PHYSICAL REVIEW B **72**, 045405 (2005)

A first-principles study of Group IV dimer chains on Si(100)

Tzu-Liang Chan,[1] C. Z. Wang,[1] Zhong-Yi Lu,[1,2] and K. M. Ho[1]
[1]*Ames Laboratory-U.S. DOE. and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[2]*Institute of Theoretical Physics, Chinese Academy of Sciences, P.O. Box 2735, Beijing 100080, China*

(Received 16 October 2004; published 5 July 2005)

First-principles calculations of Pb and Sn dimer chains on Si(100) are performed up to 0.5 ML coverage, including the possibility of mixed PbSi and SnSi dimer chains. Simulated STM images for pure Pb and Sn dimer chains are found to have a better agreement with experimental observations. In order to understand whether the STM images are influenced by the dynamics of the dimer chains, we have studied the rocking barriers of dimer chains on Si(100). The rocking frequencies of Pb dimer chains are found to be small, therefore the dynamics of the Pb dimer chain will have little effects on the STM images. However, a dynamical effect may have to be taken into account for Sn dimer chains due to their higher rocking frequency. We have also studied the tendency of intermixing of Ge, Pb, and Sn with Si on a Si(100) surface. Our analysis shows that the formation of mixed dimers depends on the source of Si atoms available for Pb and Sn to carry out the intermixing. Mixed dimer chains are energetically more favorable than the pure dimer chains only when Si atoms are codeposited with Pb or Sn, or the dimer chains are formed near step edges of the Si(100) substrate. A mechanism similar to Ge intermixing with Si on Si(100) is not favored by Pb and Sn, and there is a lack of a favorable channel for Pb and Sn to intermix with Si to form mixed dimers when Si is not deposited epitaxially in experiments, which can hinder the formation of PbSi and SnSi dimer chains.

DOI: 10.1103/PhysRevB.72.045405 PACS number(s): 68.35.Bs, 73.20.Hb, 71.15.Mb

I. Introduction

Group IV elements on Si(100) have been intensively studied because of their importance in both technological applications and a fundamental understanding of the 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.[1,2] Si *ad* dimers are located on the top of the substrate dimer row and rotate between two orthogonal orientations.[3,4] At around 400 K, Si dimer chains perpendicular to the substrate dimer rows with the individual dimers located in the trough are observed.[5] One-dimensional dense dimer chains at epitaxial positions grow into long chains perpendicular to the underlying Si dimer rows at around 500 K.[6,7] These experimental observations aroused a lot of theoretical studies on the dynamics and nucleation of Si *ad* dimers on Si(100).[8,9] 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,[10] the "rocking barrier" to flip between its two degenerate buckling states is small.[11] 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 the intermixing of Ge with Si to form a mixed GeSi dimer, and the observed buckling flips are the results from 180 deg rotational motion of the mixed GeSi *ad* dimers.[11] Intermixing between Ge and Si on the surface also leads to interesting diffusion kinetics which has also been studied experimentally and theoretically.[12,13] Recently, Pb/Si(100) has received considerable attention. It has been shown by STM experiments[14–17] that small amount of Pb($\leqslant$0.5 ML) 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[18] 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.[19] For Sn on Si(100), similar behavior as that of Pb/Si(100) has also been observed by STM at low coverage.[20] 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.[21,22] However, our recent study[23] of Pb on Si(100) showed that mixed PbSi dimer chains up to a coverage of 0.125 ML are energetically more favorable than pure Pb dimer chains by 0.19 eV per Pb atom. In this paper, we will show that the mixed dimer chain is still energetically favorable, even at a higher 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 we 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 a 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 paper is divided into eight sections. The calculation method is briefly discussed in Sec. II. In Sec. III, 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 Sec. IV. A comparison with STM experiments will be made in Sec. V by simulating STM images for different models that we have discussed in the previous sections. In Sec. VI we discuss our calculation of the "rocking" barrier of a pure Pb and Sn dimer chain on Si(100) to investigate the dynamical effects in STM images. Finally, in Sec. VII we will resolve the apparent discrepancy between experimental results and our theoretical predictions by comparing the intermixing energetics between Ge/Sn/Pb and Si.

