PHYSICAL REVIEW B VOLUME 39, NUMBER 17 15 JUNE 1989-I

Thermal amplitudes of surface atoms on Si(111) 2×1 and Si(001) 2×1

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(Received 25 January 1989)

Atomic displacement-displacement correlation functions for the surface atoms of the Si(111) 2×1 and Si(001) 2×1 surfaces are calculated using phonon energies and eigenvectors obtained from a tight-binding theory of the lattice dynamics of Si. The temperature dependence and the possible anisotropies of the amplitudes of vibration of the surface atoms are investigated. For the π-bonded chain model of Si(111) 2×1 it is found that the surface atoms have larger vibrational amplitudes perpendicular to the surface than parallel to it, and this anisotropy (1.8 in the mean-squared amplitudes at 270 K) increases rapidly with increasing temperature. This is attributed to the existence of a small-wavelength acoustic phonon with an unusually low energy. For the surface atoms on Si(001) 2×1 the anisotropy between perpendicular and parallel vibrations is not as marked. The interatomic vibrational correlations between surface atoms reveal the strength of the new bonds that are formed in the reconstruction of these surfaces.

I. INTRODUCTION

The vibrational excitations of semiconductor surfaces provide a direct probe of the structural and bonding properties that result from their reconstruction. Moreover, studies of the vibrational properties of surfaces are also necessary in order to understand dynamical processes that occur on them, such as the kinetics of adsorbates, diffusion and desorption, epitaxial growth, and possibly surface melting. The thermal fluctuations of the surface atoms are directly related to these phenomena. Furthermore, the analysis of a number of experimental probes requires a detailed knowledge of the vibrational amplitudes and correlations of the surface atoms. The Debye-Waller factors which appear in the expressions for the intensity of radiation scattered from a surface, and the displacement-displacement correlations of the surface atoms enter in the interpretation of ion scattering and other experiments. New developments in a number of experimental techniques that study vibrational properties of surfaces have generated further interest and the need for realistic calculations and a better theoretical understanding. Among these are He-atom scattering, high-resolution electron-energy-loss spectroscopy, surface infrared spectroscopy, medium- and high-energy ion scattering, and surface extended x-ray-absorption fine-structure experiments. From the theoretical point of view, an underlying formalism for surfaces exists within the general framework of the theory of lattice dynamics,[1] but few realistic calculations have been done for specific surfaces.

In this work we present results of calculations of the atomic displacement-displacement correlation functions for atoms on the Si(111) 2×1 and Si(001) 2×1 surfaces. Both of these surfaces have been the subject of intense research for many years, and even though much progress has been made, there are still unresolved questions regarding their structure and their basic excitations. In particular, the study of their dynamical properties is an area of growing interest. Here we investigate the thermal fluctuations of the atoms on these surfaces. Specifically, we will discuss the anisotropy of the vibrational amplitudes of the surface atoms between vibrations parallel and normal to the surface plane, their temperature dependence, and the interatomic vibrational correlations. As a basic input in our calculations we use phonon energies and eigenvectors that are obtained from a semiempirical tight-binding theory for structural energies in Si. This theoretical approach has been previously used by Allan and Mele[2] and Alerhand and Mele[3,4] (henceforth collectively referred to as AAM) to study phonons and other vibrational excitations on Si surfaces.

A similar study of Si(001) 2×1, to the one presented here, has been reported by Tiersten, Ying, and Reinecke.[5] They used classical Keating interatomic potentials to model the lattice dynamics of Si, and pointed out the importance of doing these types of studies. However, classical potentials cannot be reliably applied to surfaces in general. A Keating model for interatomic potentials has also been used by Yamaguchi and Harada[6] to calculate the thermal diffuse scattering in low-energy electron diffraction on the Si(111) 2×1 surface, where the atomic amplitudes of vibration enter in the calculation. Here we discuss both Si(111) 2×1 and Si(001) 2×1 in order to investigate possible variations in amplitudes on different surfaces of the same material.

