

# Molecular dynamics simulations of the metallic behavior of the Si(001) surface at high temperatures

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We perform molecular dynamics simulations to study the temperature-induced metal-semiconductor transition and the solid-liquid phase transition in the Si(001) surface. Our calculations indicate that driven by temperature, the Si dimers in the surface flip-flop, accompanied with the creation of some longer and shorter Si dimers. The concentration of both longer and shorter dimers increases with rising temperature. Once the concentration is larger than about 20% (at  $\sim 800$  K), the metal-semiconductor transition in the Si(001) surface takes place. In addition, we find that when the temperature reaches about 1200 K, the topmost layer in the surface transforms to liquid; such a liquid state is responsible for the metallic behavior of the surface at  $T > 1200$  K.

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## I. INTRODUCTION

It has been well established that the Si(001) surface with reconstruction of  $(2 \times 1)$ ,  $c(4 \times 2)$ , or  $p(2 \times 2)$  characterizes a semiconducting feature below room temperature, while it becomes metallic when temperature is above a critical value  $T_{sm}$ , at which the metal-semiconductor transition in the Si(001) surface occurs. Such  $T_{sm}$  was reported by several groups in experiment. Typically,  $T_{sm} \sim 600$  K (Ref. 1) was estimated in terms of the photoemission spectroscopy and 900 K was derived from high-resolution electron-energy-loss spectra.<sup>2</sup> On the other hand, experiment revealed that when the system was further heated to a higher temperature  $T_{im}$ , which was reported to be about 1400 K,<sup>3</sup> the Si(001) surface underwent an incomplete melting. Note that the melted silicon surface characterizes a liquid state, which is naturally responsible for the metallic feature of the Si(001) surface at  $T > T_{im}$ . However, for  $T_{sm} < T < T_{im}$ , the mechanism of the metallic behavior in the Si(001) surface is not so explicit. Gavioli *et al.*<sup>4</sup> suggested that such surface metallization was originated from the instantaneous symmetriclike dimer configuration at the surface. Hwang *et al.*<sup>1</sup> argued that diffusion of Si adatoms at the surface was the reason for the temperature-induced metallization. Later on, Fukaya and Shigeta<sup>2</sup> attributed the Si(001) surface metallization to the symmetric dimer structure.

On the theoretical side, Cho and Kim<sup>5</sup> proposed a novel model, in which the symmetric dimers being alternately displaced up and down along the dimer rows in a Si(001) surface formed a  $p(2 \times 2)$  reconstruction. Their calculated total energy showed that this reconstructed surface was stable energetically, and the band structure demonstrated its metallic feature. The authors<sup>5</sup> speculated that the symmetric dimers move up and down, keeping parallel to the surface at a finite temperature. This was used to explain the metallization of the Si(001) surface at 20 K as well as at high temperatures ( $< T_{im}$ ).<sup>5,6</sup> It is worth noting that Cho and Kim's argument was made in terms of the total energy calculations at  $T = 0$  K. In fact, at a finite temperature ( $> 120$  K), each atom vibrates around its initial position randomly, resulting in the

distortion of the symmetric dimers to some extent. In other words, this symmetric dimer structure in the Si(001) surface cannot keep well at high temperatures. Therefore, it is difficult for this model to explain the metallic feature of the Si(001) surface at high temperatures. In order to theoretically reveal the mechanisms of the temperature-induced metal-semiconductor transition and the solid-liquid phase transition in a convincing way, it is necessary to study the structures and electronic structures of the Si(001) surface at finite temperatures.

In this paper, we perform tight-binding molecular dynamics (TBMD) to simulate the Si(001) surface at temperatures ranging from 300 to 1400 K. We find that at  $T > 1200$  K, the metallization of the Si(001) surface is indeed resulted from the liquidlike structure at the top atomic layers, while at  $800 \text{ K} \leq T < 1200 \text{ K}$ , the metallization is mainly stemmed from the shorter and longer Si dimers generated from temperature effect in the surface. More importantly, the concentration of the shorter and longer Si dimers in the surface plays a critical role in the metal-semiconductor transition of the surface.

## II. COMPUTATIONAL DETAILS

A slab consisting of 12 atomic layers is selected to mimic the surface, where there are 32 silicon atoms in each layer.<sup>7</sup> Periodic conditions are imposed in the directions parallel to the surface. Since the size of the slab is large enough, one  $k$ -sampling point in the Brillouin zone is chosen in our simulations. In this work, a tight-binding potential model for silicon,<sup>8</sup> which was developed through correcting the bonding environment around each chemical bond, is employed. This model not only deals with a large system but also provides the electronic property of the system at finite temperatures. The benchmark calculation demonstrated that this tight-binding potential described many properties of the bulk silicon and various reconstructions of Si(001) and Si(111) surfaces very well. Previously, it has been used to study a grain boundary in silicon,<sup>9</sup> the electronic properties of defected Si(111)( $7 \times 7$ ) surface,<sup>10,11</sup> and silicon clusters.<sup>12</sup>