II. Calculation Method

Our first-principles calculations are based on DFT under local density approximations (LDA).[24] Pseudopotential and plane wave bases are being used. The Ceperley-Alder functional[25] parametrized by Perdew and Zunger[26] 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 that consists of 8 layers of Si passivated by H at the bottom and a vacuum space of at least 12 Å. The top surface of Si(100) is arranged to have a $c(4\times2)$ reconstruction. The bottom layer of Si atoms is 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.[27]

III. Pb on Si(100)

The energies of Pb on Si(100) at low Pb coverage ($\leqslant 0.25$ ML) have been presented in our previous short paper.[23] The main results are summarized below.

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 configurations A, B, C, and D, and are illustrated in Fig. 1. The energies of these four configurations obtained from our calculations are listed in Table I. The lowest energy configuration is the Pb dimer B, and it is buckled with a buckling angle of 11.26 deg. 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 I. For all four configurations, the mixed dimers are buckled with the Pb adatoms higher than the Si adatoms.

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

$$\Delta E_{dimer} = E_{total} - E_{sub} - N_{\mathrm{Pb}}\mu_{\mathrm{Pb}} - N_{\mathrm{Si}}\mu_{\mathrm{Si}}, \qquad (1)$$

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 $c(4\times2)$ surface reconstruction, $\mu_{\mathrm{Pb}}(\mu_{\mathrm{Si}})$ is the chemical potential of Pb(Si) atoms that is taken as the energy of bulk Pb(Si) per atom in a fcc(diamond) crystal structure, and $N_{\mathrm{Pb}}(N_{\mathrm{Si}})$ 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. Equation (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 the 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.

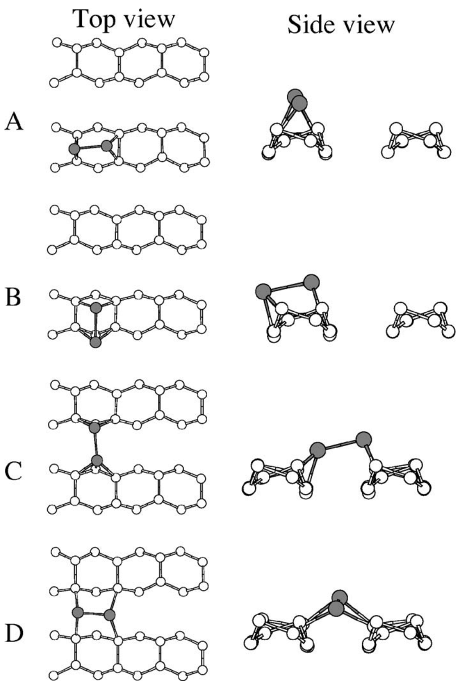

FIG. 1. Different arrangements of the Pb dimer on a Si(100) 4 × 4 unit cell. Only the first two layers of the Si substrate are shown. The Si atoms in the substrate are white. The Pb adatoms are colored gray.

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. 2. The energies of these four configurations obtained from our calculations are listed in Table I. 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 deg. These results are similar to the previous calculation results,[18] which are also included in Table I for comparison. We then consider another structural model of the dimer chain where Pb and Si intermix to form a PbSi dimer chain. Again, four different configurations are considered, which are similar to those in Fig. 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

TABLE I. 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 the Si(100) surface in four different configurations: A, B, C, and D (see figures). The data in parentheses are taken from Ref. 18. 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 deg	11.26 deg	13.03 deg	13.71 deg
	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 deg	17.47 deg	17.56 deg	21.63 deg
	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 deg	11.97 deg	14.71 deg (12.45 deg)	11.88 deg (11.42 deg)
	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 deg	20.62 deg	20.63 deg	8.96/21.61 deg
	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 deg	7.46 deg	13.46 deg	14.28 deg
	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 deg	18.70 deg	16.67 deg	20.05 deg
	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 deg	8.53 deg	15.64 deg	12.53 deg
	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 deg	19.59 deg	21.22 deg	15.88 deg
	d (Å)	2.69	2.83	2.77	2.64

in Table I. 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 the C′ configuration.