The Si(111) 2×1 surface is currently understood in terms of Pandey's π-bonding chain model.[7] According to this model the surface reconstructs by forming zigzag chains of surface atoms that run parallel to each other. The bonding along the chain is provided by the π interaction between the surface electrons. Calculations of the structure and electronic properties of this surface based on the chain model are in good agreement with a long list of experiments,[8] including the strong dispersion of the electronic surface bands, which is the signature of the chain reconstruction.[7,9,10] A side view of the surface is shown in Fig. 1. The chain model also provides a basis to understand the unique vibrational properties observed on this surface.[11,12] Its lattice dynamics is dominated by the chain geometry and by the strong coupling between the electronic surface states and the structural degrees of freedom of the zigzag chains. Indeed, the most salient features in the surface phonon spectrum are related to modes that have the form of elementary vibrational excitations of the surface zigzag chains.[4] Particularly relevant to the thermal fluctuations of the surface atoms is the appearance of a small-wavelength surface phonon with an unusually low energy. Indeed, one of the main motivations for performing the present study is to investigate the thermal effects of this mode. This intrinsic vibration of the surface, observed by Harten, Toennies, and Wöll in He-atom scattering experiments,[12] is dispersionless across the surface Brillouin zone and has an energy of $\hbar\omega = 10$ meV. Near the zone edge it is located well below the acoustic continuum. Because of the low energy of this phonon and its lack of dispersion (leading to a large contribution to the phonon density of states at that energy) this mode is thermally populated with a large probability. Thus one might expect that the vibrational amplitudes of the surface atoms on Si(111) 2×1 would be greatly enhanced. In the surface phonon spectrum we obtain from the tight-binding theory[4] this low-energy dispersionless surface phonon appears as a transverse acoustic (TA) mode where the atoms on the surface chains vibrate normal to the plane of the surface.[13] Here we find that, in agreement with these observations, the vibrational amplitudes of the surface atoms are larger perpendicular to the surface than parallel to it, *and that this anisotropy increases rapidly with increasing temperature.* At room temperature the anisotropy in the mean-squared amplitudes of vibration is 1.8. Although it is usually assumed that the thermal vibrational amplitudes of a surface atom are larger normal rather than parallel to the surface, this is not always the case, and even the opposite behavior has been observed to occur.[14]

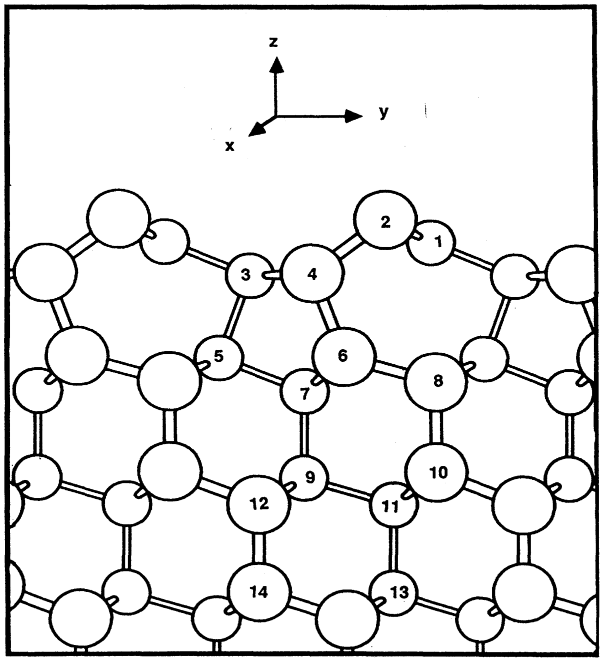

FIG. 1. Side view of the π-bonded chain model of Si(111) 2×1. The two surface atoms, numbered 1 and 2, form zigzag chains that run parallel to the [112] direction (into the page); these chains are tilted with up (2) and down (1) atoms. The Cartesian coordinates as referred to in the text are defined as follows: $\hat{\mathbf{x}}$ is $[1\bar{1}0]$, parallel to the surface chains, $\hat{\mathbf{y}}$ is $[11\bar{2}]$, parallel to the surface but normal to the chain direction, and $\hat{\mathbf{z}}$ is [111].

In contrast with this result for Si(111) 2×1, no such low-energy small-wavelength surface phonon appears in the phonon spectrum of Si(001) 2×1, and we find that for this surface the normal to in-plane anisotropy in the vibrational amplitudes of the surface atoms is much smaller. The basic building block in the reconstruction of Si(001) involves the formation of surface dimers between two neighboring surface atoms, reducing the number of dangling bonds on the surface by a half.[15-19] A side view of the surface is shown in Fig. 2. The surface dimers do not remain symmetric, but they tilt so that each dimer is formed by an up and a down atom. Within this model, the different periodicities observed on this surface [2×1, $p(2\times2)$, and $c(4\times2)$] can be understood in terms

