit cell are also tested. There are two proposed structures in Ref. [21] as shown in Fig. 3.8(a) and (b). Both contain Pb atoms adsorbed

Figure 3.6 A plot of the total energy of $1/3$ ML (3×3) distorted T4 model versus the height of the labeled Pb adatom A. The total energy is with respect to that of the undistorted ground state structure. The inset shows the T4 model of the $1/3$ ML β -phase in a (3×3) unit cell, which is used for the calculations. The dotted line and the dashed line indicate the (3×3) and $\sqrt{3} \times \sqrt{3}$ unit cells respectively. The scheme for coloring the atoms is the same as Fig. 3.2.

at T1 location but displaced a little bit off-site. If the Pb atoms displace towards H3 site, the resultant structure is called T^+ model. If it is towards T4 site, it is called T^- model. We found that it is energetically stable for the Pb atoms to be displaced either towards T4 or H3 site. The bond length between Pb atoms in a trimer is $3.68 \text{ \AA}$ for T^+ model and $3.74 \text{ \AA}$ for T^- model, compared to $3.84 \text{ \AA}$ if the Pb atoms are located exactly at the T1 sites. The geometries of the T1 model and the trimer models are very similar. For both trimer models, the Pb-Si bond length is $2.68 \text{ \AA}$, which is slightly bigger than the T1 model, and the distance between the first and second Si layers is both $0.81 \text{ \AA}$. An interesting difference between the T^- model and the other two models is that the second layer of the Si substrate of the T^- model is not completely flat. For the T^- model, the

Figure 3.7 (a) T1-B model, (b) T4-H3 model, (c) T4-T4 model, (d) H3-H3 model, and (e) T1-T1 model for 2/3 ML Pb coverage. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

second layer Si atoms directly below the center of the Pb trimers is $0.02\text{\AA}$ lower than the rest of the Si atoms in the second layer.

Figure 3.8 The top view of (a) 1 ML T^+ and (b) T^- model. Their side view diagrams look exactly the same, and is illustrated in (c), please refer to the text for a subtle difference between them. The top view and the side view are not in the same scale. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

Simulated STM images for the trimer models are shown in Fig. 3.9. For filled states images, clear distinct bright spots from Pb atoms can be observed for both T^+ and T^- models. While for empty states images, the bright spots are displaced away from the

H3(T4) site and the intensity is low at H3(T4) position for the $T^+(T^-)$ model, although the Pb adatoms are displaced towards H3(T4) site structurally. At the same bias voltage of 1.0 V, the T^+ structure is about twice as bright as the T^- structure. If T^+ domain and T^- domain coexist in the same structure, they can be differentiated by their apparent height in STM empty state images.

Figure 3.9. Simulated STM images of the T^+ model with a bias voltage of (a) -1.0 V, and (b) 1.0 V. Simulated STM images for the T^- model is shown in (c) and (d) with a bias voltage of -1.0 V and 1.0 V respectively. The dashed lines indicate the same $\sqrt{3} \times \sqrt{3}$ unit cells as in Fig. 3.8(a) and (b). (b) and (d) are plotted under the same gray scale. The bright spots in (b) are around twice as bright as those in (d).

Based on the results of Ag/Si(111)[28] and Au/Si(111)[29], missing-top-layer(MTL) models for Pb/Si(111) may be possible. MTL models are structures with the first layer of the Si substrate removed such that each Si atom of the top layer has three dangling bonds. Four different MTL models are tested. The honeycomb-chained-trimer(HCT)

model that has been observed in Ag/Si(111) is shown in Fig. 3.10(a). The structure consists of chained Pb trimers with the centers of the trimers forming a honeycomb network. A related model is called inequivalent-triangle(IET)[30]. The difference between HCT and IET is that for the IET model, the Pb and Si trimers are twisted such that the mirror plane symmetry along the $[11\bar{2}]$ direction is lost, while the three fold symmetry is preserved. We found that IET is not energetically stable and it relaxed to HCT. Another related structure is the conjugate-HCT(CHCT) model[29]. Instead of Pb atoms forming chained trimers, CHCT has the top layer of Si forming chained trimers instead. Our calculations found that CHCT is not energetically stable and reduced to HCT upon relaxation. The fourth MTL model that we considered is the substitution model(MTLs). We start with a Si(111) substrate with a top double layer. Then the first Si layer is replaced by Pb atoms such that the bonds of the second Si layer are all saturated. We found that MTLs is energetically stable and it is shown in Fig. 3.10(b).

Figure 3.10 (a) HCT model, and (b) MTLs model for 1 ML α -phase. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

3.1.3.5 Structure Models at 6/5 ML

At low temperature and with a Pb coverage of 6/5ML, a $\sqrt{3} \times \sqrt{7}$ phase have been observed. In our present calculations, the structure from X-ray diffraction experiment[23]

is adopted as shown in Fig. 3.11(a). There are six Pb atoms in a unit cell, one of them is at H3 site, the others are at T1 site or off-centered T1 site. We called this structure H3 model. As we will show later in this section when the energetics of different structures are compared, the energy difference between placing a Pb adatom at H3 or T4 site is very small when the Pb coverage is above 1 ML, we therefore tested a competitive model in which the H3 Pb adatom is placed at T4 site instead. The resultant structure is called T4 model and is shown in Fig. 3.11(b). Both structures are energetically stable. A detailed description of the structure of H3 model can be found in Ref. [23] and theoretical studies on this structure has been done as well[31]. This calculation is repeated together with our newly proposed T4 model. From our calculations, the bond lengths between the H3 Pb adatom with the other Pb adatoms are 3.01Å and 3.04Å, which is close to the Pb-Pb covalent bond length of 2.94Å. While the other Pb-Pb bond lengths not involving the H3 Pb adatom are greater than 3.2Å, which is closer to the metallic Pb bond length of 3.50Å. The corrugation of the Pb overlayer is 0.14Å. Our result is consistent with the previous theoretical study[31] and experimental observations in Ref. [23], which also observed that there may be more than one equilibrium height for the H3 Pb adatom. Calculations are done to search for other possible heights for the H3 Pb adatom, but another equilibrium position cannot be found. For the T4 model, similar observations can be made that the bond lengths between the T4 Pb adatom and the other Pb adatoms are close to the Pb-Pb covalent bond length, while the other Pb-Pb bond lengths are more metallic. The corrugation of the Pb overlayer in the T4 model is 0.13Å.

Simulated STM images for the H3 model are shown in Fig. 3.12. For empty states image(Fig. 3.12(a)), a bright spot corresponding to the H3 Pb adatom and a weaker spot corresponding to an off-site T1 Pb atom can be seen. For filled states images(Fig. 3.12(b) and (c)), five spots which seem to come from T1 position can be found in a unit cell. The relative brightness of these spots depend on the bias voltage. For the -0.35V filled states image in Fig. 3.12(b), a trimer-like feature is observed, which is highlighted

Figure 3.11 (a) H3 model, and (b) T4 model based on $\sqrt{3} \times \sqrt{7}$ unit cell for the 6/5 ML Pb coverage. The dotted line and dashed line indicate the $\sqrt{3} \times \sqrt{3}$ and $\sqrt{3} \times \sqrt{7}$ unit cells respectively. The labeling of the Pb adatoms for the H3 model is the same as that of Ref. [23]. The Pb adatoms of the T4 model is labeled in the same way except that the Pb adatom 1 denotes the T4 Pb adatom instead of the H3 Pb adatom. The dotted circles denotes Pb adatom 2 in the adjacent unit cell. The scheme for coloring the atoms is the same as Fig. 3.2.

in the figure. The simulated STM images for the T4 model is also calculated as shown in Fig. 3.13. As in H3 model, a bright spot corresponding to the T4 Pb adatom can be observed in the empty states image. For the filled states image, spots corresponding to the other T1 Pb adatoms can be seen and their relative brightness also depend on the bias voltage, as shown in Fig. 3.13(b) and (c). We again noticed a trimer-like feature when the bias voltage is -0.35V, but the orientation is different from that of the H3 model. Therefore, both H3 and T4 models should produce very similar features in STM images, and they can only be differentiated by the registry of the bright spots with respect to the underlying Si(111) substrate. In Fig. 3.14, the Si(111) lattice (small spheres) and the Pb

adatoms (big spheres) are overlaid on top of both the experimental and theoretical data. Fig. 3.14(a) presents a high-resolution STM image of the $\sqrt{3} \times \sqrt{7}$ phase at a bias voltage of 1.3V. Bright spots can be observed in between H3 Pb adatoms and the adjacent T1 Pb adatoms, this feature is reproduced accurately by our calculation as shown in Fig. 3.14(b). If the T4 model is the correct structure, the bright spots mentioned above would have to shift along the $(11\bar{2})$ direction by approximately half of the $\sqrt{3}$ lattice constant. This illustrates unambiguously that the H3 model fits the experimental STM results better than the T4 model. It can be noticed that there are other bright spots corresponding to T1 Pb adatoms in the experimental STM image, which are absent in the theoretical calculation. However, these extra spots are also absent in a recent STM experiment of the $\sqrt{3} \times \sqrt{7}$ phase[31]. The reason for the difference between the results of the two STM experiments is not clear.

Figure 3.12 Simulated STM images of the 6/5 ML H3 model with a bias voltage of (a) 1.5 V, (b) -0.35 V, and (c) -1.0 V. The dashed lines indicate the same $\sqrt{3} \times \sqrt{7}$ unit cells as in Fig. 3.11. The triangle in (b) denotes a trimer-like feature that can be observed in the filled states image.

Figure 3.13 Simulated STM images of the 6/5 ML T4 model with a bias voltage of (a) 1.5 V, (b) -0.35 V, and (c) -1.0 V. The dashed lines indicate the same $\sqrt{3} \times \sqrt{7}$ unit cells as in Fig. 3.11. The triangle in (b) denotes a trimer-like feature that can be observed in the filled states image. Note that it is pointing in the opposite direction when compared to Fig. 3.12(b).

3.1.3.6 Structures of $\sqrt{3} \times \sqrt{3}$ H3 and T4 models at 4/3 ML

For 4/3 ML coverage, we consider structures based on $\sqrt{3} \times \sqrt{3}$ unit cells with four Pb atoms in each unit cell. The first structure is called H3 model, in which one Pb atom is located at H3 site and the other three at off-centered T1 location forming a trimer. It is energetically stable and is shown in Fig. 3.15. The Pb overlayers essentially form a flat surface, which is about 2.6Å above the Si substrate. The vertical distance between the first and second layer Si substrate is 0.82Å. The H3 Pb adatom has a bond length of 3.03Å with its nearest Pb adatoms. The trimers formed by the off-centered T1 Pb adatoms have a length of 3.38Å. By replacing the H3 Pb atom by a Pb atom on the T4 site, we obtain another model called the T4 model. It is also energetically stable and is shown in Fig. 3.16. The Pb overlayer is again very flat, with a corrugation of 0.23Å, and about 2.6Å above the Si substrate. The vertical distance between the first and second layer of Si substrate is 0.86Å, with the second layer Si atoms which are directly below the T4 Pb adatoms 0.1Å higher than the rest of Si atoms in the same layer. The T4

Figure 3.14 Si(111) lattice and Pb adatoms overlaid on top of (a) a high-resolution STM image of $\sqrt{3} \times \sqrt{7}$ phase with a bias voltage of 1.3 V, and (b) simulated STM image of the H3 model at the same bias voltage. The small spheres represents the Si(111) lattice and the big spheres are the Pb adatoms. Bonds are drawn in between the H3 Pb adatoms and their adjacent T1 Pb adatoms, where the bond lengths are approximately 3Å.

Pb adatom has a bond length of 3.09Å with its nearest Pb adatoms. The trimers has a length of 3.45Å for this case.

Simulated STM images are shown in Fig. 3.17(a)-(d). Empty states images show bright spots corresponding to H3(T4) Pb atom for the H3(T4) model. From Fig. 3.17, we can see that the H3 model gives brighter spots than the T4 model. If a H3 domain and a T4 domain coexist on the same structure, they can be differentiated by their apparent height in STM. For occupied states images, bright spots corresponding to the other three Pb atoms on the T1 sites can be seen for both models. But the occupied states image of the H3 model has substantial intensity at the H3 positions, while very little intensity is seen at the T4 positions in the T4 model.

Figure 3.15 (a) The top view and (b) side view of the 4/3 ML H3 model. The gray-bordered triangle in (a) illustrates the trimers formed by the off-centered T1 Pb adatoms as mentioned in the text. The side view illustrates the Pb adatom at H3 position (the labeled Pb adatom) and its nearest Pb adatoms. The top view and the side view are not in the same scale. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

We also found another energetically stable structure which is neither H3 nor T4, but look similar to them. It has a Pb atom at an off-site T4 location and another at off-site H3 as shown in Fig. 3.18. The Pb adatoms form chain-like structures along the $[11\bar{2}]$ direction. We call this structure the intermediate(Int) phase, as it looks like a transition state between the H3 and T4 model. The Pb overlayer has a corrugation of $0.15\text{\AA}$ and it is around $2.58\text{\AA}$ above the Si substrate. As shown in Fig. 3.18(a), the bond length between Pb-1 and Pb-2 is $3.20\text{\AA}$, $3.19\text{\AA}$ between Pb-2 and Pb-3, and $2.94\text{\AA}$ between Pb-3 and Pb-1. The vertical distance between the first two layers of the Si substrate is $0.81\text{\AA}$. The Si atoms in the second layer of the substrate below Pb-1 are slightly higher than the rest of the Si atoms in the same layer by $0.1\text{\AA}$.

Simulated STM images of the Int phase are shown in Fig. 3.17(e) and (f). One bright spot and one weaker spot can be found in a unit cell in the empty states image. The brighter spots come from the off-site T4 Pb atom and the weaker spots come from the off-site H3 Pb atoms. The filled states image gives three spots in a unit cell, two bright spots and a weaker elongated spot. The weaker spots come from the off-site H3 Pb atom

Figure 3.16 (a) The top view and (b) side view of the 4/3 ML T4 model. The gray-bordered triangle in (a) illustrates the trimers formed by the off-centered T1 Pb adatoms as mentioned in the text. The side view illustrates the Pb adatom at T4 position (the labeled Pb adatom) and its nearest Pb adatoms. The top view and the side view are not in the same scale. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

and extend to T1 site towards the off-site T4 Pb atom, which does not give a bright spot in the filled state image. The two bright spots come from the other two Pb atoms located near the T1 sites in the unit cell.

As for 1 ML, we also consider the possibility of MTL models. A simple extension from the MTL models of 1 ML to 4/3 ML is by adding one extra Pb adatom to the $\sqrt{3} \times \sqrt{3}$ unit cell. In this way, we obtained energetically stable HCT-adatom models (HCTa1, HCTa2) and MTL-substitution-adatom models (MTLsa-H3, MTLsa-T4) as shown in Fig. 3.19. Since these four models are obtained by putting an additional Pb adatom on top of the existing 1 ML MTL models, the Pb overlayer has a large corrugation. Structural models with small corrugations of the Pb overlayer are also constructed simply removing the first Si layer in the Si(111) substrate of the 4/3 ML H3 and T4 models. The Pb overlayer from the H3 and T4 models are lowered to a reasonable height and laterally displaced as a whole with respect to the missing-top-layer substrate. Since it is not obvious what lateral displacement will give the lowest energy structure, we generated many $\sqrt{3} \times \sqrt{3}$ MTL models with flat Pb overlayer and the only difference between

Figure 3.17 Simulated STM images of the 4/3 ML H3 model with a bias voltage of (a) 1.5 V, and (b) -1.5 V. For the 4/3 ML T4 model, the simulated STM images are shown in (c) for 1.5 V and (d) for -1.5 V. While for the 4/3 ML Int model, it is (e) and (f) for 2.0 V and -1.5 V respectively. The dashed lines indicate the same $\sqrt{3} \times \sqrt{3}$ unit cells as in Fig. 3.15 for H3 model, Fig. 3.16 for T4 model, and Fig. 3.18 for the Int model. It should be noted that (a) and (c) are plotted under the same gray scale. We can see that the H3 spots are brighter than the T4 spots.

them is the Pb overlayer being laterally displaced as a whole with respect to the MTL substrate. Among the flat MTL models that we have generated in the above manner, the most energetically favorable one after optimization is shown in Fig. 3.19(a), which we called MTL1. Finally, we consider the H3 and T4 models with stacking fault(H3sf, T4sf) on the Si(111) substrate. The relative energetics of these structures will be considered in the following section.

Figure 3.18 (a) The top view and (b) side view of the 4/3 ML Intermediate model. The top view and the side view are not in the same scale. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

3.1.4 Relative Stabilities and discussion

We have calculated the formation energies of the structures discussed in the previous section in order to compare their relative stabilities. The formation energy is defined as:

$$E_s = (E - E_{sub} - N_{Pb} \times E_{Pb} - N_{Si} \times E_{Si})/A, \quad (3.1)$$

where E is the total energy of the structure, E_{sub} is the total energy of Si(111) substrate, $N_{Pb}(N_{Si})$ is the number of Pb(Si) adatoms in a unit cell, $E_{Pb}(E_{Si})$ is the total energy of a bulk Pb(Si) atom in fcc(diamond) structure, and A is the surface area of the Si(111) substrate. This formula measures the stability of a structure with respect to a clean Si(111) substrate and with Pb and Si adatoms in their respective bulk environment. If the formation energy is negative, it is energetically favorable to form that particular structure.

For structures based on MTL models, their formation energies are not obtained from (1). Since the Si(111) substrate with a missing top layer has three dangling bonds per surface atom, it has a much higher energy than a substrate with a top double layer. A direct application of (1) to MTL models does not allow a fair comparison with other models. We use an indirect method to infer the formation energies of MTL models. For a given MTL model, a corresponding structure with inversion symmetry is generated,

Figure 3.19 (a)MTL1 model, (b)HCTa1 model, (c)HCTa2 model, (d)MTLsa-H3 model, and (e)MTLsa-T4 model for the 4/3 ML α -phase. The scheme for coloring the atoms and outlining the unit cells is the same as Fig. 3.2.

such that hydrogen passivation at the bottom of the substrate is not necessary. Then we pick another non-MTL structure at the same Pb coverage and generate a structure with inversion symmetry. These two structures with inversion symmetry should have the same number of Pb and Si atoms in a unit cell, such that the total energies can be directly compared. Since the formation energy of the other chosen structure is known from (1), the formation energy of the MTL model can be inferred from the total energy difference. For MTL models to be formed, the top layer of the Si(111) has to be removed when Pb is deposited. The physical interpretation of the formation energy for MTL models is that the removed top Si atoms are assumed to go to a bulk diamond Si environment.

The formation energies of all the structures mentioned in Section 3.1.3 are summarized in Table 3.1 and illustrated in Fig. 3.20. For 1/6 ML, the mosaic phase has a negative formation energy, therefore it is energetically favorable to form this structure. For 1/3 ML, the T4 model has the lowest formation energy, which is 0.14 eV lower than the H3 model. The T1 model is not energetically favorable. This agrees with the experimental observations that the β -phase consists of Pb atoms adsorbed at T4 sites. For 2/3

ML, coexistence between the β -phase and the $\sqrt{3} \times \sqrt{7}$ phase is observed experimentally. From our calculations, the T1-B and T4-T4 models are the lowest energy structures and they are degenerate in energy. If a stable phase at $2/3$ ML can be observed, T1-B is a possible candidate apart from the T4-T4 model proposed by Le Lay et al[10]. For 1 ML, the T1 model and the trimer models(T^+ , T^-) are the most favorable and they are degenerate in energy. In contrary to Ag/Si(111) and Au/Si(111), MTL models are not as favorable in this case. For $6/5$ ML, the H3 model is slightly lower in energy than the T4 model by 0.01 eV per 1×1 unit cell. Experimentally, only the H3 model is observed. Despite the similarity between the adsorption energies at H3 and T4 sites of the $\sqrt{3} \times \sqrt{7}$ phase, only domains with H3 sites are observed both in X-ray and STM experiments. However, as we have shown in a recent publication for the HIC structure[32] which has $\theta=1.25$ ML(built with $\sqrt{3} \times \sqrt{3}$ unit cells in the domain interior and essentially the $\sqrt{3} \times \sqrt{7}$ phase in the domain walls), both the H3 and T4 sites are observed. It is still not clear why the binding site of the $\sqrt{3} \times \sqrt{7}$ phase is only H3 while for the HIC phase, which easily evolves from the $\sqrt{3} \times \sqrt{7}$ phase with the addition of few monolayer percent of Pb, both sites are occupied.