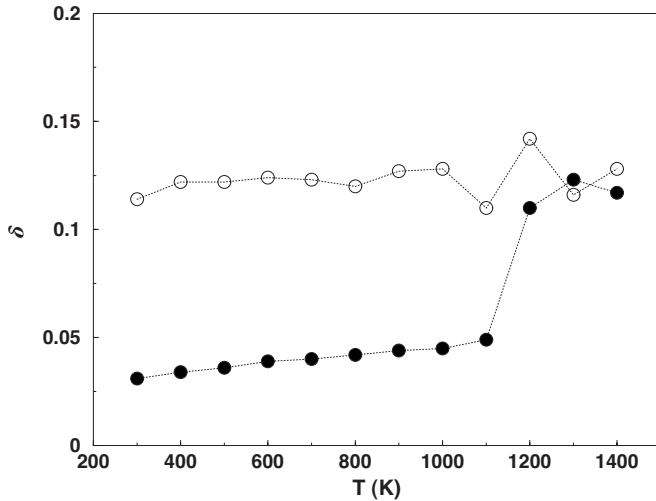


FIG. 1. The root mean square of the bond length fluctuation varying with the kinetic temperature for two top layers (solid circles) and three top layers (open circles) in the Si(001) surface.

Therefore, this tight-binding potential is reliable to handle the large and complex systems we concern in this work. In order to simulate the concerned system at finite temperatures, the tight-binding potential is combined with the molecular dynamics, where the equation of motion is integrated using the Gear algorithm.<sup>13</sup> The time interval of each TBMD step is  $8 \times 10^{-4}$  ps.

### III. RESULTS AND DISCUSSION

We start our investigation with the full relaxation of the structural model of symmetric dimers Si(001) $p(2 \times 2)$ .<sup>5</sup> Our calculated surface energy of about 1.14 eV/( $1 \times 1$ ), being comparable to those of the buckled  $p(2 \times 2)$  and  $c(4 \times 4)$  reconstructed surfaces,<sup>8</sup> indicates that this reconstructed surface is quite stable at  $T=0$  K. Furthermore, the calculated local electronic density of states of this reconstruction shows that this reconstructed surface characterizes a metallic feature, which is predominantly attributed to the symmetric dimers in the surface. To go further, we simulate the symmetric dimer  $p(2 \times 2)$  reconstructed surface<sup>5</sup> at finite temperatures ranging from 300 to 1400 K, with a step of 100 K. At each temperature, we perform MD runs of 20 000 steps to equilibrate the system, followed by MD runs of 10 000 steps within the microcanonical ensemble. During the microcanonical ensemble MD runs, the coordinates of the atoms in the slab are recorded.

According to the recorded data, we calculate the root mean square of bond length fluctuation ( $\delta$ ) (Ref. 14) for top atomic layers in the Si(001) surface at temperatures ranging from 300 to 1400 K, which is shown in Fig. 1. Clearly, the value of  $\delta$  corresponding to two top layers increases with rising temperature. At 1200 K or so,  $\delta$  increases abruptly. This just indicates the occurrence of the first order phase transition (solid-liquid transition) in the atomic layers. Thus, the melting point of the dimer layer in the Si(001) surface is estimated to be about 1200 K, lower by  $\sim 400$  K than the melting point of bulk silicon. On the other hand, the calcu-

lated  $\delta$  corresponding to top three layers at each considered temperature (seen in Fig. 1) exhibits that the variation of the  $\delta$  value at  $\sim 1200$  K is quite small. Therefore, the melting of the surface occurs mainly in the two top layers, which is the so-called incomplete melting in the surface. Such an incomplete melting feature is strongly dependent on the heating temperature and the length of the heating time. If the kinetic temperature is above 1200 K and the heating time is long enough, the semi-infinite system will be molten completely.

Further, we employ the pair distribution function  $g(r)$  to make sure the solid-liquid transition predicted by the calculated  $\delta$ . Our calculated pair distribution functions  $g(r)$  of the two top layers at considered temperatures show that the structure of the two top layers characterizes a liquidlike feature above the incomplete melting temperature and an amorphouslike feature below the incomplete melting temperature. These evidences indicate that the two top layers undergo a solid-liquid transition at about 1200 K.

Next, we turn to the electric properties of the surface at finite temperatures. It is noted that the measured data in a STM experiment were obtained within about  $10^{-2}$  s,<sup>5</sup> during which the information of a lot of instantaneous configurations was included. Because of this, we calculate the averaged density of states (DOS) of selected 19 instantaneous configurations within the time interval of 8 ps at each temperature to explain the experimental observations as follows:

$$\bar{\rho} = \frac{1}{M} \sum_i \rho_i. \quad (1)$$

Here,  $M$  is the number of the selected instantaneous configurations and  $\rho_i$  is the density of states of the  $i$ th instantaneous configuration.