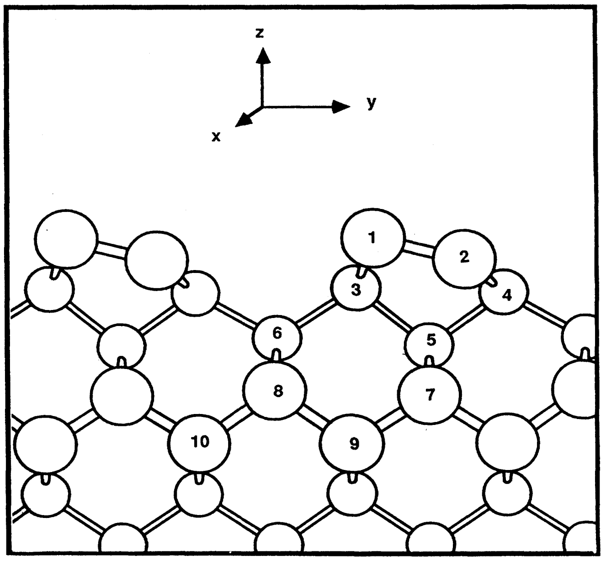

FIG. 2. Side view of the tilted dimer model of Si(001) 2×1. The Cartesian coordinates as referred to in the text are defined as follows: $\hat{\mathbf{x}}$ is $[\bar{1}10]$ parallel to the surface and perpendicular to the direction of the surface dimers, $\hat{\mathbf{y}}$ is $[\bar{1}10]$ parallel to the surface along the direction of the surface dimers, and $\hat{\mathbf{z}}$ is [001].

of different ordered arrangements of the tilted surface dimers.[19,20] We find that the normal modes of vibration of the higher-order reconstructions $p(2\times2)$ and $c(4\times2)$ are essentially the same as for the 2×1 reconstruction,[3] since essentially the surface phonons are characterized by the vibrations of the nearly isolated surface dimers.[21] Here we will report results only for the 2×1 reconstruction.

The rest of this paper is organized as follows. In the next section an outline of the calculations is given. In Sec. III the atomic amplitudes of vibration, their temperature dependence, and the interatomic correlation functions that we obtain are presented. Finally, the results are summarized and discussed in Sec. IV.

II. DISPLACEMENT-DISPLACEMENT CORRELATION FUNCTIONS

In the harmonic approximation the correlation function between the displacement $u_{i\nu}$ of atom i along the direction μ (from its equilibrium position), and the displacement $u_{j\nu}$ of atom j along the direction ν, can be expressed in terms of the phonons or normal modes of the system:[1]

$$\langle u_{i\mu}u_{j\nu}\rangle = \frac{\hbar}{2N(M_iM_j)^{1/2}} \times \sum_{\mathbf{q},\lambda} \frac{e_{i\mu}(\mathbf{q},\lambda)e^{*}_{j\nu}(\mathbf{q},\lambda)}{\omega_\lambda(\mathbf{q})} \times e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\{1+2n[\omega_\lambda(\mathbf{q})]\} , \qquad (1)$$

where the sum is over normal modes λ and wave vectors $\mathbf{q}$ in the Brillouin zone, $\omega_\lambda(\mathbf{q})$ and $e(\mathbf{q},\lambda)$ are the phonon frequencies and eigenvectors, respectively, $\mathbf{R}_i$ denotes the two-dimensional lattice vector of the surface unit cell where atom i is located, M_i is its mass, and N is the number of unit cells within the periodic boundary conditions used in the calculations. The temperature T enters through the Bose-Einstein distribution function $n[\omega]$.

The main difficulty in the evaluation of Eq. (1) is that it requires the knowledge of the phonon energies and eigenvectors of the system over the entire Brillouin zone. Because of this, the calculation of vibrational correlation functions is most often limited to simple systems where the normal modes are determined by symmetry, and Eq. (1) is usually approximated by low- and high-temperature expansions where models for the dispersion of phonon energies and the density of states, like the Debye model, are used.[22] In order to make reliable predictions and to extract microscopic information from the thermal vibrational amplitudes of the system, its phonon energies and eigenvectors must be accurately represented in Eq. (1). For semiconductor surfaces, this problem is further complicated by the fact that their reconstruction leads to bonding configuration that can be quite different from the bulk, so that dynamical properties cannot be simply described using force constants calculated for the bulk and transferred to the surface. A realistic theory must be used to calculate phonon energies and eigenvectors for each particular reconstructed surface. In this work we use the results obtained by AAM, who have studied vibrational excitations of Si surfaces using a formalism based on a semiempirical tight-binding theory for structural energies in semiconductors.[15] A detailed description of the formalism and their results is found in Refs. 3 and 4. To explain the model briefly, the total energy of the system is expressed in terms of the band-structure energy, an empirical potential energy of interionic interactions, and the Coulomb energy of on-site electronic repulsions. The band-structure energy is calculated using an sp^3 tight-binding representation of the valence electrons, and the interionic interactions are approximated with a sum of pairwise potentials. The on-site Coulomb repulsion term for the electrons is added in order to incorporate the effects of charge transfer. Using this model the dynamical matrix of a system can be calculated using perturbation theory, where the bare ion-ion forces are renormalized by the electron polarizability; exponentially decaying interatomic forces are generated by the exchange of virtual electron-hole pairs between lattice distortions at different sites on the lattice. This approach has the advantage that it incorporates the effects of reconstruction into the lattice dynamics of the surface, and it has been successful in providing a description of the vibrational properties of Si surfaces.[2-4]