For $4/3$ ML, the T4, H3 and the Int models are the lowest energy structures and they are nearly degenerate in energy. There are a few interesting implications from our results for $4/3$ ML. The first point is that although for a clean Si(111) (1×1) surface, the energy for a stacking fault is 0.04eV as shown in Table 3.1, the Pb overlayer seems to stabilize the stacking fault. The energies of T4sf and H3sf models are only 0.01 eV higher than their unfaulted counterpart. It is generally believed that when Pb is deposited on Si(111) (7×7), stacking fault will be removed. Our calculations show that this might not be the case. The second point is the apparent height difference between the H3 and T4 models in STM empty states image and their degeneracy in energy can be used to explain the features observed in HIC phase. The HIC is believed to be composed of alternating domains of H3 and T4 models. This will be further discussed elsewhere[32].

Figure 3.20 A plot of the formation energies of various models against Pb coverage on Si(111). Linear interpolation is done between certain lowest energy structures with different coverage. An explanation for the interpolation can be found in the text.

Finally, the Int model bears close resemblance to the T4 and H3 models as described in Section 3.1.3. In addition, its energy is nearly degenerate with the T4 and H3 models. The Int model may act as a bridge between T4 domains and H3 domains. In particular, the Int model may be related to the domain wall structure of the HIC phase.

The third point is that the MTL models are not as energetically favorable as the other models as in 1 ML. The lowest energy structure among the MTL models is the MTL1. One of the differences between MTL1 and the other MTL models is that the Pb overlayer in MTL1 has a smaller corrugation, while the others are highly corrugated as mentioned in Section 3.1.3. This feature is shared by the H3, T4, Int and the stacking faults models, in which the corrugation of the Pb overlayer is less than $0.25\text{\AA}$. These structures may comprise the wetting layer on which 3D Pb islands can grow. The flatness

may provide low diffusion barrier which facilitates the growth of 3D islands[33, 34, 35]. Fig. 3.21 shows an STM image of the SIC phase which consists of $\sqrt{3} \times \sqrt{3}$ domains separated by meandering domain walls, which are essentially $\sqrt{3} \times \sqrt{7}$ unit cells[35]. The coverage is slightly above 4/3 ML. The smoothness of this image is consistent with the above calculated value. Growth of additional Pb on top of this phase at even lower temperatures, $100 < T < 240\text{K}$, results in the formation of well-ordered regular structures extending up to 100nm in linear size. First, networks of planar triangular Pb clusters will form when small extra amount of Pb is deposited ($\Delta\theta < 1$ ML). For larger amount of Pb deposited ($\Delta\theta > 1$ ML) with increasing temperature, (111)-oriented Pb islands grow by bilayer height increments as a result of quantum-size effects(QSE). Fig. 3.22 shows the result of the growth after depositing ~ 2.5 ML of Pb on top of the well-annealed α -phase at 150K. A 2-step film grows first, extending over the whole $147 \times 95\text{nm}^2$ image, with the next 4-step layer forming on top of it, thus providing experimental evidence for the low corrugation of the $\sqrt{3} \times \sqrt{3}\alpha$ phase and also the low diffusion barrier of this phase. The modulation observed on top of the islands is an electronic effect related to variations at the metal/semiconductor interface discussed elsewhere[36].

Figure 3.21 Different domains of $\sqrt{3} \times \sqrt{3}$ separated by meandering domain walls which are essentially $\sqrt{3} \times \sqrt{7}$ unit cells. The corrugation of the phase is 0.05nm in good agreement with the calculation.

Figure 3.22 $147 \times 95 nm^2$ STM image showing the formation of a long flat 2-step film with few 4-step islands on top at $T=160K$ and $\theta=4ML$ (including the amount of Pb in the $\sqrt{3} \times \sqrt{3}\alpha$ phase). This is an indication of the high Pb mobility on the α -phase.

Up till now, we are comparing structures with the same coverage. Comparison of structures with different coverage can be done as follows. From Fig. 3.20, the points corresponding to the lowest energy structures of $1/6$ ML, $1/3$ ML, and $4/3$ ML are linearly interpolated. The interpolation between $1/3$ ML and $4/3$ ML, for example, represents domains with $1/3$ ML coexisting with domains with $4/3$ ML. If we assume the domain wall density is low, the energy associated with them can be neglected. This justifies the use of linear interpolation between structures. The structures with $2/3$ ML, 1 ML, $6/5$ ML are above the interpolated curves. This implies that they are susceptible to segregation into domains of $4/3$ ML and $1/3$ ML, and therefore, they are not stable coverage. The conclusion for $2/3$ ML agrees with the fact that nearly all experimental groups did not observe a stable $2/3$ ML phase. Although the 1 ML phase is observed experimentally, it is not a stable coverage according to our analysis. This discrepancy may be due to the fact that our energetics are based on local $\sqrt{3} \times \sqrt{3}$ or (1×1) geometries assuming negligible contribution from domain walls. This may not be applicable to the experimentally observed 1 ML phase. It is also possible that the observed 1 ML phase is metastable. Our results show that the $6/5$ ML models are not stable, this is contradictory to the experimental fact that the $\sqrt{3} \times \sqrt{7}$ H3 model is observed upon cooling at a Pb coverage between $1/3$ ML and around 1.2 ML. A reversible phase transition at $T \sim$

270K has been found with several techniques(X-ray and STM) with $\sqrt{3} \times \sqrt{7}$ being the stable phase at 6/5 ML and $T < 270\text{K}$. It is still not clear what the high temperature phase for $T > 270\text{K}$ and the nature of the phase transition is, whether it is the HIC[12] or the disordered (1×1) phase[15]. In addition, in the range of $1/3 < \theta < 6/5$ ML, experimentally there is coexistence between the $1/3$ ML 3×3 phase and the $\sqrt{3} \times \sqrt{7}$ phase at low temperature. One possibility for the discrepancy between experimental and theoretical results is that there is a different structure for the $\sqrt{3} \times \sqrt{7}$ phase than the one we have used in the calculation, i.e. the one based on the H3 binding site and 6/5 ML is not the lowest energy structure. Although our calculations for this model yield good agreement with both X-ray and STM experiments[31], it is possible that another lower energy structure exists which can produce similar diffraction and STM results. We adopted the proposed structure directly from Ref. [23] without an extensive search for other possible geometries at this coverage. Since the $\sqrt{3} \times \sqrt{7}$ phase is only about 20meV above the interpolated curve, it is also possible that LDA cannot resolve such a small energy difference. Yet another clue as to why in the calculation the $\sqrt{3} \times \sqrt{7}$ phase is above the interpolated energy between the $1/3$ ML β -phase and the $4/3$ ML α -phase can be obtained from the recent discovery of numerous ordered phases in the range $1.2 < \theta < 1.33$ ML, differing by minute amounts in coverage and built hierarchically according to the formation rules of the “devil’s staircase”[37]. Such phases are built by combining integral numbers n, m of the two generating phases of coverages θ_1 and θ_2 , i.e. the $\sqrt{3} \times \sqrt{7}$ phase with $\theta_1 = 1.2\text{ML}$ and the $\sqrt{3} \times \sqrt{3}\alpha$ phase with $\theta_2 = 1.33\text{ML}$. Any such phases will have coverage $\theta = 1 + \frac{n+m}{5n+3m}$ within the range $1.2 < \theta < 1.33$. Twelve such phases have been resolved by STM within $\Delta\theta \sim 0.1$ ML, one of the best realizations of the “devil’s staircase” so far. More details of how the phases are constructed can be found elsewhere[37], but the important observation for our current discussion is that these phases result from long range elastic interactions because of the large mismatch between Pb and Si lattice constants($\sim 9\%$). The energy due to these elastic interactions

falls off with distance $J(r) \sim \frac{1}{r^2}$, and it is not included in our calculated energy of the structures, which extends only up to one unit cell with the periodic boundary conditions being imposed. This missing part of the elastic energy is repulsive and favors larger unit cells with larger average separation between the atoms. The contribution of the elastic energy will raise the energy of a structure by an amount which increases with the nominal coverage of the structure, since the average atom separation decreases with increasing nominal coverage, i.e. the energy of the $4/3$ ML $\sqrt{3} \times \sqrt{3}$ structures will increase more than the energy of the $6/5$ ML $\sqrt{3} \times \sqrt{7}$ structures. The repulsive elastic energy of the structure with coverage θ_2 being higher than that with θ_1 is a necessary condition for the numerous phases corresponding to the “devil’s staircase” to form. The net result is to reduce the slope of the coexistence straight line between $1/3$ ML and $4/3$ ML. This will therefore raise the energy corresponding to the phase with the $1/3$ ML and the $4/3$ ML structures coexisting higher than the energy of the $\sqrt{3} \times \sqrt{7}$ H3 structure. In addition, as discussed before, the region $6/5 < \theta < 4/3$ ML is not simply phases of coexisting regions between the $\sqrt{3} \times \sqrt{7}$ and $\sqrt{3} \times \sqrt{3}\alpha$ phases, but an infinite number of phases with the coverage equal to any rational number between θ_1 and θ_2 . Because the system experiences long range interactions, the energy of the system is lowered if the separation between the unit cells of the two generating phases are arranged in well-defined patterns, i.e. the separation between the unit cells of one type is as uniform as possible for a given coverage. This will be discussed in detail elsewhere[37].

3.1.5 Conclusion

By using first-principles calculations, various models of Pb/Si(111) from $1/6$ ML to $4/3$ ML are studied, including existing proposed models, MTL models, and models with stacking fault. Our theoretical results have good agreement for both $1/6$ ML and $1/3$ ML. And we successfully predict that $1/6$ ML and $1/3$ ML are stable Pb coverage while $2/3$ ML is not. Between 1 ML and $4/3$ ML, our calculations indicate that energetically

favorable structures consist of very flat Pb overlayer, missing-top-layer models are not likely, and models with stacking fault may be possible. Further studies with more extensive search of possible structures at these coverage are required.

Table 3.1 Formation energies of the energetically stable structures from 1/6 ML to 4/3 ML. The formation energy of stacking fault is included as a reference.

Coverage	Unit cell	Name of structure	E_s (eV per 1×1 unit cell)
0	1×1	stacking fault	0.04
1/6	$2\sqrt{3} \times 2\sqrt{3}$	mosaic	-0.43
1/3	$\sqrt{3} \times \sqrt{3}$	T4	-0.51
		H3	-0.37
		T1	0.16
2/3	$\sqrt{3} \times \sqrt{3}$	T1-B	-0.34
		T4-T4	-0.34
		H3-H3	-0.26
		T4-H3	-0.23
		T1-T1	-0.06
1	1×1	T1	-0.47
		H3	-0.21
		T4	-0.20
	$\sqrt{3} \times \sqrt{3}$	T ⁺	-0.47
		T ⁻	-0.47
		HCT	-0.39
		MTLs	-0.14
6/5	$\sqrt{3} \times \sqrt{7}$	H3	-0.70
		T4	-0.69
4/3	$\sqrt{3} \times \sqrt{3}$	T4	-0.76
		H3	-0.75
		Int	-0.76
		T4sf	-0.75
		H3sf	-0.74
		HCTa1	-0.23
		HCTa2	-0.17
		MTLsa-H3	0.01
		MTLsa-T4	-0.06
		MTL1	-0.40

3.2 Nanoscale corrugation of Pb islands on Si(111)

3.2.1 Introduction

The formation of Pb islands with flat tops and steep edges on Si(111) surface is an intriguing feature in the epitaxial growth of metallic nanostructures on semiconductor surfaces[38]. Similar island formations have also been observed for Ag on GaAs(110)[39, 40, 41] and Ag on Si(111)[42]. It is believed that the stability of metal films with specific thickness has an electronic origin and can be explained by the “quantum size effect” (QSE) due to the electron confinement in the direction perpendicular to the surface[43, 44, 45]. However, detailed information about the electronic structure of Pb islands on Si(111), which would provide conclusive evidence for QSE, is still lacking.

Recently, a hexagonal corrugation pattern (Moire pattern) with a periodicity between 30-40Å are observed by STM experiments for Pb islands on Si(111) surface [48, 46]. Jian et. al.[46] showed that for ultrathin (3-4 atomic layers) Pb islands grown on $\alpha - \sqrt{3} \times \sqrt{3}$, the contrast of the Moire patterns does not show significant bias dependence throughout the range from -3 to +3 V. They also observed two types of islands with the same height but opposite STM contrasts. The experimental observation was explained by the charge oscillation in the out-of-plane direction which originates from electron scattering by the in-plane potential variation at the Pb/Si interface, similar to the models of Kobayashi[49] and Altfeder et. al.[48]. In these studies, the Pb atoms in the island and at the Pb/Si(111) interfaces are assumed to be in their ideal bulk crystalline positions, and effects due to rearrangements at the interface were not taken into account because the atomic structure at the interface is not known.

In this section, we attempt to study the effect of interface relaxations with nanoscale system size using quantum mechanical simulations. We observed significant atomic rearrangements at the Pb/Si(111) interface which has strong impact on the electronic structures of the Pb overlayers. The interface relaxation leads to an STM voltage-dependent

Moire patterns which are consistent with STM experiments, but are qualitatively different from that predicted by previous models where ideal bulk crystalline structure at the interface is assumed.

3.2.2 Calculation method

Interatomic interactions in our calculation are described by environment-dependent tight-binding potentials[2, 50]. The Pb/Si(111) system is modeled by a periodically repeating 9×9 supercell of the Si substrate, with a repeat distance of $34.6 \text{ \AA}$. Our choice of the supercell size is guided by LEED experiments[51]. The initial structure consists of a flat 10×10 Pb slab on top of the 9×9 Si substrate. The Si substrate consists of four Si layers and the bottom Si layer is passivated by H. The Pb overlayer is aligned by having one of its lattice vectors along the $\langle \bar{1}10 \rangle$ direction of the Si substrate, and positioning a Pb atom in the wetting layer to be at T4 position of the substrate. The Pb overlayer is slightly compressed when compared to the bulk Pb lattice constant.

The tight-binding calculations use one s and three p atomic orbitals for each atom in the structure. The wavefunctions $\psi_i(\mathbf{r})$ with energy E_i can be constructed by superposition of the atomic valence s and p orbitals of Pb and Si. Our calculations can be compared to STM experiments by approximating the STM tunneling current $j(\mathbf{r})$ using

$$j(\mathbf{r}) \sim \int_{E_f}^{E_f - eV} \rho(\mathbf{r}, E) dE, \quad (3.2)$$

where

$$\rho(\mathbf{r}, E) = \sum_i |\psi_i(\mathbf{r})|^2 \delta(E_i - E). \quad (3.3)$$

$\rho(\mathbf{r}, E)$ is the local density of states at the STM tip position, which is set to be $8 \text{ \AA}$ above the Pb film[26]. E_f is the Fermi energy, and V is the STM tip bias voltage.

3.2.3 Moire pattern on atomically flat Pb islands

We first calculated the STM images for unrelaxed flat 3-layer and 4-layer Pb films on Si(111) respectively. The left column in Fig. 3.23 shows our results for the 3-layer structure at applied voltages of +2V and -2V. While the period and orientation of the Moire pattern agree well with observation, the contrasts are very sensitive to the bias voltage and the thickness of the Pb film. There are reversals of contrasts when the bias voltage is reversed or when the thickness changes. The strong bias dependence of the contrasts of the 3- and 4-layer Pb island is inconsistent with STM experiments (see Ref. [46] and our experimental results which will be shown later). These results indicate that the nanoscale corrugation images observed in the STM experiment cannot be explained solely by the wavefunction phase shift due to the in-plane potential variation at the interface as assumed in the previous studies [46].

Figure 3.23 Simulated STM images for flat 3-layer and 4-layer Pb film on Si(111) without relaxation. The left column shows the STM images for 3-layer Pb film, and 4-layer Pb film is on the right.

3.2.4 Moire pattern on corrugated Pb islands

The above calculations lead us to conjecture that the relaxation of the Pb island on Si(111) surface will play an important role in determining the STM corrugation patterns. Using tight-binding molecular dynamics simulations, we studied the relaxation of Pb films on Si(111) surface with various thickness up to 7 layers of Pb. The system is relaxed from its initial configurations by the steepest descent method until the force on each atom is smaller than $0.01 \text{ eV}/\text{\AA}^2$. The simulation results show that the heights of the Pb islands deviate from the ideal bulk-Pb island thickness, and the deviations exhibit an oscillatory behavior which is also observed in STM experiments[47]. Similar oscillatory behavior is also observed in calculations for free standing Pb(111) films, hence the oscillations can be understood by QSE. However, the Pb overlayers are also found to be corrugated after the relaxation and the Pb atoms on the top of the T1 sites of the silicon substrate are found to be elevated from its original bulk positions as shown in Fig. 3.24(a). Simulated STM images calculated from the relaxed 3-layer and 4-layer structures are shown in Fig. 3.24(b). Indeed, the simulation results show that the locations of the bright spots do not change with applied bias voltage, in contrast to the case of unrelaxed island as discussed above.

3.2.5 Comparison with experiments

In order to further confirm our conjecture and the experimental observation of Ref. [46], we have performed experiment to study the topographic STM images for thin layers of Pb on Si(111) surface for different bias voltages. Fig. 3.25(a) shows a 2-step island on top of the $\alpha - \sqrt{3} \times \sqrt{3}$ for $\theta=3\text{ML}$ and $T=180\text{K}$. The white areas are single step islands on top of the 2-step islands. The images corresponding to the outlined region shown in Fig. 3.25(a) with three different bias voltages $+2.5$, $+1.5\text{V}$, and -2.5V respectively are shown in Fig. 3.25(b). From the comparison, it is clear that the position of the bright

Figure 3.24 (a) Side view of a 3-layer Pb film on 9×9 Si substrate after relaxation. (b) Simulated STM images for 3-layer and 4-layer Pb film on Si(111) with relaxation. The left column shows the STM images for 3-layer Pb film, and 4-layer Pb film is on the right.

spots observed in our experiment is independent of the bias voltage. Our calculation results with relaxation agrees qualitatively with our experiments and that of Ref. [46] as well. Our study shows that although STM Moire patterns can be produced by electron scattering from the in-plane potential at the interface, the contrast of the Moire patterns are strongly influenced by atomic relaxation at the interface. Comparison of our calculation with experiments suggests that the Pb/Si(111) interface exhibit significant vertical relaxations, and the STM Moire patterns observed on the ultrathin Pb/Si(111) is dominated by the geometric corrugation of the Pb overlayers due the atomic relaxation at the Pb/Si(111) interface.

Figure 3.25 (a) An experimentally measured STM image of a 2-step island on top of the $\alpha - \sqrt{3} \times \sqrt{3}$ phase for $\theta=3\text{ML}$ and $T=180\text{K}$. (b) STM images corresponding to the outlined region in (a) with applied voltages of +2.5V, +1.5V and -2.5V respectively.