Examination of the averaged local density of states (LDOS) at Fermi level shows that the Si(001) surface is semiconducting at  $T=300-700$  K [Figs. 2(a) and 2(b)], while it becomes metallic at  $T \geq 800$  K [Figs. 2(c) and 2(d)]. This agrees well with the observations in experiments.<sup>1,2</sup> Noticeably, the metallic behavior of the system at  $T=800$  K is essentially originated from the two top layers [they contribute to the nonzero DOS at the Fermi level, Fig. 2(c)]. As the temperature increases, more atomic layers at the surface contribute to the states at the Fermi level, which can be observed in the representative case at 1200 K [Fig. 2(d)]. So, we may conclude that higher temperature drives more atomic layers in the surface to be metallic.

Interestingly, combining the calculated LDOS with the calculated root mean square of the bond length fluctuation as mentioned above, we can immediately find that the metallic behavior at higher temperatures (above the incomplete melting temperature) is indeed due to the presence of liquidlike silicon at the two top layers, just supporting the mechanism proposed in the previous work.<sup>3</sup>

However, the mechanism of the metallization of the surface below the incomplete temperature cannot be straightforwardly illustrated from the amorphouslike silicon structure in the surface. We believe that the metallic behavior of the surface in this temperature range does tightly couple with some structural feature of the surface. Therefore, we carefully ex-

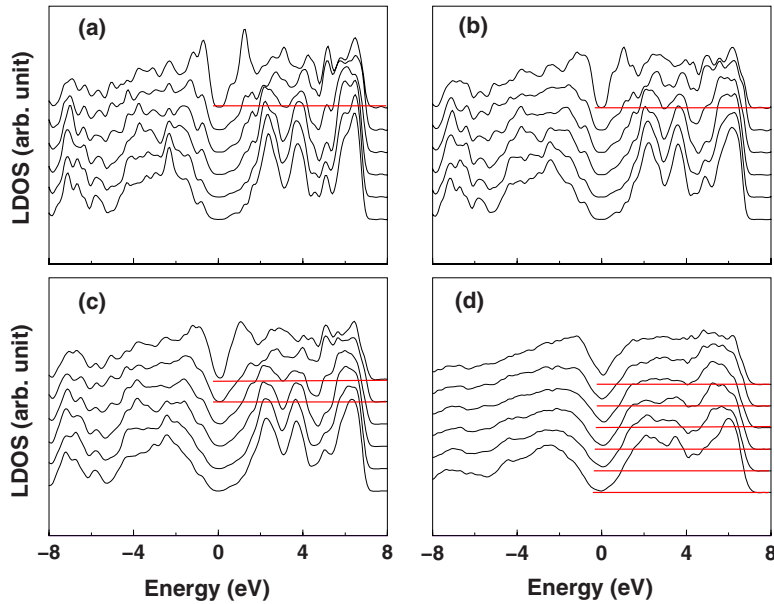


FIG. 2. (Color online) The calculated LDOS of the different atomic layers in the Si(001) surface at (a)  $T=300$  K, (b)  $T=700$  K, (c)  $T=800$  K, and (d)  $T=1200$  K. The curves from top to bottom correspond to the atomic layers from the first to the sixth layer of the surface. The Fermi levels are at 0.0 eV. The horizontal lines within each figure are used to guide the eyes.

amine the structure of the surface at concerned temperature and find that the Si dimers which are associated with the nonzero LDOS at the Fermi level are neither broken nor parallel to the surface but buckled. Furthermore, we find that the correlation of the buckled angles of the dimers with the metallic feature of the surface is very weak.

For the buckled dimers associated with the nonzero LDOS at the Fermi level ( $800 \text{ K} \leq T \leq 1200 \text{ K}$ ), we observe that the bond lengths of the dimers are either longer than  $2.5 \text{ \AA}$  or shorter than  $2.25 \text{ \AA}$ , significantly deviating from the equilibrium bond length ( $2.33 \text{ \AA}$ ) of the dimers in the Si(001) ( $2 \times 1$ ) surface. We speculate that the dimers with a large deviation of bond length in the surface may be closely relevant to the metallic behavior. To confirm this speculation, we check the bond lengths of some Si dimers in several instantaneous configurations at 300 and 700 K at which the surfaces are semiconducting. Surprisingly, we also observe the longer and shorter Si dimers at 300 and 700 K. These observations indicate that these special dimers may play a critical but not a unique role in the metal-semiconductor transition. We then move our eyes to the concentration of these special dimers. Interestingly, it is found that the total number of longer and shorter Si dimers in the cases above 800 K is larger than that below 800 K. Moreover, the concentration increases with rising temperature. These observations imply that the electric property, either the metallic or the semiconducting behavior, of the surface is critically dependent on the concentration of both longer and shorter dimers in the surface. To estimate the threshold of the concentration corresponding to the metal-semiconductor transition, we count the number of Si dimers with longer (bond length  $\geq 2.5 \text{ \AA}$ ) and shorter (bond length  $\leq 2.25 \text{ \AA}$ ) bond lengths from all configurations at each temperature in the time interval of 8 ps, averaged by the number of the configurations at this temperature. For convenience, the averaged numbers of longer and shorter dimers are named as NL and NS, respectively. Our calculation reveals that NL nearly does not vary with the temperature (below 1200 K) [seen in Fig.