Before we present the results, we comment on two approximations in our calculations. First, we have assumed that phonon energies do not depend on temperature. The second approximation is related to a technical aspect of the calculations. In order to represent a surface we use a slab geometry. For Si(111) 2×1 we used a slab with 14 layers, a slab thick enough so that at its center the atoms are essentially bulklike (i.e., their vibrational amplitudes have the same values as for atoms in the bulk). This is not the case for Si(001) 2×1, where a ten-layer slab is used. The large unit cells of the higher-order reconstructions of this surface make it computationally demanding to use thicker slabs. Thus in the case of Si(001) 2×1 the vibrational amplitudes of the atoms at the center of the slab have not yet decayed to the bulk value. Nevertheless the surface-surface coupling in the slab is very small,[23] and the values we report for the vibrational amplitudes of the surface atoms are correct, within the uncertainties of the theory.[24] We note that our calculations reproduce the experimental value of root-mean-squared (rms) amplitudes of vibration $\langle u_{i\mu}^2\rangle^{1/2}$ for an atom in the bulk; at room temperature this value is 0.075 Å.[25] Tiersten *et al.*[5] avoided this problem by using an elegant Green's-function formalism to treat a semi-infinite surface. While this is possible for the Keating interatomic potentials they used in their dynamical model, it is more tractable to consider a slab geometry when the quantum-mechanical treatment of the electrons is included.

III. RESULTS

A. Vibrational amplitudes

The on-site vibrational correlation functions yield the atomic amplitudes of vibration. In Tables I and II we list the root-mean-squared amplitudes of vibration $\langle u_{i\mu}^2\rangle^{1/2}$

TABLE I. Atomic rms amplitudes of vibration (in Å) for Si(111) 2×1 at $T=270$ K. The atom numbers and Cartesian directions are defined in Fig. 1. For an atom in the bulk $\langle u_\mu^2\rangle^{1/2}=0.075$ Å at $T=270$ K.

Layer	Atom	$\langle u_{ix}^2\rangle^{1/2}$	$\langle u_{iy}^2\rangle^{1/2}$	$\langle u_{iz}^2\rangle^{1/2}$
Surface	1	0.096	0.088	0.120
	2	0.100	0.095	0.133
Second	3	0.082	0.081	0.087
	4	0.082	0.083	0.088
Third	5	0.077	0.074	0.083
	6	0.078	0.075	0.082
Fourth	7	0.078	0.077	0.077
	8	0.076	0.073	0.078
Fifth	9	0.075	0.073	0.076
	10	0.075	0.074	0.075
Sixth	11	0.074	0.073	0.074
	12	0.075	0.073	0.075
Seventh	13	0.074	0.073	0.074
	14	0.074	0.073	0.074

at room temperature ($T=270$ K) for Si(111) 2×1 and Si(001) 2×1, respectively. The atoms are listed from the surface down to the middle of the slab, which corresponds to seven layers below the surface for Si(111) 2×1 and five layers for Si(001) 2×1. We discuss next these results for each surface independently, starting with Si(111) 2×1.

The 2×1 unit cell of the π-bonded chain model of Si(111) 2×1 has two surface atoms, which are labeled 1 and 2 in Fig. 1. Both of these surface atoms have amplitudes of vibration that are larger in the direction normal to the surface than parallel to the surface plane. This anisotropy is 1.35 on the average for the rms vibrational amplitudes, or 1.8 in the mean-squared amplitudes $\langle u_{i\mu}^2\rangle$. Notice that the two surface atoms in the chain reconstruction are inequivalent, since the surface chains are tilted so that atom 1 is up and atom 2 is down. In the tight-binding equilibrium geometry this tilt is $z_2-z_1=0.6$ Å.[4] Experimentally it is found that $z_2-z_1 \sim 0.4$ Å.[26,27] Here we obtain that the two surface atoms have also different amplitudes of vibration, and therefore different effective cross sections in relation to scattering experiments. At $T=270$ K these effective sizes are $\langle \mathbf{u}_1^2\rangle^{1/2}=0.096\hat{\mathbf{x}}+0.088\hat{\mathbf{y}}+0.120\hat{\mathbf{z}}$ Å and $\langle \mathbf{u}_2^2\rangle^{1/2}=0.100\hat{\mathbf{x}}+0.095\hat{\mathbf{y}}+0.133\hat{\mathbf{z}}$ Å (the Cartesian directions are defined in Fig. 1). These cross sections are ellipsoidal and not spherical, as it is usually assumed in the analysis of experiments.[28] For any layer below the surface the two atoms in the unit cell on that layer have nearly the same vibrational amplitudes. The decay of $\langle u_{i\mu}^2\rangle^{1/2}$ as a function of penetration into the bulk is shown in Fig. 3(a), where for definitiveness we use the values corresponding to the even-numbered atom in Table I. For all three directions the vibrational amplitudes quickly decay to the bulk value of 0.075 Å, and starting from the second layer below the surface the normal and in-plane vibrations become nearly isotropic.