Note that the geometric corrugation of Pb atoms should only be localized at the Pb/Si(111) interface, and the resultant corrugation induced at the top Pb layer by the interface should decay exponentially fast as the Pb island thickness increases or else strain will build up in the island. On the other hand, the magnitude of electronic corrugation for an atomically flat Pb island decays more slowly like $\frac{1}{l}$ obtained from previous QSE models[49], where l is the number of Pb layers. Our calculations show that for very thin Pb films on Si(111), the Moire pattern can be dominated by geometric corrugation. But as the Pb islands grow thicker, the electronic contribution will take over and changes of STM Moire patterns with applied bias voltage are expected. Hence, there is a transition of the behavior of the STM Moire patterns from geometric-corrugation dominating as observed in Ref. [46] to an atomically flat QSE-like model for thicker Pb

islands as in Ref. [48] and [52]. It is interesting that apparent corrugation observed in experiment[46] varies as $\frac{1}{l^2}$, which can be reproduced by our model as shown in Fig. 3.26 from 2 Pb layers up to 7 Pb layers. The apparent corrugation(Δz) in STM experiments is simulated in our calculation by tracing the profile of constant tunneling current. The inset in Fig. 3.26 shows the same calculations but using atomically flat unrelaxed geometries instead of relaxed geometries, which shows decaying oscillating behavior due to QSE. We believe the observed $\frac{1}{l^2}$ behavior is an apparent trend for the small thickness range that were being studied, which can be explained by a fast exponential decay due to geometry

Figure 3.26 (a) A log-log plot of the simulated STM apparent corrugation Δz against the effective number of Pb layers $l + l_0$ for our atomistic model with relaxation from $l = 2$ to $l = 7$, where l_0 is -0.32. The inset shows a log-log plot of Δz against l when unrelaxed flat model is used instead.

3.2.6 Effects of Pb layer stacking on Moire pattern

From the above calculations with atomic relaxation, we know that changing the bias voltage cannot alter the position of the bright spots for ultrathin Pb films since it is

determined by the Pb atoms at the interface. It would be interesting to know if changing the stacking of the Pb layers in the film can produce different results. This study is done using a 3-layer Pb island on the Si(111) substrate. First, we consider the case in which the first Pb layer above the Si substrate remains intact but the stacking sequence of the top two layers is swapped. If we refer the fcc stacking used in the previous calculations as ABC, then the different stacking that we consider here will be called ACB, where the first letter refers to the Pb layer just above the Si substrate and the next two letters refer to the top two Pb layers with their stacking being swapped. The 3-layer Pb film on Si(111) with ACB stacking are allowed to relax and its STM images calculated. The relaxed structure are not flat, and buckled up at the locations where the first-layer Pb atoms are close to the T1 sites of the Si substrate. Fig. 3.27 shows our calculated STM images for two different bias voltages +2.0V and -2.0V. The simulated STM images for the Pb film with ABC stacking are shown in the left column for reference. We found that the location of the bright spots remains the same when compared with the Pb film with ABC stacking even though the top Pb layer is different. We then consider another case in which the top two Pb layers remain intact but only the first Pb layer just above the Si substrate is changed, and we call this stacking CBC. The structure with CBC stacking is again allowed to relax and we found that relaxed structure is not flat. Although the buckled-up locations still correspond to the area where the first-layer Pb atoms are close to the T1 sites of the Si substrate, we notice that the registry of this Pb layer is changed when compared to ABC stacking, and is illustrated in Fig. 3.27(a). Consequently, in our simulated STM images for the CBC island, the locations of the bright spots are shifted to reflect the change of the T1 locations since the bright spots always correspond to these sites. For any case, the location of the bright spots are independent of the applied voltage as before. Therefore, the bright spot locations are sensitive to the registry of the first Pb layer with respect to the Si substrate. Jian et al. observed two types of Pb films which showed opposite contrast at the same applied bias voltage[46], and it was

attributed to different stacking of the fcc structure of the Pb film, resulting in different phase shift at the Pb/Si interface and therefore different quantization condition for the two types of island. Our calculations show that different stacking may shift the location of the buckled-up region, with a corresponding shift of the bright spots, which appears to be a reversal in contrast. However, this is a purely geometrical effect due to a change in the relative registries between the Pb film and the underlying Si substrate.

Figure 3.27 (a) Schematic diagrams illustrating the registry of the first layer of Pb atoms with respect to the Si substrate for ABC and ACB stacking on the left, and CBC stacking on the right. The black atoms are Pb, the top layer of the Si substrate is colored white, and the second Si layer is colored gray. The locations where the Pb atoms are close to the T1 site of the Si substrate are marked on the figures. (b) Simulated STM images of 3-layer Pb films on Si(111) with ABC stacking on the left column, ACB in the middle and CBC on the right. The applied voltages are +2.0V and -2.0V down a given column.

3.2.7 Conclusion

In summary, we calculated the STM images of Pb film on Si(111) up to 7 layers. We found that the Pb film is not flat if the film is allow to relax. The positions of the bright spots in the simulated STM images correspond to the places where the Pb film are buckled up, and do not change with the bias voltage. These results are qualitatively different from simulated STM images from a flat unrelaxed Pb film where the location of the bright spots change their locations with the STM bias voltage or with the film thickness. Experimentally observed $\frac{1}{\sqrt{2}}$ behavior of the STM apparent corrugation can be reproduced by our calculations. Our present study demonstrates that relaxation effect in addition to quantum size effect contribute to the electronic structures of this system. We believe that relaxation effect has a significant contribution to the properties of metal/semiconductor interface, not only does it manifests itself in the Moire patterns in STM images, but also have an impact to other electronic properties of this class of systems such as Schottky barrier.

3.3 Diffusion barriers on Pb islands

3.3.1 Introduction

Quantum size effects (QSE) in the formation and stability of metallic nanostructures on semiconductor surfaces have attracted considerable attention recently[39, 42, 38, 43, 44, 46, 53, 52]. It has been shown that the formation of metal plateaus or islands of selective heights with flat tops and steep edges on the semiconductor surfaces, observed in the low temperature epitaxial growth of Ag films on GaAs[39], Ag islands on Si(111)[42], and particularly Pb islands on Si(111)[38] can be attributed to QSE due to electron confinement in the direction perpendicular to the film surface[43, 44, 46, 53, 52]. Very recently, quantum size effects were also observed in the superconducting transition temperatures of ultra-thin Pb films[54]. However, the kinetics of this intriguing “quantum” growth and the mechanisms underlying the very fast growth of Pb islands($\sim$ minutes) at low temperatures are still not well understood.

Using first-principles total energy calculations, we have studied the diffusion barrier for a Pb adatom on a free-standing Pb films as a function of film thickness. In this letter, we show that the energy barrier for an adatom to diffuse on the Pb(111) film surface is very low, which can result in very fast growth of Pb island even at low temperature. There are significant quantum size effects in the diffusion barrier, which can affect the growth morphology of Pb islands on Si(111) surface. Since so far the role of QSE has been related only to the stability of the grown structures(i.e. how the energy minima are affected), this work shows that kinetic barriers are also affected differently between stable versus unstable islands.

3.3.2 Calculation method

Our studies are carried out using the VASP[55] program which is based on first-principles density-functional theory[1]. We used ultrasoft pseudopotential[56] and plane

waves basis with an energy cutoff of 144eV. Scalar relativistic effects are included and the generalized gradient approximation(PW-91)[57] is used for the electronic exchange-correlation energy functional. A Monkhorst-Pack grid[58] of $4 \times 4 \times 1$ is used for the Brillouin-zone integration. A 4×4 unit cell is used for the Pb film, and the thickness of the film varies from 3 to 9 Pb layers in our calculations. $12\text{\AA}$ of vacuum space is included in our supercell. The bottom layer of the Pb film is kept fixed, while the rest of the Pb atoms are allowed to relax.

3.3.3 Surface energy of free-standing Pb film

We validate our setup described above by calculating the surface energy for free-standing Pb(111) film from 3 layers up to 9 layers. The surface energy is calculated using $E_s = (E_{film} - n \times E_{Pb})/2$, where E_{film} is the total energy of the Pb film, n is the number of Pb atoms in the system, and E_{Pb} is the energy of a Pb atom in its crystalline fcc structure. The results, shown in Fig. 3.28, agree well with previous first-principles study of Ref. [44]. The surface energy of a free-standing Pb film exhibits a bi-layer oscillation because the thickness of the bi-layer($2d$) is close to half integral multiples of the Fermi wavelength(λ_f) of the Pb film. When a Pb(111) film grows by two layers in height, an additional $\sim 3/2$ wavelength of the confined electrons at the Fermi level can be fitted into the film, leading to minimization of the energy of the electrons in the quantum well.

3.3.4 Potential energy surface and diffusion barrier on free-standing Pb film

In order to map out the potential energy surface for Pb atom diffusion, we place a Pb adatom on different positions of a grid mesh over the Pb(111) film. The Pb adatom is allowed to adjust its height, but not its coordinates parallel to the Pb(111) surface. All other Pb atoms in the Pb film are allowed to fully relax except the bottom layer. These calculations are carried out for Pb(111) films from 3 to 9 atomic layers. Our

Figure 3.28 The surface energy per 1×1 unit cell of a free-standing Pb film from 3 to 9 atomic layers.

results show that, except for the 3-layer film, the hcp site as indicated in Fig. 3.29 is the lowest energy location for the Pb adatom, while the fcc site is the saddle point in the diffusion pathway for the Pb adatom from one cell to another. The bridge site (the midpoint between the hcp site and fcc site) has an energy in between the lowest energy hcp site and the fcc saddle point (except the 3-layer film). For the thinnest Pb film with only 3 Pb layers, the lowest energy site for a Pb adatom is at the bridge site rather than the hcp and the fcc site, and the saddle point shifted to the hcp site as well. For all Pb films in our calculations, the top sites are the maxima of the potential energy surface.

The adsorption energies of the Pb adatom are plotted in Fig. 3.30. The adsorption energy E_{ad} is defined as $E_{ad} = E - E_{film} - E_{Pb}$, where E is the total energy of whole system containing both the Pb adatom and the film, and E_{Pb} is the energy of a Pb atom in its crystalline fcc structure. E_{film} is the total energy of the previously optimized Pb film of the same thickness without adatoms. A bi-layer oscillation of the adsorption

Figure 3.29 Diffusion pathway of a Pb adatom on a Pb film. Only the top three Pb layers are shown, with the first, second and third layer colored white, light grey and dark grey respectively. A 1×1 unit cell is outlined to illustrate the diffusion of a Pb adatom from one unit cell to another.

energies can be seen from Fig. 3.30, similar to the behavior of the surface energies of a free-standing Pb(111) film. The calculations show that the adsorption energy of a Pb adatom on an n -layer Pb(111) film is larger than the sum of the surface energies(per 1×1 unit cell) of the n - and $(n+1)$ -layer Pb(111) films. This implies that when a Pb film grows in thickness, the Pb adatoms prefer to agglomerate to form a partially complete Pb layer.

With the exception of the 3-layer Pb film, the energy barrier for a Pb adatom diffusing on the Pb(111) film is the energy difference between the fcc and the hcp site. The diffusion barriers as a function of film thickness from 3 to 9-layer Pb(111) film is plotted in Fig. 3.31. Our results show that the energy barrier for a Pb adatom diffusing on the surface of a Pb(111) film is very small, ranging from 10 to 60 meV or even smaller (less

Figure 3.30 The adsorption energies of a Pb adatom on a 3 to 9-layer Pb film at fcc(solid), hcp(dashed) and bridge site(dotted).

than 40 meV when the film is more than 7-layers thick). This result may explain the fast growth of Pb islands on Si(111) surface at low temperature ($\sim 180K$). It is interesting to note that the diffusion energy barriers also exhibit a bi-layer oscillatory behavior, due to the QSE. The oscillation in the diffusion barrier anti-correlate with that in the surface energy. For those film thickness that has lower surface energy (stable films) the diffusion barrier is higher, and vice versa. The ratio between the energy barrier for stable and unstable films is as large as 6 (4 on average). This large oscillation in the diffusion barrier between the stable and unstable Pb film would lead to the unusual growth morphology, especially the difference between nucleation on top of stable versus unstable islands, for Pb islands on Si(111) observed in the STM experiment, as we will discuss below.

Figure 3.31 The diffusion barrier of a Pb adatom on a 3 to 9-layer Pb film.

3.3.5 Discussion

Fig. 3.32 shows an STM topography image of an intermediate transient configuration of Pb/Si(111) with several island heights present, both stable and unstable, evolving towards a distribution which eventually will include only stable heights. The initial morphology (not shown) was generated by depositing 1.6ML of Pb on top of the Si(111) $\alpha - \sqrt{3} \times \sqrt{3}$ phase at 180K. At this temperature, laterally extended 3-layer islands with respect to the Si(111) substrate (i.e., 2-layer islands with respect to the wetting layer) are observed first. This is the first stable height for growth on this interface followed by 6-layer as the next stable height when the height evolution is completed. The observed stable heights below 5 layers are different from the calculated results using free-standing Pb film because the electronic phase shift at the Pb/Si interface is not accounted in calculations. However, our calculation and experiment for thicker layers on the stable heights agree with each other. With further Pb deposition, stable heights differing by

bi-layer increments are observed. On this initial 1.6 ML distribution of Pb islands of average lateral size of 100 nm, an additional amount of 1.3 ML is deposited. The islands have irregular shapes because most of them initially grow from coalescence events with separate islands merging without shape rearrangement. This shows that very fast terrace diffusion is competing with much slower edge diffusion. The outcome of this additional deposition is shown in Fig. 3.32. Several islands are shown and because of their large initial size it is possible to have a snapshot of the completion process with most of the 6-layer islands formed, but a few uncovered areas of 5-layer still exist. In a few cases, we also observe the beginning of the formation of 7-layer islands on top of the incomplete 6-layer islands.

The most striking feature of the image is the very unusual growth morphology where all the 6-layer islands complete their top by growing from the perimeter towards the center with almost constant width. The growing front follows the shape of the initial 5-layer island perimeter. On the other hand, the growth of the unstable 7-layer islands shown as white regions on the 6-layer stable islands is by nucleating small compact islands at the island center. Only in one case the 7-layer island (center right) seems to coalesce into a single extended island possibly because of the narrow "neck" at the triangularly shaped bottom part.

The observed dramatic difference in the growth morphology between stable and unstable heights can be caused by the bi-layer oscillation in diffusion barriers described above. We believe that the diffusion barrier of a Pb adatom on Pb island on Si(111) should be very similar to that on a free-standing Pb(111) film, as long as the Pb islands are more than 5-layer high. Therefore, unstable Pb islands have a lower diffusion barrier for the Pb adatoms, while stable Pb islands have a higher diffusion barrier. A schematic diagram for the energy landscape on top of the two types of Pb islands is shown at the top of Fig. 3.32. While exact calculations of the barrier for Pb adatoms diffusing out of the Pb islands is beyond the capability of DFT calculations at this point, it is reason-

Figure 3.32 Top: A schematic diagram illustrating the potential energy surface and growth morphology on stable versus unstable islands. An additional layer on stable islands grow from the center while the growth is from the periphery for unstable islands. Below: An STM image of $330\text{nm} \times 370\text{nm}$ with a total Pb coverage of 2.9 ML at 180K on Si(111) $\alpha - \sqrt{3} \times \sqrt{3}$ phase formed by stepwise deposition (i.e. 1.3 ML on top of already 1.6 ML island distribution). The numbers label the island height measured from the Si(111) substrate.

able to assume that stable Pb islands have a lower step barrier at the edge of the islands while unstable islands have a higher one because stable islands tend to grow laterally in size rather than building the next layer to form an unstable thickness, while the reverse is true for unstable islands. Therefore, Pb adatoms deposited on unstable Pb islands experience a low diffusion barrier throughout the island top, but they will nucleate at the edge of the island where a high step edge barrier is encountered. On the other hand, Pb adatoms deposited on stable Pb islands may encounter other deposited Pb adatoms before diffusing to the edge of the islands due to the higher diffusion barrier. Also Pb

adatoms close to the periphery of the stable Pb islands tend to diffuse to lower layers to increase the lateral dimension of the islands precluding any growth on top of stable films near the edge. In the experimental observations, less than 15% of the 6-layer islands are covered, far below the estimated 0.5 ML amount deposited on the almost completed 6-layer islands, i.e., less than half of the deposited amount remains on top of the 6-layer islands. The corresponding number for stable layers covering unstable height islands is 85% which illustrates that descending from unstable heights is less probable.

One may wonder whether the nucleation of 7-layer islands on the stable 6-layer islands is possible, given the very small step edge barrier for a Pb adatom on the 6-layer island. This question can be answered by studying the initial island nucleation process. After a Pb adatom lands on a Pb island of size L , the probability P_1 for it to diffuse within a distance L in time t (so it is still on top of the island) can be obtained by $P_1 = \int_{|r| \leq L} \exp(-r^2/4Dt)/4\pi Dt \, d^2r$, where D is the diffusion coefficient. D is expressed as $D_0 \exp(-E/kT)$ in which E is the diffusion barrier, T is the temperature and D_0 is typically taken to be $1 \times 10^{12} \text{Å}^2 \text{s}^{-1}$. Hence, P_1 is the probability that the first Pb adatom is on top of the island. The probability of a second Pb adatom to land within $l = 15 \text{nm}$ around the first adatom at time t obeys the Poisson statistics $P_2 = \lambda^t \exp(-\lambda)/t!$, where $\lambda = 1/F(l/a_0)^2$ is the average time interval between two consecutive Pb adatoms lands which can be estimated by the deposition rate F , and $(l/a_0)^2$ is the number of sites on the island within the radius l . The probability of the first Pb adatom remaining on the island without diffusing to the edge while the second adatom lands close to it can be calculated by $P = \int_0^\infty P_1(t)P_2(t)dt$. If the second adatom does not land close to the first one, the probability for them to meet each other is very small, then these two Pb adatoms are likely to diffuse out of the stable island or nucleate at the edge of the unstable islands as discussed above. By using a deposition rate of 1 ML/min, a typical island size of 100 nm, and a temperature of 180 K, P is found to be 3×10^{-5} for a stable island with a diffusion barrier $E = 0.05 \text{ eV}$, while $P = 4 \times 10^{-6}$ for unstable

height Pb island with $E = 0.015$ eV. On the other hand, after depositing 0.5 ML(out of the total 1.3 ML), there will be approximately 4×10^4 Pb adatoms landing on the $100 \text{ nm} \times 100 \text{ nm}$ Pb island. Although the probability is small for two consecutive Pb adatoms meeting each other without diffusing to the edge, the probability for the two Pb adatoms to meet after 4×10^4 attempts can be significant. Our calculations show that there is a probability of 75% for two successively deposited Pb adatoms to meet each other without diffusing to the edge after depositing 0.5 ML on stable height island, but only 16% chance for unstable height island. This nucleation probability is a measure of possible island nucleation close to the center of the island. Hence, our calculations illustrate that nucleating a Pb layer close to the center of a stable Pb island top is more probable than on unstable island. For unstable island, most of the Pb adatoms diffuse to the edge of the island without meeting other deposited Pb adatoms on their way, and nucleate at the edge of the island because the step edge barrier is higher for the unstable islands as discussed previously.

Finally, we note that for most of the islands on which small 7-layer islands are seen, there is a single island on top, except for the island at the bottom right corner of Fig. 3.32 where three 7-layer islands have formed. The average distance between these three islands is 50nm, which is a third of the estimated diffusion length at 180K. The process of island nucleation is commonly described by the scaling theory[59] with the island density fully determined by the ratio D/F and the critical cluster size i_c , where D is the terrace diffusion coefficient, F is the flux rate and i_c is the minimum stable island size. It is possible that the nucleation on top of this particular 6-layer island to have three 7-layer islands(instead of a single island) is an unlikely event, but once completed it promotes very efficiently the aggregation of the deposited adatoms. For the island at top left, we see that Pb adatoms deposited nucleates a small 7-layer island instead of diffusing to the 5-th layer, this indicates that a small step barrier might be present.