3(a)], while NS significantly changes with the temperature [Fig. 3(b)]. With the definition of the concentration,  $C = (NL+NS)/N$  ( $N$  is the number of all Si dimers in the surface at a temperature), of these dimers in the surface, we find that the evolution of the concentration with temperature can be divided into three parts, ranging with 300–700 K, 800–1200 K, and  $T > 1200$  K, as shown in Fig. 3(c). In the first two parts, the concentrations linearly increase as the temperature rises, with different slopes; the inflection point between the first two parts is at about 700 K, corresponding to the metal-semiconductor transition, where the concentration of both longer and shorter dimers in the surface is close

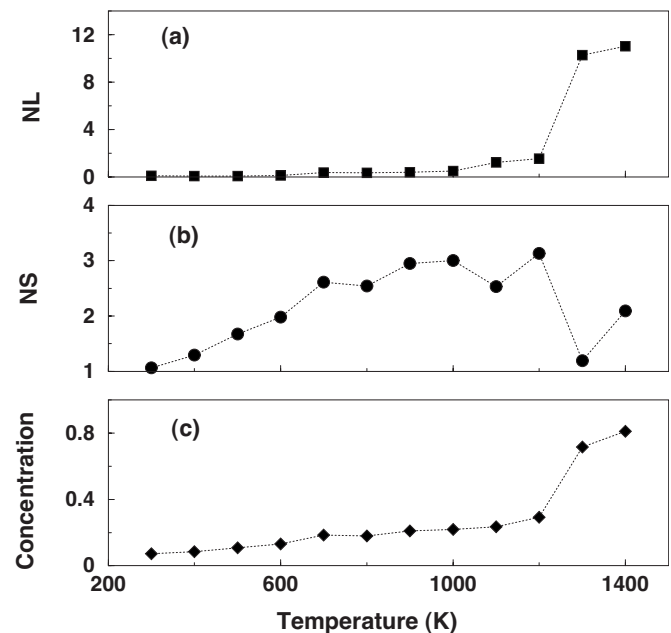


FIG. 3. The averaged number of (a) longer dimers and (b) shorter dimers in the two top layers vs temperature. (c) The concentration of the longer and shorter dimers in the two top layers vs temperature.

to 20%. This predicts that the surface shows a semiconducting behavior when  $C < 20\%$ , while a metallic behavior when  $C > 20\%$ . Therefore, the temperature-induced metal-semiconductor transition in the Si(001) surface is essentially dependent on the concentration of the shorter and longer Si dimers at the surface.

The finding above can be rationalized as below. Driven by temperature effect, the Si dimers of the Si(001) surface flip-flop randomly,<sup>6</sup> during which some of dimers are elongated and some are shortened. Generally, the strained Si dimers create new bonding states and antibonding states that are all different from those of the dimers with averaged bond length. The eigenvalues corresponding to the new antibonding states distribute mainly around the conduction band edge, and those of the new bonding states around the valence band edge, of which some new antibonding states position below the conduction band edge and some new bonding states are above the valence band edge. Thus, the strained dimers make the conduction band edge move down and the valence band edge move up, narrowing the band gap. This was also observed in the  $\alpha$ -Si system reported by Fedders.<sup>15</sup> With rising temperature, the concentration of both longer and shorter dimers increases, generating more states at band tails and

thus narrowing the band gap much more. When the concentration reaches a threshold, both tails overlap in the band gap, resulting in the metallization of the surface.

#### IV. CONCLUSION

In summary, our TBMD simulation shows that at  $T \geq 1200$  K, the metallic behavior of the Si(001) surface indeed attributes to the liquid state of the two top layers. In the case of  $800 \text{ K} \leq T < 1200 \text{ K}$ , the metallization of the Si(001) surface is from the shorter dimers and longer dimers, where the concentration of the stretched dimers is predicted to be larger than 20%.

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Si(100) $(2 \times 1)$  surface remains at  $T=300$  K and the surface exhibits metallization at  $T=800$  K. This testing supports that the used supercell as mentioned in the text is suitable to simulate the Si(100) surface.

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