The two surface atoms of Si(001) 2×1 have also vibrational amplitudes that are larger perpendicular to the surface than parallel to it (Table II). These two surface atoms, labeled 1 and 2 in Fig. 2, are inequivalent since the surface dimers are tilted. In the tight-binding equilibrium geometry this asymmetry is $z_1-z_2=0.6$ Å (tilt angle of 22°).[3] Experimentally this tilt is believed to be about 0.3 Å.[18] For the up atoms the ratio of $\langle u_{i\mu}^2\rangle^{1/2}$ between normal and in-plane vibrations is 1.1, and for the down atoms this ratio is 1.2. These anisotropies are smaller than for the surface atoms on Si(111) 2×1. Notice that the two surface atoms forming a dimer have nearly the same vibrational amplitude normal to the surface, but the in-plane vibrations of the down atoms are smaller than those for the up atoms by approximately 10%. At $T=270$ K the "effective sizes" of the surface atoms 1 and 2 are $\langle \mathbf{u}_1\rangle^2=0.094\hat{\mathbf{x}}+0.101\hat{\mathbf{y}}+0.107\hat{\mathbf{z}}$ Å and $\langle \mathbf{u}_2\rangle^{1/2}=0.087\hat{\mathbf{x}}+0.087\hat{\mathbf{y}}+0.105\hat{\mathbf{z}}$ Å. The decay of $\langle u_{i\mu}^2\rangle^{1/2}$ as a function of penetration into the bulk is shown in Fig. 3(b). It is interesting to note that in the direction parallel to the surface along the dimers (y direction in Fig. 2) the atoms in the third layer below the surface have larger vibrational amplitudes than those in the second layer below

TABLE II. Atomic rms amplitudes of vibration (in Å) for Si(001) 2×1 at $T=270$ K. The atom numbers and Cartesian direction are defined in Fig. 2. The numbers in parentheses are from the calculations of Tiersten *et al.* (Ref. 5); the range in values reported for $\langle u_{2z}^2\rangle^{1/2}$ corresponds to different tilt angles of the surface dimers considered in their calculations (12° to 24°). For an atom in the bulk $\langle u_\mu^2\rangle^{1/2}=0.075$ Å at $T=270$ K.

Layer	Atom	$\langle u_{ix}^2\rangle^{1/2}$	$\langle u_{iy}^2\rangle^{1/2}$	$\langle u_{iz}^2\rangle^{1/2}$
Surface	1	0.094 (0.085)	0.101 (0.098)	0.107 (0.097)
	2	0.087 (0.081)	0.087 (0.100)	0.105 (0.136–0.168)
Second	3	0.087	0.078	0.096
	4	0.089	0.080	0.099
Third	5	0.083	0.081	0.086
	6	0.078	0.075	0.085
Fourth	7	0.081	0.071	0.083
	8	0.078	0.074	0.081
Fifth	9	0.076	0.073	0.079
	10	0.076	0.075	0.079

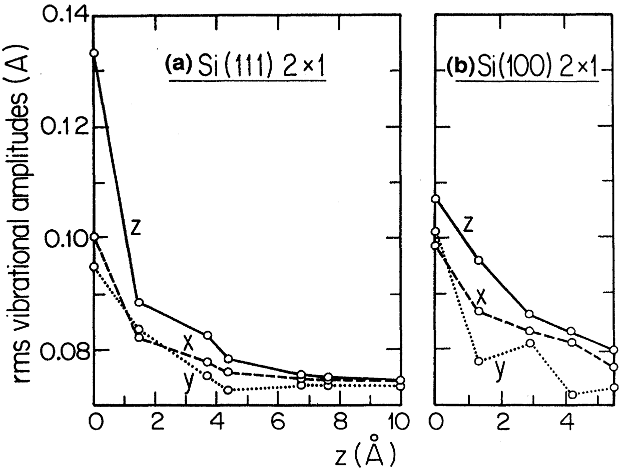

FIG. 3. Atomic rms vibrational amplitudes at $T=270$ K as a function of penetration from the surface for (a) Si(111) 2×1 and (b) Si(001) 2×1. The Cartesian directions are defined in Figs. 1 and 2, respectively.