3.3.6 Conclusion

In summary, we calculated the diffusion barriers of a Pb adatom on 3 to 9-layer free-standing Pb film. Except for the 3-layer Pb film, the lowest energy site for a Pb adatom is the hcp site. The diffusion pathway of a Pb adatom starts from the hcp site, passes through the bridge site over the fcc saddle point, and then to the next hcp site in the neighboring cell. The surface energies, adsorption energies and the diffusion barriers all show a bi-layer oscillation due to QSE, with the unstable odd-layer Pb film having a higher surface energy but lower diffusion barrier while for the stable height islands the opposite is true. The growth morphology of Pb islands on Si(111) can be affected by QSE not only through modification of the energy minima as commonly discussed in the literature, but also clearly through the single atom terrace diffusion barrier oscillation. This leads to a dramatic and unconventional growth mode not observed previously. The growth of an additional layer on a stable Pb island is likely to start from the center while it starts from the periphery for unstable Pb island as confirmed from detailed experimental observation.

CHAPTER 4. Pb and Sn on Si(100)

4.1 Group IV metal dimer chains on Si(100)

4.1.1 Introduction

Group IV elements on Si(100) have been intensively studied because of their importance in both technological applications and fundamental understanding of homoepitaxial/heteroepitaxial interface. For low coverage deposition of Si on Si(100) at room temperature, Si ad-dimers are found to form on the surface[60, 61]. Si ad-dimers locate on the top of the substrate dimer row and rotate between two orthogonal orientations[62, 63]. At around 400K, Si dimer chains perpendicular to the substrate dimer rows with the individual dimers located in the trough are observed[64]. One-dimensional dense dimer chains at epitaxial positions grow into long chains perpendicular to the underlying Si dimer rows at around 500K[65, 66]. These experimental observations aroused a lot of theoretical studies on the dynamics and nucleation of Si ad-dimers on Si(100)[67, 68]. For Ge deposition on Si(100) at low coverage, isolated dimers are formed on the top of the substrate dimer row with their dimer bonds oriented parallel to the substrate dimer row direction. The ad-dimers are buckled and flipping of the buckling state has also been seen by STM. First-principles calculations using density functional theory (DFT) show that although Ge ad-dimers on Si(100) are buckled[69], the “rocking barrier” to flip between its two degenerate buckling state is small[70]. As a result, the time scale of the rocking motion is much smaller than the time resolution of STM. This led to the

conclusion that the observed buckling is due to intermixing of Ge with Si to form mixed GeSi dimer, and the observed buckling flips are the results from 180° rotational motion of the mixed GeSi ad-dimers[70]. Intermixing between Ge and Si on the surface also leads to interesting diffusion kinetics which has also been studied experimentally and theoretically[71, 72]. Recently, Pb/Si(100) has received considerable attention. It has been shown by STM experiments[73, 74, 75, 76] that small amount of Pb($\leq 0.5ML$) deposited onto Si(100) surface form isolated dimers and chains of dimers. The dimer chains also run perpendicularly to the underlying Si dimer rows, and the dimers in the chain are buckled but located in the trough between the Si dimer rows. Theoretical calculations[77] based on DFT showed that Pb dimer chains on Si(100) surface with the buckled configurations are energetically stable. The Pb dimer chain model is also supported by the recent core-level photoemission study [78]. For Sn on Si(100), similar behavior as that of Pb/Si(100) has also been observed by STM at low coverage[79]. It is believed that the observed dimer chains for both Pb and Sn on Si(100) are similar to that of Group III metals on Si(100), in which the dimer chains are made up of pure metal dimers[80, 81]. In this section, we will show that the mixed PbSi dimer chain on Si(100) is energetically favorable up to a Pb coverage of 0.5 ML. Therefore, the buckling of the dimers observed in the STM experiments could also be due to the presence of mixed PbSi dimers. In order to further clarify this situation, we have performed first-principles calculations to study the rocking barrier of pure Pb dimer chains on Si(100), as previously did for the Ge/Si(100) system. The stability of the dimers against the “rocking” motion will provide us with useful insights into the composition of the buckled dimer chains observed in the STM experiments, and can be used to infer the different structural models for the dimer chains on Si(100) surface. We also carried out similar analysis for Sn on Si(100) in order to have a more comprehensive picture of how Group IV metals behave on Si(100) at low coverage.

This section is divided into eight parts. The calculation method is briefly discussed

in Section 4.1.2. In Section 4.1.3, we will present various configurations of isolated Pb dimers, Pb dimer chains, and their intermixed PbSi counterparts on Si(100) along with their relative energetics. Results for isolated Sn dimers, isolated mixed SnSi dimers, Sn dimer chains and mixed SnSi dimer chains on Si(100) will be shown in Section 4.1.4. Comparison with STM experiments will be made in Section 4.1.5 by simulating STM images for different models that we have discussed in the previous sections. Section 4.1.6 discusses our calculation of the “rocking” barrier of pure Pb and Sn dimer chain on Si(100) to investigate the dynamical effects in STM images. Finally, Section 4.1.7 will resolve the apparent discrepancy between experimental results and our theoretical predictions by comparing the intermixing energetics between Ge/Sn/Pb and Si.

4.1.2 Calculation method

Our first-principles calculations are based on DFT under local density approximations (LDA) [1]. Pseudopotential and plane wave basis are being used. The Ceperley-Alder functional [24] parametrized by Perdew and Zunger [25] is used for the exchange-correlation energy functional. The kinetic energy cutoff is set to be 12 Ryd. The Si(100) surface is modeled by a periodically repeating 4×4 slab which consists of 8 layers of Si passivated by H at the bottom and a vacuum space of at least $12\text{\AA}$. The top surface of Si(100) is arranged to have a $c(4 \times 2)$ reconstruction. The bottom layer of Si atoms are kept fixed to simulate the bulk environment. Four k points are used to sample the Brillouin zone. Simulated STM images are calculated according to the theory of Tersoff and Hamann[26].

4.1.3 Pb on Si(100)

We first consider isolated Pb dimers on Si(100). Four different ways of putting a Pb dimer on the 4×4 unit cell are called configuration A, B, C, and D, and are illustrated in Fig. 4.1. The energies of these four configurations obtained from our calculations

are listed in Table 4.1. The lowest energy configuration is the Pb dimer B, and it is buckled with a buckling angle of 11.26° . For isolated mixed PbSi dimers on Si(100), four different configurations A, B, C, and D are also studied. The lowest energy mixed PbSi dimer is configuration C, which is only slightly lower in energy than configuration B as shown in Table 4.1. For all four configurations, the mixed dimers are buckled with the Pb adatoms higher than the Si adatoms.

Figure 4.1 Different arrangements of Pb dimer on a Si(100) 4×4 unit cell. Only the first two layers of the Si substrate are shown. The Si atoms in the substrate are white. The Pb adatoms are colored gray.

To compare the relative stability of Pb dimer and mixed PbSi dimer on Si(100), we consider their formation energies as follows. The formation energy is given by

$$\Delta E_{dimer} = E_{total} - E_{sub} - N_{Pb} \mu_{Pb} - N_{Si} \mu_{Si}, \quad (4.1)$$

where E_{total} is the total energy of the system under consideration, E_{sub} is the total energy of Si(100) 4×4 substrate with $c(4 \times 2)$ surface reconstruction, $\mu_{Pb}(\mu_{Si})$ is the chemical potential of Pb(Si) atoms which is taken as the energy of bulk Pb(Si) per atom in fcc(diamond) crystal structure, and $N_{Pb}(N_{Si})$ is the number of Pb(Si) adatoms in the unit cell. This formula is a measure of the energy gain when Pb and Si atoms form a dimer on the Si(100) surface when Pb and Si are deposited epitaxially, or Si adatoms come from step edges of the Si substrate. Eq. (4.1) gives an upper bound for the formation energy since under equilibrium conditions the maximum possible values for μ_{Pb} and μ_{Si} are equal to their chemical potentials in the bulk phase for the source of Pb and Si adatoms mentioned above. The formation energies of Pb dimer in configuration B and mixed PbSi dimer in configuration C are found to be -0.33 eV per Pb atom and -0.06 eV per Pb atom respectively. Therefore, it is energetically favorable to form pure Pb dimers instead of mixed PbSi dimers.

Next, we consider isolated Pb dimer chains on Si(100). Four different ways of putting a Pb dimer chain on the 4×4 unit cell, configuration A, B, C, and D, are considered, as illustrated in Fig. 4.2. The energies of these four configurations obtained from our calculations are listed in Table 4.1. The lowest energy configuration is the dimer chain C, which runs perpendicularly to Si dimer rows with each Pb dimer located in the trough between the dimer rows. The individual dimers are buckled with a buckling angle of 14.71° . These results are similar to the previous calculation results [77] which are also included in Table 4.1 for comparison. We then consider another structural model of dimer chain where Pb and Si intermix to form PbSi dimer chain. Again, four different configurations are considered, which are similar to those in Fig. 4.2, but with each Pb dimer replaced by a mixed PbSi dimer. These configurations are called PbSi dimer chain A, B, C, and D respectively. Their relative energies are shown in Table 4.1. The lowest energy configuration is found to be the chain C again and all the mixed dimers are buckled with the Pb atoms favor the higher positions. Interchange the Pb and Si atoms

of the PbSi dimer chain C such that all Si are higher than Pb atoms (we call the resultant configuration C') will result in 0.57 eV/dimer higher in energy. Since this energy is much higher than the thermal energy for room temperature, we conclude that the PbSi mixed dimer chain should mainly be observed in the C rather than C' configuration.

Figure 4.2 Different arrangements of Pb dimer chains on a Si(100) 4×4 unit cell. The Pb adatoms are in gray.

Using Eq. (4.1), the formation energy of mixed PbSi dimer chain C is calculated to be -0.70 eV per Pb atom, while that of pure Pb dimer chain C is -0.51 eV per Pb atom. Therefore, the formation energy of the mixed PbSi dimer chain is 0.19 eV per Pb atom lower than that of the pure Pb dimer chain. In order to see which factor contributes most to the stability of the mixed PbSi dimer chain, we decompose the formation energies of the dimer chains obtained by (4.1) into the formation energies of individual dimers

ΔE_{dimer} and the coupling U between dimers along the chain, i.e., $\Delta E_{chain} = 2(\Delta E_{dimer} + U)$. As we discussed above, the formation energies of the individual ad-dimer in the configuration C are calculated to be -0.06 eV/Pb-atom for mixed PbSi ad-dimer and -0.21 eV/Pb-atom for pure Pb ad-dimer. Our analysis results show that the dimer coupling energy U is -0.64 eV/Pb-atom for the mixed PbSi dimer chain, which is much larger than -0.30 eV/Pb-atom for the pure Pb dimer chain on Si(100) surface. Therefore, the stability of mixed PbSi dimer chain C is provided mainly by the coupling between PbSi dimers along the chain, although the individual mixed PbSi dimer is not as favorable as the Pb dimers.

It should be noted that PbSi dimer chain C corresponds to a Pb coverage of 0.125ML, the same coverage as a Pb ad-dimer in a 4×4 unit cell. It is necessary to show that the mixed dimer chain is also energetically more favorable than the formation of just a Pb dimer per 4×4 unit cell. As discussed above, the formation energy of a Pb ad-dimer in configuration B is -0.33 eV per Pb atom, which is also smaller than the formation energy of PbSi dimer chain C.

In this section, we have also studied the structures of Pb on Si(100) at higher Pb coverage of 0.5 ML. Experimentally, it is observed that close packed Pb dimer chains are formed at 0.5ML of Pb coverage[75, 77, 82, 83]. The close packed dimer chains run perpendicularly to the underlying Si dimer rows, and the separation between the dimer chains is 3.84Å, which is the Si(100) surface lattice constant. The surface will have a (2×2) symmetry if the buckling of adjacent Pb dimer chains is in phase, while (4×2) symmetry is obtained if buckling is anti-phase. It was observed experimentally that (2×2) and (4×2) can coexist [82]. We have performed calculations for both (2×2) and (4×2) structures consisting of Pb dimer chain C separated by one Si(100) surface lattice constant, as shown in Fig. 4.3. The Pb dimer bond length for the (2×2) structure is 3.04Å with a buckling angle of 14.02°, while for the (4×2) structure, the Pb dimer bond length is 3.03Å with a buckling angle of 14.17°. For both cases, the Pb dimer bond

length and the buckling angle are very similar to that of the Pb dimer chain C at the coverage of 0.25 ML. We found that the total energy of the (4×2) structure is only 0.86 meV/dimer lower than that of (2×2) . Therefore, the two structures can be considered degenerate in energy under LDA.

Figure 4.3 Close packed Pb dimer chains on a Si(100) 4×4 unit cell with (a) (2×2) and (b) (4×2) symmetry. Each Pb dimer chain is in the configuration C, as shown in Fig. 4.2, but the chains are packed such that they are separated by one Si(100) surface lattice constant.

Another possibility of closed packed dimer chain is the close packed mixed PbSi dimer chain. We also consider both (2×2) and (4×2) structures which are similar to Fig. 4.3 but with each Pb dimer replaced by a mixed PbSi dimer. For both cases, the ground state structures consist of mixed dimers with Pb adatoms higher than Si adatoms. For the (2×2) structure, the Pb-Si ad-dimer bond length is 2.84Å and the buckling angle is 19.53°. In the (4×2) case, the Pb-Si ad-dimer bond length is also 2.84Å but the buckling angle is 19.95°. The total energy of the (2×2) structure is 1.9 meV/dimer lower in energy than that of (4×2) , and they can be considered as degenerate under LDA. The other buckling state which corresponds to Si adatoms higher than Pb adatoms has an energy of 0.57 eV/dimer higher than the ground state structure for both (2×2)

and (4×2) structures. Therefore, the Pb atoms should stay in the higher positions if mixed dimer chains are formed. The energies of close packed Pb and mixed PbSi dimer chains can be compared by using Eq. (4.1). The formation energy is -0.53 eV/Pb atom and -0.72 eV/Pb atom for closed packed pure Pb dimer chain and mixed PbSi dimer chain respectively. Therefore, up to 0.25ML, mixed PbSi dimer chains are still energetically more favorable than pure Pb dimer chains.

4.1.4 Sn on Si(100)

In the similar way as Pb dimer on Si(100), we studied four different ways of putting a Sn dimer on the 4×4 unit cell, which we called configuration A, B, C and D as in Fig. 4.1, but with the Pb dimers replaced by Sn dimers. As shown in Table 4.1, the lowest energy structure is configuration B, with a Sn dimer bond length of 2.99Å, and a buckling angle of 7.46°. Its formation energy by using Eq. (4.1) is -0.26 eV per Sn atom. For mixed SnSi dimer, the lowest energy configuration is C with a Sn dimer bond length of 2.75Å. The mixed dimer structure is buckled with Sn atom higher and a buckling angle of 16.67°. The formation energy of an isolated mixed SnSi dimer is +0.03 eV per Sn atom. Therefore, it is energetically not favorable to form isolated SnSi dimers.

Similarly, we studied Sn dimer chain on the 4×4 unit cell in four configurations A, B, C and D as in Fig. 4.2, but with the Pb dimers replaced by Sn dimers. As shown in Table 4.1, the lowest energy structure is configuration C, with a Sn dimer bond length of 2.94Å, and a buckling angle of 15.64°. Calculations are also done for a mixed SnSi dimer chain in four different configurations similar to Fig. 4.2, but the Pb dimers are replaced by SnSi dimers. Again, configuration C has the lowest energy as shown in Table 4.1. The Sn-Si dimer bond length is 2.77Å. The ground state structure has Sn adatoms higher than Si adatoms with a buckling angle of 21.22°. The other buckling state, in which the Si adatoms are higher than Sn adatoms, is 0.42 eV/dimer higher in energy than the ground state structure. In fact, the structures of the other three mixed

dimer chain configurations(i.e. A, B, and D) are all buckled with the Sn adatoms higher than the Si adatoms. We compared the relative stabilities of Sn dimer chain and mixed SnSi dimer chains using their formation energies(see Eq. (4.1)). We found that the formation energies of the Sn dimer chain and mixed SnSi dimer chain are -0.50 eV/Sn atom and -0.59 eV/Sn atom respectively. The mixed dimer chain is again energetically more favorable, but the difference between the formation energies is not as large as the difference between Pb dimer chain and mixed PbSi dimer chain.

Table 4.1 The energies per dimer E (relative to that of the lowest energy configuration), the buckling angle θ , and the bond length d of the ad-dimers and dimer chains on Si(100) surface in four different configurations A, B, C, and D(see figures). The data in parenthesis are taken from Ref. [77]. There are two buckling angles and bond lengths for the PbSi dimer chain in configuration D because this configuration has a broken bond in the substrate which makes the two ad-dimers asymmetrical.

		A	B	C	D
Pb ad-dimer	E (eV)	0.32	0.	0.24	0.70
	θ	8.75°	11.26°	13.03°	13.71°
	d (Å)	2.94	3.16	3.03	2.96
PbSi ad-dimer	E (eV)	0.11	0.01	0.	0.84
	θ	20.34°	17.47°	17.56°	21.63°
	d (Å)	2.87	2.73	2.81	2.68
Pb dimer chain	E (eV)	0.69(0.57)	0.31(0.15)	0.(0.)	0.94(0.84)
	θ	10.28°	11.97°	14.71°(12.45°)	11.88°(11.42°)
	d (Å)	2.97	3.21	3.01(3.13)	2.93(2.97)
PbSi dimer chain	E (eV)	0.73	0.60	0.	1.01
	θ	17.68°	20.62°	20.63°	8.96/21.61°
	d (Å)	2.73	2.89	2.81	2.67/2.69
Sn ad-dimer	E (eV)	0.24	0.	0.16	0.64
	θ	8.93°	7.46°	13.46°	14.28°
	d (Å)	2.89	2.99	2.94	2.89
SnSi ad-dimer	E (eV)	0.08	0.03	0.	0.78
	θ	17.15°	18.70°	16.67°	20.05°
	d (Å)	2.69	2.79	2.75	2.62
Sn dimer chain	E (eV)	0.71	0.43	0.	0.98
	θ	9.30°	8.53°	15.64°	12.53°
	d (Å)	2.89	3.04	2.94	2.86
SnSi dimer chain	E (eV)	0.69	0.62	0.	1.15
	θ	17.27°	19.59°	21.22°	15.88°
	d (Å)	2.69	2.83	2.77	2.64

4.1.5 Comparison with STM experiments

We have shown that for Pb and Sn dimer chains on Si(100), the most energetically favorable structure is configuration C, in which the chain runs perpendicularly to the underlying Si dimer rows, and the dimers in the chain are located in the trough between the Si dimer rows. On the other hand, both mixed PbSi and SnSi dimer chains also have their lowest energy structure in configuration C. Therefore, in terms of geometry, both pure metal and mixed dimer chains are possible structures for Pb and Sn on Si(100) at low coverage. In this section, we will present our simulated STM images to see how the different models compare with experiments. For our simulation, the STM tip is assumed to position at a height of 2Å above the highest atom in the structure, and the images are calculated with a surface bias voltage of -1.0 V for the occupied states and 1.0 V for the empty states respectively.