Using Eq. (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. An analysis to understand why isolated mixed PbSi dimers are not stable while the mixed PbSi dimer chain is favorable can be found in our previous study.[23] The conclusion there is that 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 0.125 ML, 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 paper, we have also studied the structures of Pb on Si(100) at a higher Pb coverage of 0.5 ML. Experimentally, it is observed that close packed Pb dimer chains are formed at 0.5 ML of Pb coverage.[16,18,28,29] The close packed dimer chains run perpendicularly to the underlying Si dimer rows, and the separation between the dimer chains is 3.84 Å, 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 antiphase. It was observed experimentally that (2×2) and (4×2) can coexist.[28] 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. 3. The Pb dimer bond length for the (2×2) structure is 3.04 Å with a buckling angle of 14.02 deg, while for the (4×2) structure, the Pb dimer bond length is 3.03 Å with a buckling angle of 14.17 deg. For both cases,

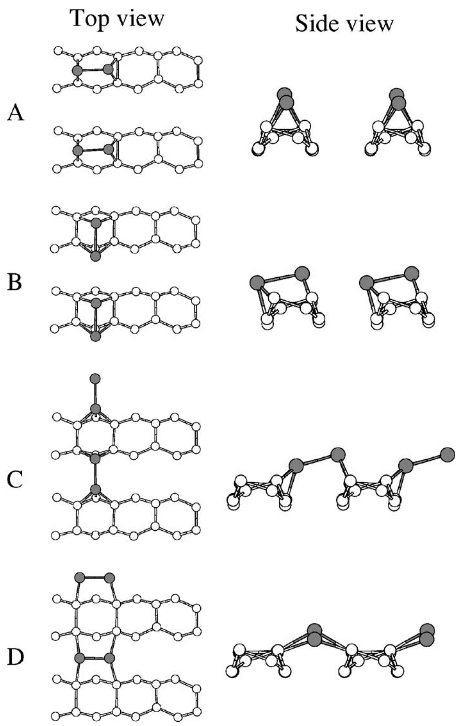

FIG. 2. Different arrangements of Pb dimer chains on a Si(100) 4×4 unit cell. The Pb adatoms are in gray.

the Pb dimer bond length and the buckling angle are very similar to that of the Pb dimer chain C at a 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.

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 that are similar to Fig. 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 2.84 Å and the buckling angle is 19.53 deg. In the (4×2) case, the Pb-Si *ad*-dimer bond length is also 2.84 Å but the buckling angle is 19.95 deg. 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 that 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. (1). The formation energy is −0.53 eV/Pb atom and −0.72 eV/Pb atom for a closed packed pure Pb dimer chain and mixed PbSi dimer chain, respectively. Therefore, up to 0.25 ML, mixed PbSi dimer chains are still energetically more favorable than pure Pb dimer chains.

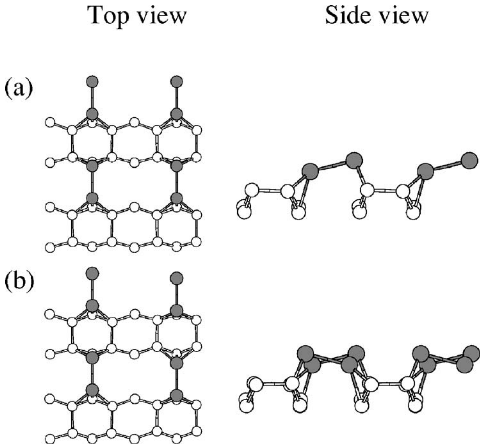

FIG. 3. Close packed Pb dimer chains on a Si(100) 4×4 unit cell with (a) (2×2) and (b) (4×2) symmetry. Each Pb dimer chain is in the configuration C, as shown in Fig. 2, but the chains are packed such that they are separated by one Si(100) surface lattice constant.