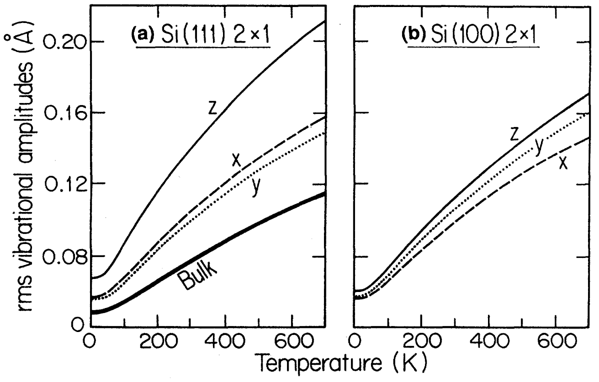

FIG. 4. Atomic rms vibrational amplitudes of surface atoms on (a) Si(111) 2×1 (surface atom 2) and (b) Si(001) 2×1 (surface atom 1) as a function of temperature. The bold line (a) is for a bulk atom.

the surface. In the slab representation we have used for Si(001) 2×1 the vibrational amplitudes have not decayed to their bulk value at the center of the slab (fifth layer). Nevertheless, our results for the atoms at or near the surface can be compared with those obtained for Si(111) 2×1, and correspond to consistent results within the uncertainties of the theory.

We now compare our results for Si(001) 2×1 with those obtained by Tiersten *et al.*[5] Their calculated values for $\langle u_{i\mu}^2\rangle^{1/2}$ at $T=251$ K are given in parentheses in Table II. The most important discrepancy is in the vibrational amplitudes normal to the surface. Whereas they find that the two surface atoms that form a dimer have very different vibrational amplitudes normal to the surface, we find that these are nearly identical. This is not only a numerical difference, but it is a qualitative one. It is still being disputed in the literature whether the surface dimers on Si(001) are symmetric or asymmetric, and the use of our results or those of Tiersten *et al.* would yield different results in the analysis of experiments precisely regarding the degree of asymmetry of the surface dimers.

B. Temperature dependence

The temperature dependence of $\langle u_{i\mu}^2\rangle^{1/2}$ for the surface atoms on Si(111) 2×1 and Si(001) 2×1 are shown in Figs. 4(a) and 4(b), respectively. We discuss first the results for Si(111) 2×1. The values plotted in Fig. 4(a) correspond to the surface atom 2 (the up surface atom). The same behavior is observed for the surface atom 1. Also shown in Fig. 4(a) is the corresponding temperature dependence for an atom in the bulk. Notice that, regardless of orientation, the vibrational amplitudes of the surface atom increase faster with increasing temperature than the vibrational amplitude of a bulk atom. However, the vibrations normal to the surface have the strongest temperature dependence, and the anisotropy between normal and in-plane vibrations grows quickly with increasing values of T. For temperatures larger than approximately 200 K the mean-squared amplitudes of vibration $\langle u_{i\mu}^2\rangle$ follow the classical high-temperature linear relation

$$\langle u_{i\mu}^2\rangle \sim \alpha_{i\mu} T \ . \tag{2}$$

The corresponding proportionality constants $\alpha_{i\mu}$, averaged over the two surface atoms and normalized by the bulk-atom values, are

$$\begin{aligned} &\alpha_x/\alpha_{\text{bulk}}=1.34, \quad \alpha_y/\alpha_{\text{bulk}}=1.27 \ , \\ &\alpha_z/\alpha_{\text{bulk}}=2.21 \ . \end{aligned} \tag{3}$$

It is usually expected that the vibrations of a surface atom will be larger normal to the surface than parallel to it, since at the surface the atoms have reduced coordination in the normal direction. However, the rate of increase of the normal vibrational amplitudes for Si(111) 2×1 is a unique characteristic of this surface [compare with the results for Si(100) 2×1, Fig. 4(b)]. This temperature enhancement of the normal to in-plane anisotropy is related to the low-energy TA surface phonon that was discussed in the Introduction and observed by Harten *et al.*[12] Most of the vibrational character of this mode is localized on the surface atoms, which vibrate normal to the surface plane. This, together with the fact that this surface phonon has a very low energy and a large contribution to the density of states, and therefore it appears predominantly in the phonon sum of Eq. (1), explains why the anisotropy between normal and in-plane vibrations has the strong temperature dependence shown in Fig. 4(a).

We note that for temperatures above 600 K our results have to be considered with caution, since Si(111) undergoes an irreversible phase transition at ~600 K from a 2×1 to a 7×7 reconstruction.[29] The 7×7 reconstruction[30] involves drastic changes in the bonding configuration of the surface, and the transition cannot be described through a soft-phonon mechanism starting from the 2×1 phase. This transition is yet to be understood. At 600 K the rms vibrational amplitudes of the surface atoms normal to the surface are about 8% of the equilibrium bulk interatomic distance d_0 (2.35 Å), and the in-plane vibrational amplitudes are on the average 6% of d_0. According to the Lindemann criteria, melting occurs when the rms vibrational amplitudes are 10–12 % of d_0 (the melting temperature of Si is 1683 K). The fluctuations normal to the surface, 8% of d_0, are nearly twice as large as thermal fluctuations for a bulk atom at the same temperature, 4.5% of d_0. Thus we can conclude that near the transition temperature the surface atoms undergo significant excursions out of their equilibrium positions in the direction perpendicular to the surface. No further insight is obtained, but this simple observation may help to gain an understanding of the 2×1 to 7×7 transition of the Si(111) 2×1 surface.