The simulated STM images for isolated Pb dimer chain C and the close packed Pb dimer chains on Si(100) are shown in Fig. 4.4 and 4.5 respectively. For both cases, bright spots corresponding to the higher Pb adatom positions are observed in filled states image. While both atoms of the Pb dimer give bright spots in the empty states, the spots corresponding to the lower Pb adatom positions are larger. The appearance of each individual Pb dimer chain in STM at 0.5ML is very similar to an isolated Pb dimer chain. We have also calculated the simulated STM images for the isolated mixed PbSi dimer chain C and close packed mixed dimer chain as shown in Fig. 4.6 and 4.7 respectively. The occupied states images show bright spots corresponding to the Pb atoms of the mixed PbSi dimers. The empty states images exhibit bright spots corresponding to the Pb atoms and also weak spots corresponding to the Si atoms of the mixed dimers. In STM experiments, Ref. [75] observed that the bright spots coming from the buckled-up Pb adatom in the filled states image shifted to the buckled-down Pb adatom positions in the empty states image. Our calculated STM images for pure Pb dimer chains in

Fig. 4.4 corresponds well with the experimental observations. On the other hand, our calculation of Fig. 4.6 shows that the buckled-up Pb adatoms in the mixed dimer chains give bright spots for both filled states and empty states images, while the buckled-down Si adatoms only contribute weak spots in the empty states image. Therefore, the mixed dimer chain model cannot explain the shift of the bright spots upon reversing the bias as observed in the experiments.

Figure 4.4 Simulated STM images of Pb dimer chain C with a surface bias voltage of (a) 1.0 V and (b) -1.0 V. H denotes the higher Pb adatom position and L denotes the lower Pb adatom position.

For isolated Sn dimer chains and mixed SnSi dimer chains on Si(100), our STM simulation is shown in Fig. 4.8. For Sn dimer chain in configuration C(Fig. 4.8(a) and (b)), there are bright spots at the higher Sn adatom positions in both empty states and filled states images. While the lower Sn adatoms give slightly weaker spots in empty states image, they are almost not visible in the filled states images. While for the mixed SnSi dimer chain C(Fig. 4.8(c) and (d)), both filled states and empty states images show bright spots corresponding to the Sn adatom positions, the Si adatoms only give very weak spots in the empty states image. Ref. [79] observed that for Sn on Si(100) the circular spots in the filled states image became elongated in the empty

Figure 4.5 Simulated STM images of (2×2) close packed Pb dimer chain with a surface bias voltage of (a) 1.0 V and (b) -1.0 V, and (4×2) close packed Pb dimer chain with a surface bias voltage of (c) 1.0 V and (d) -1.0 V. H denotes the higher Pb adatom position and L denotes the lower Pb adatom position.

states image, and high-resolution image of the elongated spots revealed buckled dimers. Therefore, the simulated STM images for pure Sn dimer chain have a better agreement with experimental STM observations.

4.1.6 “Rocking” barrier of dimer chain

Our calculations above do not involve the dynamics of the dimer chains. However, information about the dynamics of the dimer chains would be very useful for understanding the experimental STM images. If the time scale of atomic motion is much shorter than STM scanning frequency, the observed STM images will correspond to time-averaged structures rather than the static structures. In this section, we will study the “rocking” motion of dimer chains on Si(100). There are two degenerate buckling

Figure 4.6 Simulated STM images of mixed PbSi dimer chain C with a surface bias voltage of (a) 1.0 V and (b) -1.0 V. H denotes the Pb adatom position and L denotes the Si adatom position.

states in the pure Pb(or Sn) dimer chain structure because the dimers are made up of the same type of atom. We call the motion to flip its buckling state as “rocking”, and the associated energy barrier as the “rocking barrier”. If the rocking barrier is small, the dimers will rock so fast that the rocking cannot be resolved by STM and the dimers will look as if they are not buckled. Therefore, our study of the rocking barrier will provide useful information for interpreting results from STM experiments. Note that our study of the rocking motion is for pure Pb and Sn dimer chains. Since the two buckling states of the mixed dimer chains are not degenerate in energy, the mixed dimer chains will mostly stay in the lower energy buckling state.

There are different ways for a dimer chain to flip its buckling. The rocking barrier between the two degenerate buckling states for the Pb dimer chain in configuration C are calculated as follows.

We first consider the type of rocking in which all the dimers in the chain are correlated such that they flip their buckling state at the same time. The saddle point for this type of correlated rocking motion should be a non-buckled dimer chain with all the adatoms at

Figure 4.7 Simulated STM images of (2×2) close packed PbSi dimer chain with a surface bias voltage of (a) 1.0 V and (b) -1.0 V, and (4×2) close packed PbSi dimer chain with a surface bias voltage of (c) 1.0 V and (d) -1.0 V. H denotes the Pb adatom position and L denotes the Si adatom position.

the same height. The saddle point can be found by calculating the energy of the system as a function of the height of the chain with respect to the Si substrate. The rocking barrier calculated in such a manner is found to be 0.31 eV/dimer. In order to study the effect of the interchain separation on the rocking barrier, the above calculation for the Pb dimer chain are repeated using 2×4 and 8×4 unit cells, in which the separation between the chains are halved and doubled respectively. The rocking barrier is found to be 0.27 eV/dimer with the 2×4 unit cell and 0.29 eV/dimer for the 8×4 unit cell. Therefore, the rocking barrier is not sensitive to interchain separation. The calculation with 4×4 unit cell is repeated using GGA-PW91[57] with the VASP[55] code and ultrasoft pseudopotential. The rocking barrier is found to be 0.27 eV/dimer under the GGA-PW91. Since the Si(100) substrate between the Pb dimer chain C are exposed, the

Figure 4.8 Simulated STM images of Sn dimer chain with a surface bias voltage of (a) 1.0 V and (b) -1.0 V, and mixed SnSi dimer chain with a surface bias voltage of (c) 1.0 V and (d) -1.0 V. H denotes the higher Sn adatom position. L denotes the lower Sn adatom position in (a) and (b), and the Si adatom position in (c) and (d).

substrate Si dimers in this open region should allow to adopt different buckling. We have studied the effect of different buckling states of these Si dimers on the rocking barrier of Pb dimer chain. We found that the rocking barrier is changed by only 5 meV/dimer. Therefore, the effect of substrate buckling on the rocking barrier is not significant.

It should be noted that the energy required to flip the buckling state of the entire infinite chain in this correlated way is actually infinity. Therefore, the rocking motion that flip an infinite chain of dimers at the same time is impossible. Nevertheless, the correlated rocking of a finite chain is possible. In fact, the dimer chains observed in STM experiments all have finite length. Unfortunately, calculations for various finite lengths are not feasible with the first-principles method. Instead, we calculated the rocking

barrier E_{B1} of the Pb dimer chain C having a length of just one Pb dimer, which is the other extreme case. This structure is simply an isolated Pb ad-dimer in a 4×4 unit cell. The barrier is found to be 0.08 eV/dimer, which is significantly lower than that of an infinite chain. This is because for the isolated Pb ad-dimer, the underlying Si dimers are allowed to buckle and consequently able to lower the energy of the saddle point, while the underlying Si dimers for an infinite Pb dimer chain are unbuckled.

The rocking dynamics of Sn dimer chain on Si(100) is also studied. The rocking barrier of an infinite Sn dimer chain C in the above correlated manner is calculated to be 0.28 eV/dimer, and the rocking barrier E_{B1} of an isolated Sn ad-dimer is found to be 0.06 eV/dimer, which are similar to that of Pb for both cases.

While the above calculations can provide rough estimates to the rocking barriers of dimer chains on Si(100), we resort to the following model calculation in order to obtain the variation of rocking frequency of a dimer chain with a finite length. Our model calculation is based on a cascade of dimer flipping in the dimer chain. The individual dimer in the dimer chains is assumed to rock independently and there are no correlation between each other. The ground state of a dimer chain of length L , which we refer as S_0 , has all its dimers with the same buckling. The rocking of the dimer chain starts off with the state S_1 in which a dimer at one of the ends of the dimer chain is being flipped. The energy difference between S_1 and S_0 is approximated by $\frac{E_1}{2}$, where E_1 is the energy of one flipped dimer in an infinitely long dimer chain. E_1 is found to be 0.22 eV and 0.16 eV for Pb and Sn respectively from our first-principles calculations. The energy barrier from S_0 to S_1 is approximated by $E_{B1} + \frac{(E'_{B1} - E_{B1})}{2}$, where E'_{B1} is the rocking barrier of flipping only one dimer in an infinitely long dimer chain. This equation adds the contribution of the adjacent dimer to the energy barrier of an isolated dimer. The calculation of E'_{B1} is done by using a 4×8 unit cell, in which the dimers to be flipped is separated by three other dimers along the dimer chain in configuration C. Therefore, the dimers to be flipped are well separated and can be considered uncorrelated. Using

this setup, E'_{B1} is found to be 0.41 eV[84] and 0.33 eV for Pb and Sn respectively with LDA. After the first dimer is flipped, the adjacent dimer next to it will follow to flip, resulting to the state S_2 and its energy approximated by $\frac{E_1}{2}$ with respect to S_0 . The energy barrier from S_1 to S_2 is assumed to be E'_{B1} . This cascade of dimer flipping will continue till the other end of the dimer chain, with the energy of S_i equals to $\frac{E_1}{2}$ higher than that of S_0 and the energy barrier from S_{i-1} to S_i equals to E'_{B1} for $2 \leq i \leq L-1$. S_L is the other ground state of the dimer chain and the energy barrier from S_{L-1} to S_L is the same with the one from S_0 to S_1 .

After knowing all the intermediate states and their associated energy barriers, we can calculate the rocking frequency f_L of a dimer chain with length L recursively by $f_L = f_{L-1,L}(\frac{f_{L-1}}{f_{L-1}+f_{L-1,L}})$, where $f_{L-1,L}$ is the rocking frequency between S_{L-1} and S_L . The meaning of this recursive relation is that if we know the rocking frequency between S_0 and S_{L-1} , then the rocking frequency between S_0 and S_L can be obtained by multiplying the rocking frequency between S_{L-1} and S_L by a prefactor factor, which takes into account that a dimer chain can both flip a dimer in its dimer chain or have one of its flipped dimer reverting back to the original buckling. The rocking frequency $f_{L-1,L}$ is given by the Arrhenius relation[59] $f_{L-1,L} = p(L-1)f_0 \exp \frac{-\Delta E}{k_B T}$, where $p(L-1)$ is the relative population of S_{L-1} specified by the Boltzmann factor and ΔE is the energy barrier between S_{L-1} and S_L . In order to use the Arrhenius relation, the typical phonon frequency f_0 for Si(100) has to be found. For a bare Si(100) substrate, it is known that an extensive $c(4 \times 2)$ reconstruction can be observed at 144K [85], except near defects where symmetric Si dimers can be seen. We have calculated the energy barrier to flip a single Si dimer in the Si(100) substrate with $c(4 \times 2)$ reconstruction. This barrier is found to be 0.25 eV. If the typical time resolution of STM is taken to be 1000 s^{-1} [86], we can infer from the Arrhenius relation that f_0 is $5.6 \times 10^{11} \text{ s}^{-1}$ for Si(100). Knowing f_0 , the result of our simulation under this framework at room temperature is illustrated in Fig. 4.9 for $L=4$ to 10, which are typical lengths of dimer chains observed in experi-

ments. We found that the rocking frequency of a dimer chain decreases with its length as expected. For Pb dimer chains, the rocking frequencies are two order of magnitude smaller than that of the Sn dimer chains. If we adopt 1000 s^{-1} as the cutoff below which rocking can be resolved by experiments, then Pb dimer chains should be observed to be buckled in STM experiments independent of their length. This result is not sensitive to whether LDA or GGA is being used as the exchange-correlation functional. On the other hand, the rocking frequencies of Sn dimer chain are considerably higher, we expect some influence of dynamical effects due to rocking motion in STM observations. For example in the experiment of Ref. [79], height profiles of Sn dimer chains reveal certain symmetric dimers in the chain. However, there is probably pinning due to defects and the ends of the dimer chains may help to stabilize the buckled dimer against rocking.

Figure 4.9 Simulated rocking frequency of Pb dimer chain(solid line) and Sn dimer chain(dashed line) versus the length of the dimer chain.

4.1.7 Tendency of intermixing

Despite our calculations in Section 4.1.3 and 4.1.4 show that it is energetically favorable to form mixed PbSi and SnSi dimer chains on Si(100), it is unlikely that the experimental STM images are corresponding to the geometries of mixed dimer chains as discussed in Sections 4.1.5 and 4.1.6. In order to investigate this discrepancy between our theoretical calculations and experimental observations, we further consider the intermixing energetics of pure ad-dimers with Si to form mixed dimers, since the individual dimer is the building block for the whole dimer chain. We summarized in Table 4.2 the formation energies of isolated dimers and dimer chains on Si(100) using Eq. (4.1) including the pure Ge dimer and mixed GeSi dimer. It is experimentally verified that Ge will intermix with Si to form mixed dimers after Ge deposition on Si(100). A comparison between Ge, Sn and Pb can give us a hint on how intermixing occurs. From Table 4.2, we can find that it is not energetically favorable to form mixed dimers when compared with pure dimers using Eq. (4.1) for all cases, including Ge, which contradicts with experimental observation. One should note that the formation energy calculated using Eq. (4.1) is a measure of the energy released in forming an ad-dimer on Si(100) when compared to a clean Si(100) substrate with an infinite source of atoms for the ad-dimer, in which the only cost in extracting an atom from the source is measured by the chemical potential. We are approximating the chemical potentials by bulk energies to obtain an upper bound for the formation energy. However, in experiment Si is not deposited epitaxially onto the Si(100) surface, and it is very unlikely that bulk-like Si islands are formed in experiments. In addition, the observed dimer chains may be formed far away from step edges of the Si substrate. Therefore, our estimates of the formation energies of the mixed dimers on Si(100) may not reflect the true experimental conditions.

One possible source of Si atoms is Si ad-dimers on Si(100). A Si ad-dimer can react with an ad-dimer formed by the deposited atoms to produce mixed dimer. The

Table 4.2 The formation energies of dimers and dimer chains on Si(100) calculated using Eq. (4.1). The letter in bracket refers to the atomic configuration illustrated in Fig. 4.1 and Fig. 4.2.

Si ad-dimer(A)	+0.27 eV/Si
Ge ad-dimer(A)	+0.005 eV/Ge
Sn ad-dimer(B)	-0.26 eV/Sn
Pb ad-dimer(B)	-0.33 eV/Pb
Ge-Si ad-dimer(A)	+0.21 eV/Ge
Sn-Si ad-dimer(C)	+0.03 eV/Sn
Pb-Si ad-dimer(C)	-0.06 eV/Pb
Sn ad-dimer chain(C)	-0.50 eV/Sn
Pb ad-dimer chain(C)	-0.51 eV/Pb
Sn-Si ad-dimer chain(C)	-0.59 eV/Sn
Pb-Si ad-dimer chain(C)	-0.70 eV/Pb

associated energy release can be calculated by $\Delta E_{mix} = E_{mixed} - E_{pure}/2 - E_{Si-Si}/2$, where E_{mixed} and E_{pure} are the total energy of the mixed ad-dimer and pure Ge(or Sn, Pb) ad-dimer on Si(100) respectively, with E_{Si-Si} being the total energy of pure Si ad-dimer on Si(100) surface in configuration A. ΔE_{mix} is calculated to be -0.06, +0.014, and +0.002 eV per mixed dimer for Ge, Sn and Pb respectively. Hence, if we consider the mixed dimers being formed by two different ad-dimers, then the formation of GeSi mixed dimers are favorable, but SnSi and PbSi are not. While this mechanism produces a conclusion that agrees with experimental observation, we note that the amount of Si ad-dimers on Si(100) is very limited, and cannot act as a source of Si for large domains of dimer chains observed in the experiment.

Another source of Si atoms is from the Si(100) substrate. It has been observed experimentally that Ge ad-dimers on Si(100) can exchange one of its Ge atoms with the Si(100) substrate to form mixed GeSi ad-dimers. A detailed kinetic pathway of how this intermixing mechanism can occur has already been described in detail in a previous publication[71]. The formation energy of such reaction can be calculated as follows:

$$\Delta E' = E_{mixed} + E'_{sub} - E_{sub} - E_{pure}, \quad (4.2)$$

where E_{sub} is the total energy of Si(100) 4×4 substrate with $c(4 \times 2)$ surface reconstruction, and E'_{sub} is the same as E_{sub} but the surface has one of its buckled-up surface atom replaced by Ge, Sn or Pb. $\Delta E'$ measures the energy released when one of the atom in the pure ad-dimer substitutes a surface atom in the Si(100) substrate and the substituted Si atom comes out to form a mixed ad-dimer. $\Delta E'$ are calculated to be -0.07, +0.23 and +0.28 eV per mixed dimer for the case of Ge, Sn and Pb respectively. Therefore, our calculations show that it is energetically favorable for Ge ad-dimers to intermix with Si to form GeSi ad-dimers by substituting surface Si atoms in Si(100) substrate, while this mechanism is not favored by Sn and Pb.

In order to gain more insight on the difference in behavior of Group IV elements on Si(100) surface, we can decompose Eq. (4.2) into $\Delta E' = \Delta E_{mix} + \Delta E_{substitute}$, where ΔE_{mix} is the same as above and $\Delta E_{substitute} = E'_{sub} + E_{Si-Si}/2 - E_{pure}/2 - E_{sub}$. ΔE_{mix} is a measure of the energy involved in intermixing Ge, Sn or Pb with Si to form mixed ad-dimers, and $\Delta E_{substitute}$ is a measure of the energy involved in substituting a surface Si atom in Si(100) substrate by Ge, Sn or Pb. Note that although we are using Si ad-dimer as a reference to calculate ΔE_{mix} and $\Delta E_{substitute}$, if we are comparing ΔE_{mix} or $\Delta E_{substitute}$ between two different elements, the term involving Si ad-dimer will be canceled out. Therefore, ΔE_{mix} and $\Delta E_{substitute}$ can be used to gauge the relative energetics involved in intermixing and substitution as we go down the Group IV elements. $\Delta E_{substitute}$ is -0.01, +0.21 and +0.28 eV per Ge, Sn and Pb atom respectively. Hence, Sn and Pb is much less favorable than Ge to substitute a surface Si atom in the Si(100) substrate. And from ΔE_{mix} , Ge is slightly more favorable than Sn and Pb to intermix with Si to form mixed dimers. This is probably due to the large size of Pb and Sn compared with Si, and also due to the fact that Ge has a similar electronic structures with Si. The above analysis shows that it is not favorable for pure Sn and Pb dimers to form isolated mixed dimers by extracting Si atoms from the Si(100) substrate.

We have considered two possible channels in which mixed dimers can be formed on

Si(100) when Si atoms are not epitaxially deposited nor from step edges. The limited availability of Si ad-dimers on Si(100), and the high energies involved in substituting a surface Si atom in Si(100) substrate by Sn or Pb will hinder the formation of individual mixed dimers, which are the precursors of mixed dimer chains. This explains why mixed PbSi and SnSi dimer chains are not observed in experiments. Nevertheless, if there is an external source of Si atoms by epitaxially depositing Si on Si(100) for example, or if the dimer chains are formed close to step-edges or defects on Si(100) surface, or by annealing the sample, mixed PbSi and SnSi dimer chains maybe able to form on Si(100).

4.1.8 Conclusion

As a conclusion, we have carried out first-principles calculations to study Pb and Sn dimer chains on Si(100) up to 0.5ML coverage, including the possibility of mixed PbSi and SnSi dimer chains. Our simulated STM images of pure Pb and Sn dimer chains agree with experimental observations, while that of the mixed dimer chains are not. Our calculated rocking barriers of dimer chains suggest that the rocking frequencies of Pb dimer chains are low, buckling of Pb dimer chain can be observed in STM experiments. While for Sn dimer chains, it might be necessary to take dynamical effect into account when interpreting STM results. However, there are possible pinning due to defects and the ends of the dimer chains that cannot be included in our calculation. Our analysis on the relative energetics between pure dimers and mixed dimers shows that the formation of mixed dimers depend on the source of Si atoms available for Pb and Sn dimers to carry out intermixing. In particular, substituting Si atoms in the Si(100) substrate by Sn and Pb atoms is much less energetically favorable than intermixing with Si if Si atoms are available from an external epitaxial source, while the reverse holds for the case of Ge. A lack of favorable channel for Pb and Sn to intermix with Si to form mixed dimers can hinder the formation of PbSi and SnSi dimer chains in experiments.