IV. Sn on Si(100)

In the similar way as the 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. 1, but with the Pb dimers replaced by Sn dimers. As shown in Table I, the lowest energy structure is configuration B, with a Sn dimer bond length of 2.99 Å, and a buckling angle of 7.46 deg. Its formation energy by using Eq. (1) is −0.26 eV per Sn atom. For a mixed SnSi dimer, the lowest energy configuration is C with a Sn dimer bond length of 2.75 Å. The mixed dimer structure is buckled with a Sn atom higher and a buckling angle of 16.67 deg. 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 a Sn dimer chain on the 4×4 unit cell in four configurations, A, B, C, and D as in Fig. 2, but with the Pb dimers replaced by Sn dimers. As shown in Table I, the lowest energy structure is configuration C, with a Sn dimer bond length of 2.94 Å, and a buckling angle of 15.64 deg. Calculations are also done for a mixed SnSi dimer chain in four different configurations similar to Fig. 2, but the Pb dimers are replaced by SnSi dimers. Again, configuration C has the lowest energy as shown in Table I. The Sn-Si dimer bond length is 2.77 Å. The ground state structure has Sn adatoms higher than Si adatoms with a buckling angle of 21.22 deg. 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. (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

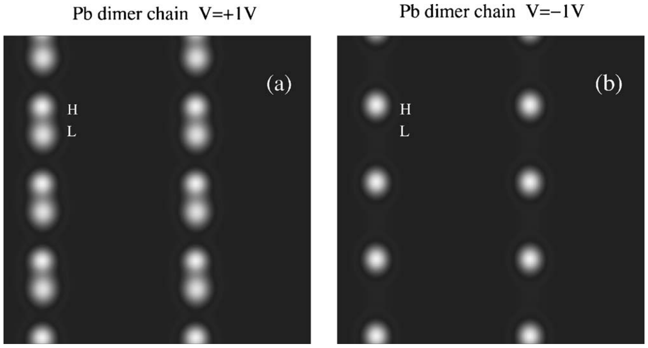

FIG. 4. Simulated STM images of Pb dimer chain C with a surface bias voltage of (a) 1.0 V and (b) −1.0 V. H denotes the higher Pb adatom position and L denotes the lower Pb adatom position.

as the difference between the Pb dimer chain and the mixed PbSi dimer chain.

V. 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 perpendicular 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 2 Å 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.

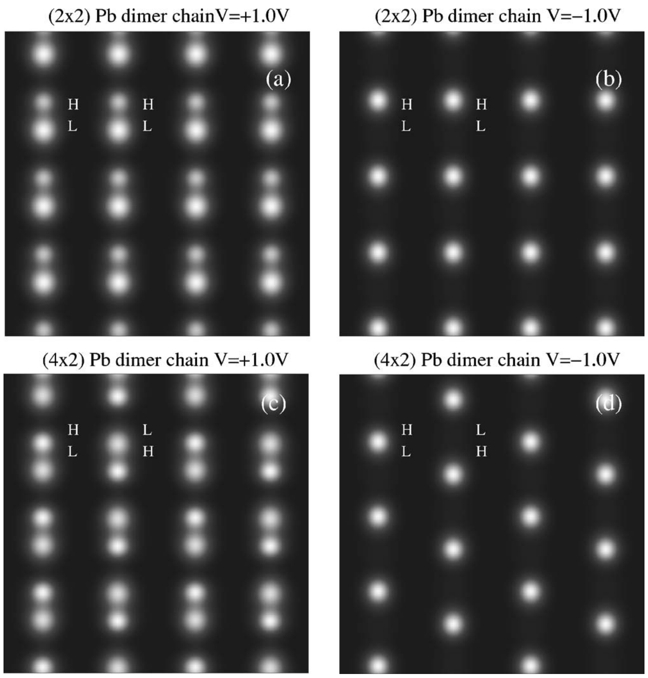

FIG. 5. Simulated STM images of a (2×2) close packed Pb dimer chain with a surface bias voltage of (a) 1.0 V and (b) −1.0 V, and a (4×2) close packed Pb dimer chain with a surface bias voltage of (c) 1.0 V and (d) −1.0 V. H denotes the higher Pb adatom position and L denotes the lower Pb adatom position.