The temperature dependence of $\langle u_{i\mu}^2 \rangle^{1/2}$ for the surface atoms of Si(001) 2×1 is shown in Fig. 4(b) (the average of the values for atoms 1 and 2 listed in Table II is used in this figure). The thermal fluctuations of the surface atoms increase faster with increasing temperature than the thermal fluctuations for a bulk atom [Fig. 4(a)]. But contrary to what happens in the case of Si(111) 2×1, the ratio between normal and in-plane vibrations does not change substantially. In the temperature regime above approximately 200 K, where the mean-squared amplitudes of vibration are linearly proportional to the temperature, the rate of increase of $\langle u_{i\mu}^2 \rangle$ is characterized by the proportionality constants α_μ [Eq. (2)]:

$$\alpha_x/\alpha_{\text{bulk}} = 1.22, \quad \alpha_y/\alpha_{\text{bulk}} = 1.56, \quad \alpha_z/\alpha_{\text{bulk}} = 1.81 . \tag{4}$$

A comparison with the values for Si(111) 2×1 demonstrates that the large anisotropy in this latter surface is not an intrinsic property of all surfaces, but a specific result for this particular case.

C. Interatomic correlations

The interatomic correlation functions are of interest in the interpretation of ion scattering experiments, and also provide information about the strength of the bonding between atoms. The normalized displacement-displacement correlation function between two atoms i and j is defined as surface atoms connected by a bond along one of the surface chains, defined as

$$C_{i\mu,j\nu} = \langle u_{i\mu} u_{j\nu} \rangle / \langle u_{i\mu}^2 \rangle^{1/2} \langle u_{j\nu}^2 \rangle^{1/2} . \tag{5}$$

TABLE III. Normalized displacement-displacement correlations $C_{1\mu,2\mu}$ between two bonded atoms on a surface chain of Si(111) 2×1.

T (K)	$C_{1x,2x}$	$C_{1x,2x}$	$C_{1z,2z}$
0	0.398	0.233	0.252
50	0.454	0.276	0.299
100	0.552	0.350	0.373
270	0.667	0.438	0.433
400	0.685	0.452	0.440
600	0.695	0.459	0.444

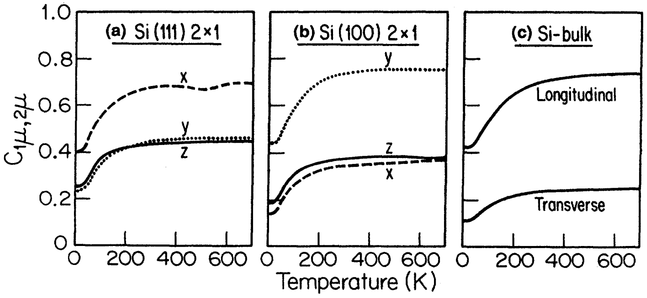

FIG. 5. Normalized displacement-displacement correlation $C_{i\mu,j\mu}$ as a function of temperature between neighboring surface atoms in (a) Si(111) 2×1 and (b) Si(001) 2×1, and (c) between two neighboring atoms in the bulk.

This correlation function between two neighboring surface atoms on a zigzag chain of the Si(111) 2×1 surface is shown in Fig. 5(a) as a function of temperature. The vibrations of the atoms along the direction of the surface chains (dashed line) are strongly correlated. This is an indication of the strong bonding along the surface chains. This intrachain bonding is generated by the π interaction of the surface electrons and are bonds that are created in the reconstruction of the surface. Indeed, this correlation is as strong as the longitudinal correlation between two neighboring atoms in the bulk, shown in Fig. 5(c). The small dip in $C_{1x,2x}$ at $T \approx 500$ K is due to a longitudinal optical vibration of the surface chains, which contributes negatively to the correlation function. For vibrations perpendicular to the chain direction the interatomic correlations are weaker, but still larger than the transverse correlation of bulk atoms. Figure 5 shows that for temperatures larger than approximately 300 K the functions $C_{1\mu,2\mu}$ remain fairly constant. Below this temperature, however, the vibrational correlations have a strong temperature dependence. This behavior must be taken into account in the analysis of experiments. We list some representative values of $C_{1\mu,2\mu}$ in Table III.