4.2 Diffusion of Pb adatom and ad-dimer on Si(100)

4.2.1 Introduction

Group IV elements on Si(100) have been intensively studied because of their importance in both technological applications and fundamental understanding of homoepitaxial/heteroepitaxial interface. When Ge atoms are deposited on Si(100) at low coverage, isolated dimers are formed on the top of the substrate dimer row with their dimer bonds oriented parallel to the substrate dimer row direction. It has been shown by both experimental and theoretical studies that intermixing between Ge and Si takes place on the surface which lead to interesting diffusion kinetics[87, 72]. It has also been observed by STM experiments [73, 74, 75, 76] that small amount of Pb($\leq 0.5ML$) deposited onto Si(100) surface form isolated dimers as well as chains of dimers. The one-dimensional Pb dimer chains run perpendicularly to the underlying Si dimer rows, and the dimers in the chain are buckled and located in the trough between the Si dimer rows. In order to understand the mechanism and have a better control of the growth of these nanoscale structures on Si(100), knowledge about the binding and diffusion of Pb adatoms and dimers on Si(100) at atomistic level is very useful and desirable. In this section, we will report our first-principles calculation results on the diffusion pathway and energy barrier of Pb adatoms and dimers on the Si(100) surface.

4.2.2 Calculation method

Our first-principles calculations are performed based on density functional theory (DFT) under local density approximations (LDA) [1]. Pseudopotential and plane wave basis are used. The Ceperley-Alder functional [24] parametrized by Perdew and Zunger [25] is used for the exchange-correlation energy functional. The kinetic energy cutoff is set to be 12 Ryd. The Si(100) surface is modeled by a periodically repeated 4×4 slab which consists of 8 layers of Si passivated by H at the bottom and a vacuum space of

at least $12\text{\AA}$. The top surface of Si(100) is arranged to have a $c(4 \times 2)$ reconstruction, which is one of the lowest energy reconstruction for the Si(100) surface. The effect of the surface Si dimer buckling is very small on the energetics of Pb dimers and dimer chains on Si(100) from our previous study.[88] A Pb adatom or a dimer was put on the top of the surface to study their diffusion. The bottom layer of Si atoms and the H atoms are kept fixed to simulate the bulk environment, while all other atoms in the substrate are allowed to relax until the force on each non-fixed atom is less $0.01\text{ eV/\AA}$. A set of four special k points are used to sample the surface Brillouin zone.

4.2.3 Diffusion of Pb adatom on Si(100)

We first consider a Pb adatom on the Si(100) surface. The lowest energy position of a Pb adatom on the Si(100) surface is found to be at M_1 located in between the Si(100) dimer rows as marked in Fig. 4.10. Starting from M_1 , the Pb adatom will climb to the top of the Si dimer row at a local minimum C and then diffuse along the dimer row through H as illustrated schematically at the top of the figure. The path from M to H and from H to the next minimum is symmetric, and the overall diffusion barrier along the path is 0.32 eV . Diffusion along the trenches of the Si(100) surface is not favorable since the energy at K is 0.49 eV relative to M_1 while the diffusion barrier up the dimer row to the local minimum at C is only 0.26 eV . The energy at the local minimum C is only 0.06 eV higher than that at M_1 , but the Pb adatom needs to overcome an energy barrier of 0.26 eV at H in order to diffuse along the Si dimer row. Overall, the diffusion along the path M_1 -C-H is less costly than diffusing along the trench in between the Si dimer row.

4.2.4 Diffusion of Pb dimer on Si(100)

We then consider the diffusion of a Pb dimer on the Si(100) surface. Our previous study showed that there are four different configurations of Pb dimers on Si(100) which

Figure 4.10 Top: A schematic diagram illustrating the diffusion pathway of a Pb adatom on Si(100). The Pb adatom starts from its minimum M_1 , then climbs to the top of the Si dimer row to a local minimum C and diffuses along the dimer row through H. The path from M to H and from H to the next minimum is symmetric. The top two layers of the Si(100) substrate is colored white, and the two next Si layers underneath is colored grey. Bottom: The energy variation of a Pb adatom from its minimum M_1 to a neighboring minimum along the path.

are called A, B, C and D.[88] Dimers A and B are on the top of the Si(100) dimer row with the dimer bond oriented parallel or perpendicular to the underlying dimer row respectively. Dimers C and D are on the trough between the Si(100) dimer rows with C oriented perpendicular and D oriented parallel to the dimer rows. Our calculation showed that the lowest energy configuration is Pb dimer B located on top of the Si(100) dimer row, followed by dimer C(0.24 eV higher), A(0.32 eV higher) and D(0.70 eV higher). In order to search for the diffusion pathway of dimer B on top of the dimer row, the positions of the two Pb atoms in the dimer are varied independently to map out the

lowest energy pathway. Some of the atomic configurations along the diffusion pathway are shown in Fig. 4.11. The diffusion of the dimer actually involves a rotation with a saddle point S_B (0.95 eV with respect to B) as illustrated in the figure, and subsequently diffuse to a local minimum M (0.43 eV with respect to B) in which the orientation of the Pb dimer becomes parallel to the underlying dimer row from this point onwards. There is a diffusion barrier of 0.20 eV from M through a second saddle point S_A to Pb dimer A, which is 0.32 eV higher than B. The energy variation along the path from B to A is the solid line in Fig. 4.12.

Figure 4.11 The atomic geometries and their energies (with respect to B) illustrating the rotation and diffusion of Pb dimer B to A which correspond to the solid line in Fig. 4.12. The grey atoms represent the Pb adatoms, and the white atoms for the Si atoms in the Si(100) substrate.

Since the Pb dimer B tends to rotate to A first before diffusing along the dimer row, we thus focus here on the diffusion of dimer A in more detail. We have performed

Figure 4.12 The energy variation of a Pb dimer rotation and diffusion from B to A(solid curve), diffusion from B to C(dotted line), and the diffusion of dimer A along the Si dimer row(dashed line). It should be noted that the rotation of dimer B share the same local minimum M as in the diffusion of dimer A, hence the two curves coincide in the right half of the figure.

extensive calculations to map out a potential energy surface(PES) for this diffusion process as shown in Fig. 4.13, which is a function of the displacements of the two Pb atoms of the dimer. The PES was generated by a 15×15 grid mesh. Due to symmetry, there are actually 64 independent configurations needed to be computed. Additional configurations were computed around the saddle point in order to get a more accurate value for the diffusion barrier. From Fig. 4.13, we can see that the Pb atoms tend to move together initially, and hence the Pb dimer diffuses as a whole at this stage. However, at around the saddle point S_A (0.31 eV with respect to A), the leading Pb atom continues the path by itself leaving the other Pb atom behind till the local minimum M (0.11 eV with respect to A) is reached. Beyond this, the lagging Pb atom catches up and both Pb atoms in the dimer diffuse together again till it reaches the neighboring stable

configuration A'. The energy variation of the diffusion process is shown in Fig. 4.12 as the dashed line. It should be noted that the path from A to M is symmetric to the path from M to A'. The corresponding principal atomic geometries illustrating the diffusion mechanism is shown on the right side of Fig. 4.13. Although the principal geometries look quite similar to those of Ge dimer diffusion on Si(100)[70], the Ge dimer diffuses in a piecewise manner in which one of the Ge atom moves first to the neighboring site but the other Ge atom is nearly frozen in the process, and then the second Ge atom will follow to form a dimer with the first atom again. While for Pb dimers, the initial and final phase of the diffusion process involves the Pb dimer moving as a whole with both Pb atoms progressing at similar speed.

Figure 4.13 Left: The potential energy surface for the diffusion of Pb dimer A on top of the Si(100) dimer row. The axes represent the displacements of the two Pb atoms in the dimer as illustrated schematically in the figure. The white curve indicates the lowest energy diffusion pathway for the potential energy surface. Right: The atomic geometries and their energies (with respect to A) corresponding to the white curve on the left of the figure and the dashed line in Fig. 4.12. The grey atoms represent the Pb adatoms, and the white atoms for the Si atoms in the Si(100) substrate.

We also investigated another pathway in which the dimer B diffuses from the top to

the trough in between the substrate dimer row. The pathway starts from B and proceeds to configuration C which has an energy of 0.24 eV higher than B and is located in the trough and with the dimer bond orientation the same as B, that is oriented perpendicular to the Si(100) dimer row. To calculate the energy barrier along this diffusion pathway, the Pb dimer is moved from B to C progressively. For each configuration along the path, the y-coordinate of the center of mass of the dimer is held fixed, while the rest of the coordinates are allowed to relax. Several configurations along the diffusion path are shown in Fig. 4.14. We found that the diffusion of B down the trough is piecewise initially. The leading Pb atom descends from the dimer row while the other Pb atom remains close to its initial position, and this is illustrated by B_1 in the figure. Shortly afterwards, the lagging Pb atom catches up with the Pb atom in the trough nearly frozen in position till the saddle point S_C is reached, which is 0.89 eV relative to B. Beyond this point, the Pb dimer diffuses as a whole to configuration C. The energy variation from B to C is shown in Fig. 4.12 by the dotted line.

4.2.5 Discussion

Our calculation results as discussed above show that if a Pb dimer is initially on top of the Si(100) dimer row at its lowest energy configuration(B), it can diffuse along the dimer row or perpendicular to the row by passing through the troughs. For diffusion from the top of the row to the trough, there is an energy barrier of 0.89 eV to a local minimum C which is 0.24 eV relative to B. However, from C back to B, there is a corresponding barrier of 0.65 eV. On the other hand, the diffusion along the top of the dimer row involves a relatively high rotation barrier of 0.95 eV to A, which is 0.32 eV with respect to B. However, with the dimer oriented parallel to the substrate dimer row, it is then less costly in energy(0.31 eV) to diffuse along the top of the row. Therefore, if the Pb dimer can overcome the initial high rotation barrier from B to A, it is easier to diffuse on the Si(100) surface.

Figure 4.14 The atomic geometries and their energies (with respect to B) illustrating the diffusion of Pb dimer B from the top of the Si(100) dimer row down the trough to C which correspond to the dotted line in Fig. 4.12. The grey atoms represent the Pb adatoms, and the white atoms for the Si atoms in the Si(100) substrate. Only the Si dimer rows are shown for the Si substrate.

Although Pb adatoms diffusing along the top of the Si(100) dimer row has a diffusion barrier of only 0.32 eV, it is energetically more favorable to form a Pb dimer on Si(100) than just isolated Pb adatoms, since the adsorption energy of the Pb dimer A on Si(100) is -0.17 eV per Pb atom [88], while the adsorption energy of a Pb adatom at the minimum M_1 is calculated to be only 2 meV per atom. Hence, if two Pb adatoms diffusing along the Si(100) dimer row meet each other, it is very likely that Pb dimer A will be formed. Since there is a high rotation barrier from A to B, the Pb dimer A may get stuck in this local minimum configuration. A comparison of a Pb dimer with other dimers composed of Group IV elements on Si(100) can be found in Table 4.3. We can see that a Pb dimer

have the lowest diffusion barrier when compared to Si, Ge and Si-Ge dimers if they are all in configuration A. When compared to the rotation of Si-Ge dimer on Si(100)[71] in Table 4.3, the Pb dimer has to overcome a larger barrier. This can be understood by the geometry of the saddle point S_B in Fig. 4.11, one of the Pb atom in the dimer has to climb over a Si dimer of the dimer row in order to rotate due to the large size of the Pb atom.

Table 4.3 Relative energies E_{dimer} between different configurations(see text) of Pb ad-dimer on the Si(100) surface, a comparison of the diffusion barriers of dimers in configuration A along the top of the Si(100) dimer row($E_{\parallel}$) and dimers in configuration B across the dimer row($E_{\perp}$) between different Group IV elements, and a comparison of the rotation barriers(E_{rot}) on the dimer row between Pb and Si-Ge ad-dimers.

	$E_{dimer}(\text{eV})$
A	0.32
B	0
C	0.24
	$E_{\parallel}(\text{eV})$
Si ad-dimer(A)	1.02 ¹
Ge ad-dimer(A)	0.77 ^a
Si-Ge ad-dimer(A)	1.12 ²
Pb ad-dimer(A)	0.31 ³
Pb ad-atom	0.32 ^c
	$E_{\perp}(\text{eV})$
Si ad-dimer(B)	1.39 ⁴
Pb ad-dimer(B)	0.89 ^c
	$E_{rot}(\text{eV})$
Si-Ge ad-dimer	0.74 ⁵
Pb ad-dimer	0.95 ^c

As a conclusion, we have studied the diffusion process of a Pb adatom and dimer on the Si(100) surface. A Pb adatom diffuses on top of the Si(100) dimer row with a barrier of 0.32 eV. A Pb dimer can diffuse across the Si(100) dimer row by passing through the trough in between with an energy barrier of 0.89 eV. Or the Pb dimer can first rotate its bond parallel to the underlying dimer row with an energy barrier of 0.95

eV(if it is not already parallel to the dimer row), and then diffuse along the top of the dimer row with only 0.31 eV barrier afterward. Although dimer B is the lowest energy configuration, there is a high energy barrier to rotate from A to B. As a result, dimer A may act as a fast mass transport unit on the surface for the self-assembly of Pb/Si(100) nano-structures at low Pb coverage.

CHAPTER 5. Highly localized quasiatomic minimal basis orbitals for Mo

5.1 Introduction

The electronic structures of periodic systems in solid-state physics are usually formulated in the reciprocal space. While it is technically elegant and simple to implement computationally, the formalism lack in providing an easy connection to the traditional chemical concepts and an intuitive picture about the bonding properties of crystal in real space. Hence, a representation of the electronic structures using localized orbitals is appealing, and also important for the modern theories of electron correlations[90] and electron polarization[91, 92]. Moreover, localized orbitals are shown to play a key role in the development of $O(N)$ methods[93, 94, 95, 96, 97] where the computational effort of electronic structure calculations scale linearly with the system size.

Wannier functions(WFs), introduced by Wannier in 1937[98], are the most widely used functions to describe the electronic structures of crystals in real space. Since WFs are constructed by a unitary transformation of the canonical electronic eigenstates of the crystal, they cover the same space as that spanned by the eigenstates from which the WFs are constructed. However, well-localized WFs exist only in large-gap insulators but not in metallic systems[99, 100]. A lot of effort has been focused on obtaining maximally localized generalized WFs[101, 102, 103, 104, 105]. In particular, Souza, Marzari and Vanderbilt have shown that it is possible to generate atomic-like Wannier orbitals by including a suitable number of unoccupied bands in addition to the occupied bands[105].

Recently, we proposed a new scheme to construct highly localized quasiatomic minimal basis orbitals (QUAMBOs) [106] for both insulating and metallic systems, using the electronic eigenstates obtained from first-principles calculations. Our scheme selects a relevant subset of anti-bonding states from a large unoccupied subspace. The anti-bonding states are chosen such that the resulting QUAMBOs are maximally localized. The QUAMBOs not only contain the adaption of the minimal basis to the environment, but also reproduce exactly the first-principles electronic structures of the occupied states. Previously, we have successfully constructed the QUAMBOs for Si and Al in diamond and fcc structures resulting in highly localized s- and p-like orbitals. In this chapter, we will demonstrate that similar algorithm can be applied to transition metals as well, in which the localized d-electrons play an important role to the electronic properties. Mo in bcc structure is chosen as our prototype system in this study. QUAMBOs of Mo in fcc structure are also calculated to compare the bonding between bcc and fcc structures.

5.2 Formalism

Given a set of Bloch eigenstates $\phi_{\mathbf{k},\mu}(\mathbf{r})$ obtained from first-principles calculations using a large basis set, with the eigenstates being labeled by the wave vector $\mathbf{k}$ in the Brillouin zone and the band number μ , we want to construct a set of quasiatomic orbitals $A_\alpha(\mathbf{r} - \mathbf{R}_i)$ for each atom i at position $\mathbf{R}_i$ in the unit cell and for each orbital type α (s, p_x, p_y, p_z etc.) by linear combinations of the Bloch eigenstates. For each wave vector $\mathbf{k}$, a total of n_{tot} bands are calculated, with $n_{occ}(\mathbf{k})$ of them being occupied and the rest $n_{vir}(\mathbf{k})$ are unoccupied. However, only a subspace of the unoccupied bands is needed and this subspace should be optimized in order to combine coherently with the occupied bands to enhance the localization of the QUAMBOs. This optimal subset of

virtual bands $\phi_{\mathbf{k},p}(\mathbf{r})$ is obtained by a linear transformation:

$$\phi_{\mathbf{k},p}(\mathbf{r}) = \sum_{\mu=n_{occ}+1}^{n_{tot}} T_{\mu p}(\mathbf{k}) \phi_{\mathbf{k},\mu}(\mathbf{r}), p = 1, 2, \dots, n_p(\mathbf{k}) < n_{vir}(\mathbf{k}), \quad (5.1)$$

where T is a rectangular matrix to be determined later which satisfies $T \cdot T^\dagger = I$ since $\phi_{\mathbf{k},p}(\mathbf{r})$ is required to be orthogonal to each other. Then the quasiatomic orbitals can be constructed by a suitable linear combination of the occupied bands and the optimized virtual bands:

$$A_\alpha(\mathbf{r} - \mathbf{R}_i) = \sum_{\mathbf{k}} \left(\sum_{\mu=1}^{n_{occ}} a_{\mu\alpha}(\mathbf{k}, \mathbf{R}_i) \phi_{\mathbf{k},\mu}(\mathbf{r}) + \sum_{p=1}^{n_p} b_{p\alpha}(\mathbf{k}, \mathbf{R}_i) \phi_{\mathbf{k},p}(\mathbf{r}) \right). \quad (5.2)$$

Our requirement is that each A_α should be as close as possible to its corresponding free-atom orbital A_α^0 , which implies the minimization of the mean square deviation $\langle A_\alpha - A_\alpha^0 | A_\alpha - A_\alpha^0 \rangle$ under the norm-conserving constraint $\langle A_\alpha | A_\alpha \rangle$. The Lagrangian minimization for this problem yields

$$A_\alpha(\mathbf{r} - \mathbf{R}_i) = D_{i\alpha}^{-1/2} \left[\sum_{\mathbf{k}} \left(\sum_{\mu=1}^{n_{occ}} \langle \phi_{\mathbf{k},\mu}(\mathbf{r}) | A_\alpha^0(\mathbf{r} - \mathbf{R}_i) \rangle \phi_{\mathbf{k},\mu}(\mathbf{r}) + \sum_{p=1}^{n_p} \langle \phi_{\mathbf{k},p}(\mathbf{r}) | A_\alpha^0(\mathbf{r} - \mathbf{R}_i) \rangle \phi_{\mathbf{k},p}(\mathbf{r}) \right) \right], \quad (5.3)$$

where

$$D_{i\alpha}^{-1/2} = \sum_{\mathbf{k}} \left(\sum_{\mu=1}^{n_{occ}} |\langle \phi_{\mathbf{k},\mu}(\mathbf{r}) | A_\alpha^0(\mathbf{r} - \mathbf{R}_i) \rangle|^2 + \sum_{p=1}^{n_p} |\langle \phi_{\mathbf{k},p}(\mathbf{r}) | A_\alpha^0(\mathbf{r} - \mathbf{R}_i) \rangle|^2 \right) \quad (5.4)$$

and is related to the root-mean-square deviation of the optimized A_α from the corresponding free-atom A_α^0 by

$$\Delta_{i\alpha} = \langle A_\alpha - A_\alpha^0 | A_\alpha - A_\alpha^0 \rangle^{1/2} = [2(1 - D_{i\alpha}^{1/2})]^{1/2}. \quad (5.5)$$

Equation (5.5) suggests that the key step to obtaining quasiatomic localized orbitals is to select a virtual band subset $\phi_{\mathbf{k},p}(\mathbf{r})$ that maximizes the sum $\sum_{i,\alpha} D_{i\alpha}$, i.e. maximizing the overall overlap between the virtual bands and the free-atom orbitals. With the subset of virtual bands chosen according to this criteria(details to be given below), QUAMBOs can then be constructed through equation (5.3).