The simulated STM images for isolated Pb dimer chain C and the close packed Pb dimer chains on Si(100) are shown in Figs. 4 and 5, respectively. For both cases, bright spots corresponding to the higher Pb adatom positions are observed in a filled states image. While both atoms of the Pb dimer give brights 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 0.5 ML 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 Figs. 6 and 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, the authors of Ref. 16 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 corresponds well with the experimental observations. On the other hand, our calculation of Fig. 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.

For isolated Sn dimer chains and mixed SnSi dimer chains on Si(100), our STM simulation is shown in Fig. 8. For a Sn dimer chain in configuration C (Figs. 8(a) and 8(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

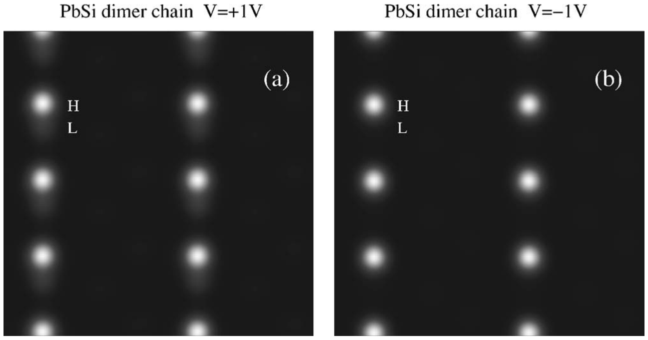

FIG. 6. Simulated STM images of mixed PbSi dimer chain C with a surface bias voltage of (a) 1.0 V and (b) −1.0 V. H denotes the Pb adatom position and L denotes the Si adatom position.

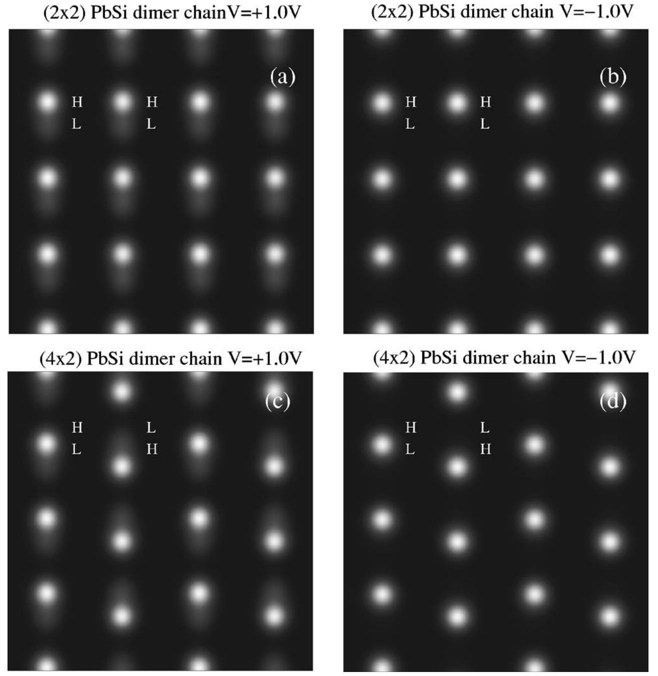

FIG. 7. Simulated STM images of a (2×2) close packed PbSi dimer chain with a surface bias voltage of (a) 1.0 V and (b) −1.0 V, and a (4×2) close packed PbSi dimer chain with a surface bias voltage of (c) 1.0 V and (d) −1.0 V. H denotes the Pb adatom position and L denotes the Si adatom position.

for the mixed SnSi dimer chain C (Fig. 8(c) and 8(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. Reference 20 observed that for Sn on Si(100) the circular spots in the filled states image became elongated in the empty states image, and high-resolution image of the elongated spots revealed buckled dimers. Therefore, the simulated STM images for a pure Sn dimer chain have a better agreement with experimental STM observations.