The temperature dependence of $C_{i\mu,j\mu}$ for two surface atoms on Si(001) 2×1 forming a dimer is shown in Fig. 5(b). The vibrations of the surface atoms along the dimer direction are strongly correlated (dotted line); this might be expected since these vibrations expand and contract the surface dimers. Indeed, this correlation is very similar to the longitudinal correlation for two atoms in the bulk. The correlation for vibrations perpendicular to the dimer direction, including the vibrations normal to the surface, are much weaker but still stronger than the transverse correlations for bulk atoms [Fig. 5(c)], similarly to the results for Si(111) 2×1. In Table IV we list some representative values of $C_{i\mu,j\mu}$ that we have calculated. For reference, we present also in this table the corresponding results obtained by Tiersten *et al.*, which are shown in parentheses. The main difference is in the nor-

TABLE IV. Normalized displacement-displacement correlations $C_{1\mu,2\mu}$ between two surface atoms on Si(001) 2×1 forming a dimer. The numbers in parentheses are from the calculation of Tiersten *et al.* (Ref. 5); the range of values corresponds to different tilt angles considered in their calculations (12° to 24°).

T (K)	$C_{1x,2x}$	$C_{1y,2y}$	$C_{1z,2z}$
0	0.136	0.438	0.189
	(0.130–0.134)	(0.420–0.572)	(0.097–0.136)
50	0.188	0.485	0.231
100	0.263	0.591	0.303
270	0.341	0.728	0.370
400	0.353	0.750	0.379
	(0.354–0.366)	(0.60–0.838)	(0.239–0.245)
600	0.364	0.754	0.476

mal vibrations $C_{iz,jz}$, where we obtain correlations which are stronger by approximately 10%.

IV. DISCUSSION

The results of our calculations indicate that for both Si(111) 2×1 and Si(001) 2×1 the surface atoms have thermal vibrational amplitudes that are larger along the direction perpendicular to the surface plane than parallel to it. Although this is usually expected since the surface atoms have reduced coordination normal to the surface, we find that the degree of anisotropy between normal and in-plane vibrations is very different for the two surfaces. Indeed, for Si(111) 2×1 we find that this anisotropy is quite large (1.8 in the mean-squared amplitudes of vibration), whereas on Si(001) 2×1 the fluctuations of the surface atoms are nearly isotropic. Furthermore, in the case of Si(111) 2×1 the anisotropy increases rapidly with increasing temperature, a feature that we attribute to the presence of a low-energy dispersionless surface phonon. No such large temperature enhancement is observed for the surface atoms of Si(001) 2×1, which does not support a similar low-energy surface phonon. The most salient feature when one compares the atomic vibrational amplitudes on the two surfaces is that in the case of Si(111) 2×1 the surface atoms have very large amplitudes of vibrations normal to the surface. The difference in the vibrational amplitudes of surface atoms on Si(111) 2×1 and Si(001) 2×1 shows that the specific microscopic properties of the surface must be considered in the calculation of the atomic vibrational correlation functions.

It is interesting to compare the decay of vibrational amplitudes as a function of penetration into the bulk for the two surfaces we have studied (Fig. 3). Clearly the phonons on Si(111) 2×1 are more sharply localized at the surface than on Si(001) 2×1. The reconstruction of Si(111) 2×1 is more drastic and leads to a surface geometry that is quite different than the underlying bulk, and thus one might expect surface vibrations which do not strongly mix with the bulk modes. Regarding the intersite vibrational correlations between two connected surface atoms, we find that in both surfaces the bonds that are formed in the reconstruction lead to strong longitudinal correlations. The weaker transverse correlations of the dimers on Si(001) can be understood from the fact that the surface dimers are not interconnected between them and can therefore have more freedom of motion parallel to the surface plane.

In summary, we have calculated vibrational correlation functions for surface atoms on Si(111) 2×1 and Si(001) 2×1, and we have studied in detail the thermal fluctuations of the surface atoms, the decay of these as a function of penetration into the bulk, and the intersite correlation between the surface atoms. One important conclusion is that the vibrational amplitudes of surface atoms are characteristic to each particular surface, indicating that accurate microscopic information must be included in the calculation of these quantities in order to make reliable predictions. Specifically, we predict the degree of anisotropy between normal and in-plane vibrations, and the difference in vibrational amplitudes between inequivalent surface atoms. Experimental techniques exist that can directly measure these variables. Perhaps the most important contribution of the calculations we have presented here is in their use in the analysis of experiments. Our calculated atomic vibrational amplitude and correlation function results might greatly reduce the uncertainties in the interpretation of scattering experiments that probe the structure of the surface; Debye-Waller factors might also be easily calculated with the information we have provided.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. JSEP Contract No. DAAL-03-86-K-0002. One of us (E.J.M.) acknowledges support from the D.O.E. Grant No. FG02-89-ER45118. We thank Dr. Douglas Allan for some useful conversations.

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