5.3 Algorithm to construct QUAMBOs for Mo

5.3.1 Calculation of Bloch eigenstates from first-principles calculations

First, the electronic eigenstates of Mo in bcc structure are calculated using first-principles density functional theory under local density approximation(LDA)[1]. The Kohn-Sham equations are solved self-consistently using pseudopotential[107] with a mixed basis of plane waves and Gaussian functions[108] to enable adequate convergence for the localized d-like orbitals. The cut-off energy is set to be 40 Ry and a Monkhorst-Pack grid[58] of $16 \times 16 \times 16$ is used for the Brillouin zone integration. A total of 70 bands are calculated for each k-point in our grid.

5.3.2 Projection of Bloch eigenstates onto free-atom orbitals

Before we can proceed to constructing QUAMBOs, the Bloch eigenstates obtained from the previous step need to be projected onto the free-atom orbitals of Mo first. We choose to use the 5s and 4d pseudo-wavefunctions as our free-atom orbitals A_{α}^0 . The pseudo-wavefunctions are obtained by atomic calculations in which the pseudo-wavefunctions are constrained to match the corresponding ground state wavefunctions exactly outside a core radius and reproduce the same atomic eigenvalues at the same time. The radial part of the pseudo-wavefunctions is designed to be nodeless inside the core radius that join smoothly to the wavefunction outside the core, and the integrated charge of the pseudo-wavefunctions is required to be normalized. Hence, a total of six QUAMBOs for Mo will be generated designed to maximize the overlap with these six free-atom orbitals $A_{\alpha}^0(\alpha = s, d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2})$. In our calculations, the eigenstates, originally given by a mixed basis of plane waves and Gaussian functions, are now re-expressed using plane waves with a cut-off energy of 80 Ry, this is because integration involving plane waves is computationally simpler. It should be noted that p-orbitals are not included in the construction as we will explain later that the six s-

and d-like QUAMBOs are sufficient to serve as a minimal basis set that reproduces the properties of Mo in a bcc crystal. We checked that the plane wave set is large enough that our studies following the QUAMBO construction, for example bonding analysis in the following sections, is converged.

5.3.3 Determination of the virtual subspace

By virtue of equation (5.4) and that the optimal virtual subset has to be orthonormal, the optimization of the virtual bands to yield the maximal overlap with the free-atom orbitals A_α^0 can be done by diagonalizing the matrix

$$B_{\mu\mu'}^k = \sum_{i,\alpha} \langle \phi_{k,\mu}(\mathbf{r}) | A_\alpha^0(\mathbf{r} - \mathbf{R}_i) \rangle \langle A_\alpha^0(\mathbf{r} - \mathbf{R}_i) | \phi_{k,\mu'}(\mathbf{r}) \rangle \quad (5.6)$$

for each k-point, where μ and μ' run over all the unoccupied states obtained in our first-principles calculation. The eigenvectors define the transformation matrix T in equation (5.1) for optimizing the virtual bands. The eigenvalues and eigenvectors are ranked in descending order with the largest eigenvalues being the first one. Hence, after the transformation, the virtual space for each k-point will have the first virtual state giving the largest overlap with the free-atom orbitals A_α^0 , and the second virtual state having the second largest overlap and so on.

A Bloch wavefunction for the QUAMBOs can be obtained by

$$\tilde{A}_{k,\alpha}(\mathbf{r} - \mathbf{R}_i) = D_{i\alpha}^{-1/2} \left[\sum_{\mu=1}^{n_{occ}} \langle \phi_{k,\mu}(\mathbf{r}) | A_\alpha^0(\mathbf{r} - \mathbf{R}_i) \rangle \phi_{k,\mu}(\mathbf{r}) + \sum_{p=1}^{n_p} \langle \phi_{k,p}(\mathbf{r}) | A_\alpha^0(\mathbf{r} - \mathbf{R}_i) \rangle \phi_{k,p}(\mathbf{r}) \right] \quad (5.7)$$

analogous to equation (5.3). The size of the virtual subspace $n_p(\mathbf{k})$ is chosen such that the sum $n_{occ}(\mathbf{k}) + n_p(\mathbf{k})$ is equal to the number of desired QUAMBOs. For Mo in bcc structure, there are only one atom in a unit cell and six QUAMBOs are being sought for this atom, hence $n_p(\mathbf{k}) = 6 - n_{occ}(\mathbf{k})$. The first n_p states from the virtual space will be chosen. Since the virtual states are ranked according to the amount of overlap with

the free-atom orbitals, the chosen virtual subspace of size n_p thus acts as good “anti-bonding” states that combine with the occupied states to produce localized quasiatomic orbitals. Special attention has to be made to ensure that the transformation of occupied and virtual states to $\tilde{A}_{\mathbf{k},\alpha}$ is invertible and numerically stable. If it is not, another choice of the virtual subspace should be made. We found that if three additional p-like QUAMBOs are desired, giving a total of nine QUAMBOs, the transformations become singular or badly conditioned no matter how the virtual subspace is being chosen. This situation happens when the six s- and d-like QUAMBOs already constitute a sufficient minimal basis set to express the system under consideration, addition QUAMBOs are redundant leading to singular transformations. Since the transformation is invertible, our QUAMBOs are ensured to reproduce all the occupied eigenstates and eigenvalues of the system. However, for metallic system like Mo, it is preferable to preserve the electronic properties not only below the Fermi level, but also slightly above the Fermi level as well. Hence, additional eigenstates up to 2 eV above the Fermi level are included into n_{occ} , with the construction of the virtual subspace obtained by higher unoccupied states rather than unoccupied states immediately above the Fermi level.

5.3.4 Construction of orthogonalized QUAMBOs

Finally, the QUAMBOs can be constructed by summing up all the $\tilde{A}_{\mathbf{k},\alpha}(\mathbf{r} - \mathbf{R}_i)$ over the first Brillouin zone:

$$A_{\alpha}(\mathbf{r} - \mathbf{R}_i) = \sum_{\mathbf{k}} \tilde{A}_{\mathbf{k},\alpha}(\mathbf{r} - \mathbf{R}_i). \quad (5.8)$$

However, the QUAMBOs are not mutually orthogonal to each other in general. The QUAMBOs belonging to the same atom can be orthogonalized by symmetric orthogonalization:

$$\hat{A}_{\alpha}(\mathbf{r} - \mathbf{R}_i) = \sum_{\alpha'} A_{\alpha}(\mathbf{r} - \mathbf{R}_i) (S^{-1/2})_{\alpha\alpha'}, \quad (5.9)$$

where $S_{\alpha\alpha'} = \langle A_\alpha(\mathbf{r} - \mathbf{R}_i) | A_{\alpha'}(\mathbf{r} - \mathbf{R}_i) \rangle$. Hence, the set $\hat{A}_\alpha(\mathbf{r} - \mathbf{R}_i)$ ($\alpha = s, d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}$) constitutes a minimal quasiatomic basis which is intra-atom orthogonal.

5.4 Results

By following the recipe described above, the s- and d-like QUAMBOs for Mo in bcc structure are obtained and a three-dimensional plot of the six QUAMBOs are displayed in Fig. 5.1. The corresponding contour plots are shown in Fig. 5.2 together with the s- and d-like QUAMBOs for Mo in fcc structure and the free-atom orbitals for comparison. Due to symmetry, $\hat{A}_{d_{xy}}$ and $\hat{A}_{d_{zx}}$ are not shown in the contour plots since they are the same as $\hat{A}_{d_{yz}}$ when projected onto the appropriate atomic plane. From Fig. 5.2, we can see that the bcc QUAMBOs are very similar to the corresponding orbitals in the free atom. The root-mean-square deviations ($\Delta_{i\alpha}$) between the bcc QUAMBOs and the corresponding free-atom orbitals are 16.4% for s, 7.5% for d_{xy}, d_{yz}, d_{zx} , and 7.0% for $d_{x^2-y^2}, d_{3z^2-r^2}$ -like QUAMBOs respectively. The deformation of the QUAMBOs are more pronounced along the bonds between the atoms. The QUAMBOs for Mo in fcc structure, although also quite similar to the free-atom orbitals, their deformation is clearly different from that of the bcc QUAMBOs with deviations of 16.5% for s, 7.2% for d_{xy}, d_{yz}, d_{zx} and 6.5% for $d_{x^2-y^2}, d_{3z^2-r^2}$ -like QUAMBOs respectively. This demonstrates that the QUAMBOs can adapt to the bonding environment in the crystal by deforming slightly from the free-atom orbitals.

As explained above, the QUAMBOs are constructed such that they can reproduce the occupied states electronic properties obtained from a first-principles calculation using a large basis set. This can be demonstrated explicitly by comparing the band structure and density of states of bcc Mo calculated using QUAMBOs as bases with those obtained from our original LDA calculation. The matrix element of the

Figure 5.1 Three-dimensional plots for the six QUAMBOs of Mo in bcc structure. A cubic unit cell of the bcc structure is also shown.

Hamiltonian under QUAMBOs is $H_{\alpha\alpha'}(\mathbf{k}) = \langle \tilde{A}_{\mathbf{k},\alpha}(\mathbf{r} - \mathbf{R}_i) | H | \tilde{A}_{\mathbf{k},\alpha'}(\mathbf{r} - \mathbf{R}_{i'}) \rangle$, where $\tilde{A}_{\mathbf{k},\alpha}(\mathbf{r} - \mathbf{R}_i) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n} e^{i\mathbf{k} \cdot \mathbf{R}_n} \hat{A}_{\alpha}(\mathbf{r} - \mathbf{R}_i - \mathbf{R}_n)$ is the Bloch sum of the QUAMBO $\hat{A}_{\alpha}(\mathbf{r} - \mathbf{R}_i)$, $\mathbf{k}$ is an arbitrary k-point in the Brillouin zone not restricted to those in the k-point grid from our first-principles calculation, and $\mathbf{R}_n$ are the lattice vectors of the bcc crystal structure. The total Hamiltonian $H = \sum_{\mathbf{k}'} \sum_{\mu=1}^{n_{tot}} |\phi_{\mathbf{k}',\mu}\rangle E_{\mathbf{k}',\mu} \langle \phi_{\mathbf{k}',\mu}|$ when expressed using the eigenstates of the system. Here, $\mathbf{k}'$ runs over the k-point grid chosen for the Brillouin zone integration in our first-principles calculation. It is straight forward to show that

$$H_{\alpha\alpha'}(\mathbf{k}) = \sum_{\mathbf{R}_n} \langle \hat{A}_{\alpha}(\mathbf{r} - \mathbf{R}_i) | H | \hat{A}_{\alpha'}(\mathbf{r} - \mathbf{R}_{i'} - \mathbf{R}_n) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_n} = \sum_{\mathbf{R}_n} \sum_{\mathbf{k}'} H_{\alpha\alpha'}(\mathbf{k}') e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_n}. \quad (5.10)$$

The first equality expresses that we have achieved a partition of the Hamiltonian into different atoms and atomic orbitals in real space, and $H_{\alpha\alpha'}(\mathbf{k})$ is in fact a Fourier transform back to the reciprocal space. The second equality provides an interpolation formula for the matrix element $H_{\alpha\alpha'}(\mathbf{k})$ at any k-point in the Brillouin zone using the matrix elements in our k-point grid. Using equation (5.10), the Hamiltonian can be calculated

Figure 5.2 Contour plot of the QUAMBOs of Mo in bcc structure shown in Fig. 5.1: (a) s-, (b) d_{yz} -, (c) $d_{x^2-y^2}$ -, and (d) $d_{3z^2-r^2}$ -like QUAMBOs with their corresponding QUAMBOs of Mo in fcc structure and free-atom orbitals for comparison. (a), (b) and (d) are plotted in the (100) plane, and (c) is plotted in the (001) plane. The outermost contour line has the value of $0.05 \text{ \AA}^{-3/2}$. The contour step is $0.02 \text{ \AA}^{-3/2}$ for (a) and $0.05 \text{ \AA}^{-3/2}$ for (b) to (d).

at any k-point with the QUAMBOs as bases and it can then be diagonalized to obtain the band structure along the symmetry directions of the Brillouin zone as shown in Fig. 5.3. Similarly, the density of states of Mo in bcc structure using the QUAMBOs as bases can be calculated as well and the result is shown in Fig. 5.4. When compared with the original LDA calculation, we can see that the QUAMBOs can reproduce exactly all the occupied states, and the states up to 2 eV above the Fermi level are well preserved. It should be noted that the same method of constructing QUAMBOs for Al resulted in an

energy gap opening up immediately at the energy where the forced reproduction of the eigenstates terminates[106], but this situation does not occur for Mo as shown in Fig. 5.4. This probably implies that the QUAMBOs for Mo are not too bad a representation for the space even beyond 2 eV above the Fermi level, although it is not designed to be so.

Figure 5.3 Electronic band structure for bcc Mo along symmetry directions calculated using a mixed-basis first-principles LDA method(solid line) and using QUAMBOs as a basis set(dotted line).

5.5 Population and bonding analysis

The occupied eigenstates $\phi_{\mathbf{k},\mu}(\mathbf{r})$ from our first-principles calculations can be expressed in terms of Bloch sums of QUAMBOs $\tilde{A}_{\mathbf{k},\alpha}$ as $\phi_{\mathbf{k},\mu} = \sum_{i,\alpha} c_{\mu,\alpha}(\mathbf{k}, \mathbf{R}_i) \tilde{A}_{\mathbf{k},\alpha}(\mathbf{r} - \mathbf{R}_i)$. This is possible because the construction of QUAMBOs is by linear combination of these eigenstates and the transformation is being ensured to be invertible. The Mulliken overlap population matrix[109] between the i -th atom of the origin cell and the j -th atom of

Figure 5.4 Electronic density of states of bcc Mo obtained by using QUAMBOs as a basis set, compared with those from the original LDA calculations.

cell $\mathbf{R}_n$ is then defined as

$$M_{i0,jn} = N^{-1} \sum_{\mathbf{k}, \alpha, \beta} P_{\alpha, \beta}^{i,j}(\mathbf{k}) S_{\beta, \alpha}^{jn, i0}(\mathbf{k}), \quad (5.11)$$

where $P_{\alpha, \beta}^{i,j}(\mathbf{k}) = \sum_{\mu}^{n_{occ}} 2c_{\mu, \alpha}(\mathbf{k}, \mathbf{R}_i) c_{\mu, \beta}^*(\mathbf{k}, \mathbf{R}_j)$ and $S_{\beta, \alpha}^{jn, i0}(\mathbf{k}) = \langle \hat{A}_{\beta}(\mathbf{r} - \mathbf{R}_j - \mathbf{R}_n) | \hat{A}_{\alpha}(\mathbf{r} - \mathbf{R}_i) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_n}$. Hence, $M_{i0,jn}$ is actually the partial trace of a density matrix $(P \cdot S)$ which is expressed under a non-orthogonal basis set (because QUAMBOs between different atoms are not orthogonalized) in reciprocal space. The trace sums over all the orbitals of i -th atom of the origin cell and the j -th atom of cell $\mathbf{R}_n$. In a similar way, the bond order index [110] for a system without spin polarization can be expressed as

$$BO_{i0,jn} = \sum_{\alpha \in i0, \beta \in jn} (PS)_{\alpha\beta}^{i0, jn} (PS)_{\beta\alpha}^{jn, i0}, \quad (5.12)$$

where $(PS)_{\alpha\beta}^{i0, jn} = N^{-1} \sum_{\mathbf{k}} (P(\mathbf{k}) \cdot S(\mathbf{k}))_{\alpha\beta} e^{-i\mathbf{k} \cdot \mathbf{R}_n}$ with $S_{\beta\alpha}^{jn, i0}(\mathbf{k}) = \langle \tilde{A}_{\mathbf{k}, \beta} | \tilde{A}_{\mathbf{k}, \alpha} \rangle = \sum_m S_{\beta, \alpha}^{jm, i0}(\mathbf{k})$. The bond order between the two atoms is the

trace of the square of the density matrix with the trace summing over the orbitals of the two atoms.

Based on equations(5.11) and (5.12), we calculated the matrix elements $M_{i0,jn}$ and the bond order indices $BO_{i0,jn}$ for Mo in bcc structure as well as fcc-Mo for comparison in Fig. 5.5. The Mulliken overlap populations are two times of $M_{i0,jn}$. We can see that the overlap population and bond order mainly concentrate on the first and second neighbors, hence the interaction between the Mo atoms are very localized. Both $M_{i0,jn}$ and $BO_{i0,jn}$ have higher magnitudes for Mo in bcc structure than in fcc, this is because fcc is close-packed and each atom in fcc structure has twelve nearest neighbors compared to eight in bcc, hence each individual bond is weaker in fcc. To further our understanding of the nature of bonding in Mo crystal, we decompose the matrix elements $M_{i0,jn}$ into contribution from overlap between different orbitals. The decomposed matrix element between the origin atom and an atom in the first neighbor($(1/2,1/2,-1/2)a$ for bcc and $(1/2,0,1/2)a$ for fcc where a is the lattice constant) $M_{0,1}$ are shown in Table 5.1, the indices i and j are omitted for clarity because there is only one atom in the primitive unit cell for both bcc and fcc structures. For bcc-Mo, we can see that the $ss-\sigma$ bond accounts for nearly 20% of $M_{0,1}$. On the other hand, $d_{zx}d_{zx}-\sigma$ and $-\delta$ bonds account for more than 25% of $M_{0,1}$ in fcc structure(it will be d_{xy} or d_{yz} if other atoms in the first neighbor are considered). This difference can be understood by the close-packed nature of fcc structure which promotes bonding between the localized d-electrons in Mo, while the $ss-\sigma$ bonding is more convenient for a slightly more open structure as in bcc. For the matrix element between the origin atom and the second neighbors, the $ss-\sigma$ anti-bonding dominates $M_{0,2}$ for both fcc and bcc structures. The $ss-\sigma$ bond contributes 80% and 70% to $M_{0,2}$ in bcc and fcc structure respectively.

In Fig. 5.6, our results for $M_{i0,jn}$ as a function of the inter-atomic distances of bcc-Mo are plotted together with those of diamond Si and fcc Al structures from our previous study[106] for comparison. The overlap population of both Si and Mo extend only up

Figure 5.5 The matrix elements $M_{i0,jn}$ (top) and bond order index $BO_{i0,jn}$ (bottom) between the origin atom and its various neighbors for Mo in bcc and fcc structures.

to the second neighbors, while the overlap population of the fcc-Al are smaller for the first neighbor but extend up to the fifth neighbors, which reflects the diffuse nature of the electronic states in Al. This implies that the electronic structures of Mo can be satisfactorily described by tight-binding approach although it is a metal.

5.6 Conclusion

As a conclusion, we have constructed a minimal basis set of localized quasiatomic orbitals (QUAMBOs) for Mo in bcc crystal structure by using the converged self-consistent

Table 5.1 The first-neighbor overlap population matrix elements for bcc and fcc Mo decomposed into overlaps between different orbitals. The matrix elements are calculated between the atom at the origin and an atom in the first neighbor: $(1/2, 1/2, -1/2)a$ for bcc and $(1/2, 0, 1/2)a$ for fcc. Only the diagonal and upper-triangle are shown because the array is symmetric.