VI. "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 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.

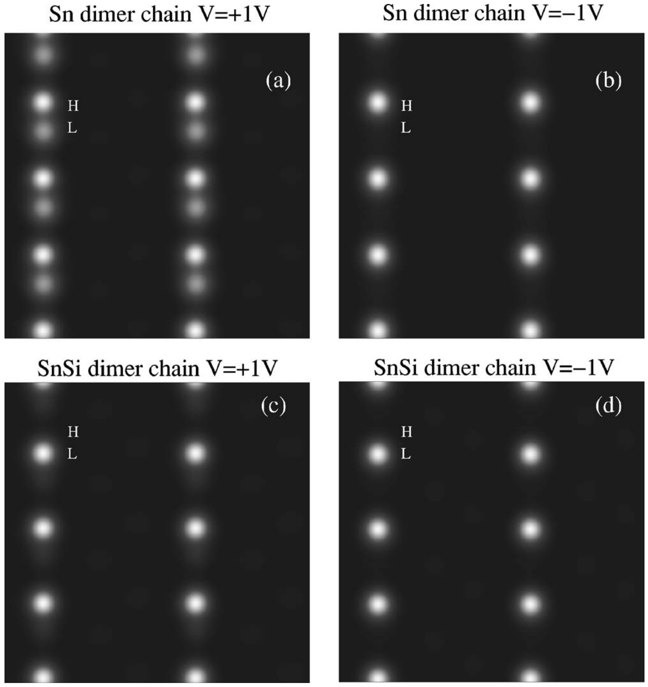

FIG. 8. Simulated STM images of a Sn dimer chain with a surface bias voltage of (a) 1.0 V and (b) −1.0 V, and a mixed SnSi dimer chain with a surface bias voltage of (c) 1.0 V and (d) −1.0 V. H denotes the higher Sn adatom position. L denotes the lower Sn adatom position in (a) and (b), and the Si adatom position in (c) and (d).

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 nonbuckled dimer chain with all the adatoms at 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 is 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 a 4×4 unit cell is repeated using GGA-PW91[30] with the VASP[31] 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 is exposed, the 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 flips 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 are 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 a 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 correlations between each other. The ground state of a dimer chain of length L, which we refer to 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 $E_1/2$, 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 $E_{B1}+(E'_{B1}-E_{B1})/2$, 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 are 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[32] 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 in the state S_2 and its energy approximated by $E_1/2$ 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 until the other end of the dimer chain, with the energy of S_i equal to $E_1/2$ higher than that of S_0 and the energy barrier from S_{i-1} to S_i equal to E'_{B1} for $2\leqslant i\leqslant L-1$. 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 $f_L=f_{L-1,L}(f_{L-1}/(f_{L-1}+f_{L-1,L}))$, 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 the fact that a dimer chain can both flip a dimer in its dimer chain or have one of its flipped dimers reverting back to the original buckling. The rocking frequency $f_{L-1,L}$ is given by the Arrhenius relation[33] $f_{L-1,L}=p(L-1)f_0\exp(-\Delta E/k_BT)$, 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 $c(4\times2)$ reconstruction can be observed at 144 K,[34] 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 $c(4\times2)$ reconstruction. This barrier is found to be 0.25 eV. If the typical time resolution of STM is taken to be 1000 s^{-1},[35] we can infer from the Arrhenius relation that f_0 is 5.6×10^{11} s^{-1} for Si(100). Knowing f_0, the result of our simulation under this framework at room temperature is illustrated in Fig. 9 for L=4 to 10, which are typical lengths of dimer chains observed in experiments. 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 orders 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 a 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. 20, 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.