$M_{0,1}$	s	d_{xy}	d_{yz}	d_{zx}	$d_{x^2-y^2}$	$d_{3z^2-r^2}$
BCC						
s	0.02114	-0.00105	-0.00105	-0.00105	0	0
d_{xy}		0.00278	0.00451	0.00451	0	0.00827
d_{yz}			0.00278	0.00451	0.0062	0.00207
d_{zx}				0.00278	0.0062	0.00207
$d_{x^2-y^2}$					0.00846	0
$d_{3z^2-r^2}$						0.00846
FCC						
s	0.00287	0	0	0.00352	0.00191	0.00064
d_{xy}		0.00084	0.00685	0	0	0
d_{yz}			0.00084	0	0	0
d_{zx}				0.01940	0.00237	0.00079
$d_{x^2-y^2}$					0.00053	0.00795
$d_{3z^2-r^2}$						0.00584

eigenstates from first-principles calculations as input. The construction follows a similar procedure as in Ref. [106], hence our method applies to both insulator and metal. In particular, our study shows that it works for transition metals with localized d-electrons as well. The Mo QUAMBOs can be used as a basis for electronic calculations that can reproduce all the occupied-states electronic properties of bcc Mo, for example the electronic band structure and density of states. Moreover, population and bonding analysis can be made that provides interpretation based on chemical bonding, and we compared the Mulliken overlap population and bond order indices between bcc-Mo and fcc-Mo, and between bcc-Mo, diamond-Si and fcc-Al.

Figure 5.6 The matrix elements $M_{i0,jn}$ between the origin atom and its various neighbors for diamond-Si, fcc-Al and bcc-Mo.

CHAPTER 6. Global search for H-passivated Si nanowires

6.1 Introduction

The continuous miniaturization of electronics industry has achieved the limit in which the interconnection of the devices in a reliable and controllable way is particularly challenging. Fervent strides are currently underway in the preparation of nanoscale wires for molecular and nano-electronics applications [112]: such wires(possibly doped or functionalized) can operate both as nanoscale devices and as interconnects [113]. Silicon nanowires (SiNW) offer, in addition to their appeal as building blocks for nanoscale electronics, the benefit of simple fabrication techniques compatible with the currently well-developed silicon technology.

The current growth methods(e.g., [114, 115, 116, 117]) can yield wires with diameters ranging from several tens of nanometers down to 1 nm. These SiNWs are usually crystalline with only a few axis orientations being observed, and have a prismatic shape bounded by facets parallel to the wire axis[115, 116, 117, 118, 119]. While remarkable progress has been achieved in terms of preparation and characterization of SiNWs, atomic-level knowledge of the structure remains necessary for a complete understanding of the device properties of these wires. At present, attempts to predict the structure of SiNWs are affected by the lack of robust methodologies (i.e. algorithms coupled with model interactions) for searching the configuration space, and most studies to date rely on heuristically proposed structures as a starting point for stability studies of SiNWs at the ab-initio level. The electronic structure calculations are too computationally de-

manding to be used in a thorough sampling of the potential energy surface of SiNWs. On the other hand, most of the empirical potentials for Si are fast, but are not sufficiently transferable to capture accurately the structure and energetics of various wire configurations. Despite these obstacles, the current theoretical efforts to find the structure of SiNWs have been very vigorous and have led to the identification of a number of low-energy configurations for pristine SiNWs[120, 121, 122, 123, 124]. In comparison, the structure of passivated nanowires has received much less attention from a theoretical perspective, although most of the experimental techniques to date yield wires that are passivated either with oxides[125, 126] or with hydrogen[117, 118].

Motivated by the elegant experiments[117] of Ma and coworkers, we have investigated the structure of thin H-passivated nanowires oriented along the $\langle 110 \rangle$ direction. To this end, we have designed a robust and efficient optimization procedure based on a genetic algorithm (GA), followed by structural refinements at the density functional theory (DFT) level. We have found that in the presence of hydrogen, the silicon atoms of the nanowire can maintain their bulk-like bonding environment down to sub-nanometer wire dimensions. Furthermore, our calculations reveal that, as the number of atoms per length is increased, there emerges three distinct types of wire configurations with low formation energies (magic wires). Two of these structures have a plate-like aspect in cross section, which have not been experimentally observed so far. The third one has a hexagonal section, which is consistent with recent experiments for Si and Ge wires[117, 127]. Given their extremely small diameter (corresponding to a few tens of atoms per unit cell), the magic structures found here by the combined GA-DFT optimization procedure cannot be predicted by thermodynamic considerations based on the Wulff construction[128]. Our procedure is generally applicable for finding the structure of any ultra-thin nanowire provided that suitable models for the atomic interactions are available and that the spatial periodicity along the wire axis is known.

6.2 Genetic algorithm

The choice of GA for the present work was motivated by our previous findings that search procedures inspired by the genetic evolution can successfully be used to determine the structure of Si clusters (0-D systems)[129] and Si surfaces (2-D systems)[130, 131]. The nanowires have intermediate dimensionality (1-D), hence our expectation that the GA would also perform well in this case. The SiNWs are modeled using a supercell periodic in one dimension, with the period chosen according to the STM experiments[117]. We choose the Hansel-Vogel (HV) empirical potential to describe the atomic interactions, for this model has been shown to reproduce well the energies of hydrogenated phases of the Si(001) surface[132].

The detail setup of our GA is as follows. The geometry of the $\langle 110 \rangle$ SiNWs are restricted to have a periodicity of $3.84\text{\AA}$ along the z -axis. Initially, Si atoms are randomly generated within this slice of $3.84\text{\AA}$. This randomly generated SiNW is then passivated by hydrogen according to the number of dangling bonds on the surface. The resultant H-passivated SiNW will be optimized to an energy minimum using the HV empirical potential. A pool of 60 structures with the same number of Si atoms in a unit cell are being maintained, a larger pool will be used for SiNWs with a larger diameter. After this initial generation, the genetic pool is evolved by performing mating operations. Such operations consist of selecting two random structures (parents) from the pool, and cutting each of the two structures at a random point by a random plane parallel to the $\langle 110 \rangle$ axis of the SiNW, then pasting parts of the parent structures that lie on the opposite sides on the cutting plane to create a new structure (child). The child structure is passivated by satisfying all its dangling bonds with H atoms, then relaxed with the HV model. The child will be allowed to replace a parent structure in the genetic pool if it is more energetically favorable. The fitness function that we use to determine the energetics will be explained in the next paragraph. Our mating operation is carried out

15 times in each generation, and a typical GA run has 50000 generations.

The fitness function that we use in our GA is the formation energy of the SiNW per Si atom. It is defined as

$$E_f = (E - \mu_H n_H - \mu_{Si} n_{Si}) / n_{Si}, \quad (6.1)$$

where E is the energy of the SiNW per unit cell, μ_H and μ_{Si} are the chemical potentials of H and Si respectively, and n_H and n_{Si} are the number of H and Si in the unit cell. μ_{Si} is taken to be the energy of a Si atom in bulk diamond structure. Our GA search is carried out at a fixed number of Si atoms, μ_{Si} simply serves as an overall shift of the formation energy. On the other hand, the number of H atoms can fluctuate during the GA search and is controlled through the H chemical potential μ_H . For H chemical potentials that are too strong, the SiNW will be etched away to form silane gas. If μ_H is too negative, i.e. the cost of extracting an H atom from an H source is too high, it is not energetically favorable to passivate the surface dangling bonds of the SiNW by H. The H chemical potential is chosen such that certain hydrogenation reactions at surfaces are thermodynamically possible. For example, the passivation of Si(111) to form a mono-hydride surface ($\text{Si}(111) + \text{H} \rightarrow \text{Si}(111)\text{-H}$) can be studied by calculating the energies of clean Si(111) and mono-hydride Si(111) surfaces at the HV empirical level. The minimal H chemical potential that makes this reaction energetically favorable can then be determined. The set of reactions that we studied is shown in Fig. 6.1 along with our two chosen values of μ_H , which is -2.32 eV and -2.42 eV. By performing GA search with μ_H higher than -2.32 eV, we found that the SiNWs are being etched away due to the strong H chemical potential. For GA search with μ_H lower than -2.42 eV, the SiNW will try to reduce the number of surface dangling bonds because of the high cost of extracting H atoms from the H source. With H chemical potentials within the range of -2.32 eV and -2.42 eV, we will later show that results comparable to experimental observations can be produced.

Figure 6.1 Choice of the chemical potential μ_H used in the genetic algorithm search coupled with the HV potential. The two vertical lines are located at $\mu_H = -2.42$ eV and $\mu_H = -2.32$ eV. The left end of each horizontal bar is the lowest μ_H value at which a given hydrogenation reaction is favorable as predicted by the HV potential[132].

Since we are doing two independent searches, one for each H chemical potential, we realize that considerable effort can be saved by adopting a GA with two fitness functions. Our modified GA with more than one fitness function also consists of a genetic pool of 60 structures in total. However, instead of optimizing these 60 structures solely by one fitness function, we divide our pool into two equal segments, each contains 30 structures. The first segment is optimized by the first fitness function, and the second segment is optimized by the second fitness function. The mating operation randomly picks two structures from the whole pool, and is not restricted to picking two structures in the same segment. The two fitness functions have the same form as Eq. (6.1), but with two different H chemical potentials as discussed above. Hence, our GA not only optimizes structures with two different chemical potentials at the same time through two different segments, but also allows structural motifs to be exchanged across different segments,

and maintains structural diversity of the genetic pool consequently.

Finally, the low energy candidates are verified and refined by ab-initio calculations using VASP[56]. The ab-initio calculations are based on density functional theory(DFT)[1] under generalized gradient approximations(PW-91[58]) with ultrasoft pseudopotential. The kinetic energy cutoff is set to be 11 Ry. The SiNW is positioned at the center of a periodically repeating supercell with a vacuum space of $12\text{\AA}$ in the x-y direction separating the periodic images of the SiNW. Each SiNW structure is optimized to its energy minimum until the forces are less than $0.01\text{ eV/\AA}$. A set of 16 k-points, centered along k_z , are used to sample the Brillouin zone of the supercell. The H chemical potentials that should be used in evaluating the formation energies in our ab-initio calculations can be different from that used in the HV potential in the GA search. We found that by choosing the H chemical potentials to be -3.35 and -3.45 eV in our DFT calculations, corresponding to -2.32 and -2.42 eV respectively for the empirical potential, we can maximize the correlation of the formation energies between DFT and HV results. In Fig. 6.2, we can see that there is good agreement between the DFT and HV energetics.

6.3 Structure of H-passivated $\langle 110 \rangle$ Silicon nanowires

The most stable structures(DFT level) that we found through the above procedure are shown in Fig. 6.3 and 6.4, where the formation energies are calculated with $\mu_H = -3.35$ and -3.45 eV for DFT. In the case of odd n , the two sides of the pool found structures that are different only in the position of one peripheral Si atom. As Fig. 6.3 and 6.4 reveal, the GA-DFT optimization finds stable structures that are made of six-atom rings (viewed along the SiNW axis), with some of the rings incomplete depending on the value of n . The six-rings can arrange themselves in chains (e.g., $n = 12$, $n = 16$); for $n > 16$ the rings form fused pairs of such chains ($n = 18$; 24 ; 30), which we call double-chains. Structures similar to the double-chains shown in Fig. 6.3 and 6.4 have also

Figure 6.2 Formation energies per Si atom at the DFT level using VASP as a function of the same quantity computed with the HV empirical potential at $\mu_H = -2.42$ eV. The chemical potential $\mu_H = -3.45$ eV for the DFT calculations was used so as to maximize the correlation between the DFT and HV formation energies over more than 422 wire configurations relaxed at both theory levels. The magic structures described in the paper lie below 0.15 eV, where the agreement between the DFT and the HV calculations is best.

been considered in recent studies of quantum confinement in SiNWs[133]. The formation energy of the most stable structures for $10 \leq n \leq 30$ retrieved is plotted in Fig. 6.7(a) as a function of n . When the value of n increases, the formation energy assumes an overall decreasing trend while displaying odd-even oscillations. The relatively larger formation energy of the odd- n structures corresponds to configurations where one Si atom protrudes from the surface of the wires, thus creating a somewhat unfavorable bonding environment.

As shown in Fig. 6.3 and 6.4, the ground state for each n has a bulk-like structure

Figure 6.3 Nanowire structures (axial view) with $n = 10$ to $n = 21$ Silicon atoms per unit cell and $\mu_H = -3.35$ and -3.45 eV, found after the genetic algorithm optimization and subsequent DFT relaxations. The Si and H atoms are shown as yellow and small white circles respectively.

with no significant reconstructions. The absence of reconstruction is due to the hydrogen environment at chemical potentials that favor no less than five hydrogenation reactions (refer to Fig. 6.1). The use of smaller μ_H values can lead to understanding the interplay between reconstruction and hydrogen coverage on the SiNW facets, an investigation which we will address in subsequent studies. For smaller values of n ($n < 17$), the common motif present in lowest energy structures is the six-atom ring. When chains of complete six-atoms rings are formed, the structures become particularly stable, as it is

Figure 6.4 Nanowire structures (axial view) with $n = 22$ to $n = 30$ Silicon atoms per unit cell and $\mu_H = -3.35$ and -3.45 eV, found after the genetic algorithm optimization and subsequent DFT relaxations. The Si and H atoms are shown as small white circles respectively.

the case of $n = 12$ and $n = 16$ SiNWs, which are made of $R = 2$ and $R = 3$ complete rings, respectively. The six-atom ring chains expose two $\{111\}$ facets with monohydride terminations. Another common feature of all (complete) chain structures is the presence of two dihydrides with the SiH_2 planes oriented perpendicular to the wire axis. For $n > 17$, the most favorable structures are the double-chains described above (and illustrated in Fig. 6.3 and 6.4), whose building blocks we call double-rings. These blocks are readily identifiable in the case of $n = 18$; 24; and 30, which correspond to a number of $D = 2$; 3, and 4 full double-rings (respectively). The double-chains expose a total of four $\{111\}$ nanofacets which form parallelogram-shaped SiNW cross sections. The complete

double-chains also contain two dihydrides, identical to those capping the chain SiNWs.

We have also conducted further optimization studies for $n > 30$ using, however, only even number of atoms n . We found that starting at $n = 60$, structures with hexagonal cross section becomes stable over the double-chain SiNWs described above. Even the smallest hexagonal SiNW ($n = 28$) has a formation energy that is only slightly higher (by 5 meV/atom) than that of the double-chain with the nearest size ($n = 30$). The hexagonal wires are bounded by two $\{001\}$ and four $\{111\}$ facets, and can be described by their number of completed concentric layers L of six-atom rings. Due to the relative stability and structural closure of the chain, double-chain, and hexagonal SiNWs, we name these configurations *magic*. The shapes of prototype magic SiNWs are illustrated in Fig. 6.5, and a description of their building blocks and number of atoms is summarized in Table 6.1. The formation energies of magic SiNWs were separately plotted as a function of n in Fig. 6.7(b,c) at both levels of theory[132, 56]. The plot reflects the structural trends described above, namely the transition between chain and double-chain at $n \sim 16$ and the transition between double-chain and hexagonal SiNW starts at $n \sim 29$. It should be noted that incomplete hexagons appear frequently in the range $28 < n < 60$, therefore the latter shape transition is not as well defined as the former.

We note that even in the absence of reconstructions, the shape of the SiNWs (refer to Fig. 6.5) departs from the equilibrium crystal shape predicted by the constrained minimization of the overall surface energy (Wulff construction[128]). The reason for this departure is that the number of surface Si atoms is larger than, or comparable to, the number of bulk-like Si atoms. In fact, for chain SiNWs there are no bulk atoms, while for double-chains the number of surface Si atoms is approximately twice as large as the number of bulk atoms. For the chain and double-chain stable magic wires, the polygonal shape itself is not preserved as only two or four facets are exposed instead of the expected six. For the hexagonal wires with diameters smaller than 2 nm, the departure from the

Wulff construction[128] is more subtle. Although the shape is same type of polygon, the relative extent of the $\{100\}$ and $\{111\}$ nanofacets is not that predicted by the surface energies since these facets contain only a very small number of their corresponding unit cells, and therefore the interactions of facet edges are significant.

Figure 6.5 Magic structures(axial and perspective view) found as formation-energy minima of nanowires with up to $n=30$ Si atoms per cell. The chain (a) and double-chain (b), are characterized by the number of rings R and double-rings D , respectively (also refer to Table 6.1). The configurations with hexagonal cross-section have a number L of full concentric layers ($L = 2$ in panel (c) above) of six-atom rings, and are consistent with recent observations of 3nm-diameter SiNWs[117].

6.4 Comparison with experiments

To our knowledge, chain and double-chain wires have not been observed so far for ultrathin SiNWs, perhaps because the wire diameters achieved in laboratory are still somewhat thicker than it is favorable for plate-like structures to form[117]. Recent experiments were successful in preparing and characterizing $\langle 110 \rangle$ SiNWs with hexagonal

Table 6.1 Building blocks and magic numbers(n) of Si atoms corresponding to the different types of low-energy SiNWs found in the global optimization. The last two columns show the number of mono-hydride and di-hydride in each case.

structure	building blocks	n	mono-H	di-H
chain	rings, R	$4(R + 1)$	$2(R+1)$	2
double-chain	double-rings, D	$6(D + 1)$	$2(D+2)$	2
hexagon	layers, L	$2L(3L + 1)$	$4L$	$2L$

section have diameters between 1.3 nm and 7 nm [117]. The thinnest hexagonal wire in our work ($n = 28$, corresponding to $L = 2$ in Table 6.1) has a diameter of approximately 1.2 nm, as estimated by the distance between its $\{001\}$ facets. The first hexagonal wire ($L = 3$) that we find to be more stable than any double-chain magic wire is about 1.8 nm in diameter, i.e. already in the range of the experimentally reported hexagonal SiNWs [117]. Pursuing further the comparison between the hexagonal wires found here and those in Ref. [117], we have simulated STM images for the facets of the $L = 5$ hexagonal wire. The simulated images are shown in Fig. 6.6 (a) for a $\{111\}$ wire-facet covered with monohydride, and for a $\{001\}$ facet covered with di-hydride. Our calculations are in agreement with the STM experiments, which also showed the exclusive presence of di-hydride species on the $\{001\}$ facets of $\langle 110 \rangle$ SiNWs. Furthermore, the striking similarity (refer to Fig. 6.6) between the simulated STM image and the experimental one brings strong support to the predictive power of the theoretical methodology used here to search for structures of H-passivated SiNWs.

6.5 Conclusion

In conclusion, we described a combined GA-DFT procedure to search for the structure of $\langle 110 \rangle$ passivated SiNWs, and presented our results for $\langle 110 \rangle$ nanowires with up to 60 atoms per unit cell. Subject to the availability of reasonable empirical potentials, this

Figure 6.6 (a) Simulated empty-state STM images(bias of +2.0V) of the $\{001\}$ and $\{111\}$ facets of an $L = 5$ hexagonal nanowire. (b) STM image of a $\{001\}$ facet from the experiments of Ma *et al.* [117], which was taken at the same bias voltage.

GA-DFT procedure can be applied for finding the structure of any type of nanowire that exhibits atomic-scale periodicity along its axis. For H-passivated $\langle 110 \rangle$ silicon wires, our calculations revealed three types of magic structures (shown in Fig. 6.5), chain, double-chain and hexagonal SiNWs. Our results for hexagonal wires of 1.8 nm diameter are consistent with recent experiments[117]. We believe that it is conceivable that the chain and double-chain structures proposed here can be observed experimentally upon pursuing the preparation of SiNWs thinner than 1.3 nm.

Figure 6.7 (a) DFT formation energies per Si atom for two values of the H chemical potential plotted as a function of n . Structures with even number of Si atoms n are local minima for both the empirical and ab-initio levels. (b, c) Formation energies per Si atom computed for specific structures of the H-passivated $\langle 110 \rangle$ nanowires: chain (dotted), double-chain (dashed), and hexagonal (solid line), computed at the level of HV potential with $\mu_H = -2.42$ eV (b), and of DFT calculations with $\mu_H = -3.45$ eV (c).

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