VII. Tendency of intermixing

Despite the fact that our calculations in Secs. III and IV 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 Secs. V and VI. 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

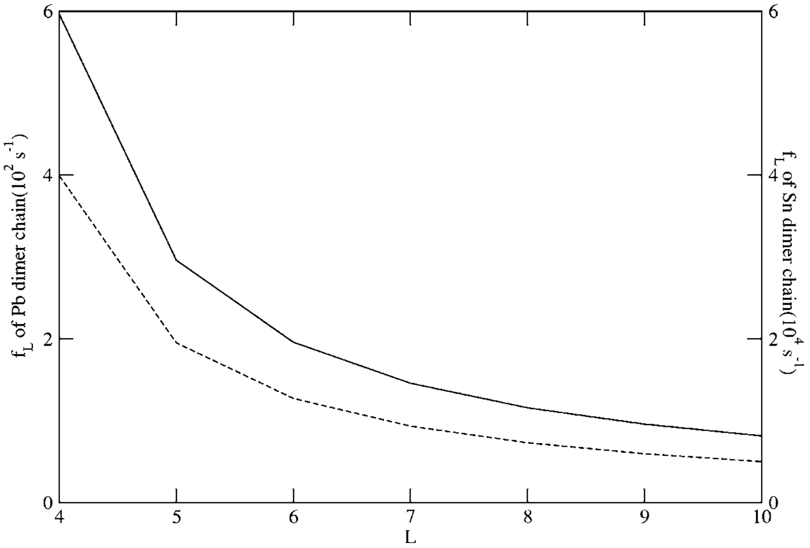

FIG. 9. Simulated rocking frequency of the Pb dimer chain (solid line) and Sn dimer chain (dashed line) versus the length of the dimer chain.

to form mixed dimers, since the individual dimer is the building block for the whole dimer chain. We summarized in Table II the formation energies of isolated dimers and dimer chains on Si(100) using Eq. (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 II, we can find that it is not energetically favorable to form mixed dimers when compared with pure dimers using Eq. (1) for all cases, including Ge, which contradicts with experimental observation. One should note that the formation energy calculated using Eq. (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.

TABLE II. The formation energies of dimers and dimer chains on Si(100) calculated using Eq. (1). The letter in brackets refer to the atomic configuration illustrated in Fig. 1 and Fig. 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

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 associated energy release can be calculated by $\Delta E_{mix} = E_{mixed} - E_{pure}/2 - E_{\text{Si-Si}}/2$, 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 $E_{\text{Si-Si}}$ being the total energy of a pure Si *ad* dimer on the 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 the 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 our previous publication.[12] The formation energy of such reaction can be calculated as follows:

$$\Delta E' = E_{mixed} + E'_{sub} - E_{sub} - E_{pure}, \qquad (2)$$

where E_{sub} is the total energy of a Si(100) 4×4 substrate with $c(4\times2)$ surface reconstruction, and E'_{sub} is the same as E_{sub}, but the surface has one of its buckled-up surface atoms replaced by Ge, Sn, or Pb. $\Delta E'$ measures the energy released when one of the atoms 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. (2) into $\Delta E' = \Delta E_{mix} + \Delta E_{substitute}$, where ΔE_{mix} is the same as above and $\Delta E_{substitute} = E'_{sub} + E_{\mathrm{SiSi}}/2 - E_{pure}/2 - E_{sub}$. 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 the 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 the 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 structure 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 the Si(100) surface, or by annealing the sample, mixed PbSi and SnSi dimer chains may be able to form on Si(100).

VIII. Conclusion

As a conclusion, we have carried out first-principles calculations to study Pb and Sn dimer chains on Si(100) up to 0.5 ML 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, the buckling of the Pb dimer chain can be observed in STM experiments. While for Sn dimer chains, it might be necessary to take a 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.

ACKNOWLEDGMENTS

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences including a grant of computer time at the National Energy Research Supercomputing Center (NERSC) in Berkeley.

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