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Phonon-mediated indirect interactions between adatoms on surfaces: O adatoms on Si(100)

S. C. Tiersten* and T. L. Reinecke
Naval Research Laboratory, Washington, D.C. 20375

S. C. Ying
Department of Physics, Brown University, Providence, Rhode Island 02912

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In an earlier paper, we presented a general treatment of the phonon-mediated interactions between adatoms on surfaces, based on a lattice-dynamics approach. There the interaction was expressed in terms of the vibrational correlation functions of the surface and the interactions of the adatom with the rigid surface. In the present paper, we give the results of model calculations for the interactions between O adatoms on the dimer sites of the Si(100) surface. The approach developed earlier for the vibrational properties of the Si(100) surface is used, and a model for the interactions of the O adatoms with the surface is obtained on the basis of recent total-energy results.

Phonon-mediated interactions between adatoms on surfaces are an important contribution to indirect substrate-mediated interactions, especially at large distances,[1] and they play an important role in surface ordering and nucleation. Most earlier work has addressed this problem in terms of continuum elasticity theory for the surface.[2] In a recent work[3] we have provided a detailed treatment of this problem in terms of the full lattice dynamics of the surface. In this way detailed studies can be made for realistic models of adatom-substrate systems. Results can be obtained for varying adatom-adatom separations beginning at nearest-neighbor separations including the anisotropy of the interaction with respect to directions on the surface. In that work we gave detailed results for the interactions between pairs of As-As dimers on the Si(100) surface and between H adatoms on the W(100) surface, and we found interesting dependences on adatom separations and surface anisotropy.

The formalism for the interactions between adatoms on surfaces begins with the expression for the energy of the substrate-adatom system:

$$E = W[\{\mathbf{r}_s\}] + V_1[\{\mathbf{r}_s\};\mathbf{R}_1] + V_2[\{\mathbf{r}_s\};\mathbf{R}_2] \; . \tag{1}$$

Here W is the interaction energy between the atoms of the clean substrate at positions $\{\mathbf{r}_s\}$, and $V_1[\{\mathbf{r}_s\},\mathbf{R}_1]$ and $V_2[\{\mathbf{r}_s\},\mathbf{R}_2]$ are the interactions between the adatoms at $\mathbf{R}_1$ and $\mathbf{R}_2$ and the substrate atoms $\{\mathbf{r}_s\}$. The displacements of the substrate atoms around their equilibrium positions are expanded to harmonic order. The key results from this development are

$$E_{\mathrm{relax},\xi} = -\tfrac{1}{2}\sum_{\lambda,\mu} V'_{\xi,\lambda}[\mathbf{R}_\xi]\underline{\chi}_{\lambda\mu}V'_{\xi,\mu}[\mathbf{R}_\xi] \; , \tag{2}$$

$$E_{\mathrm{INT}}(\mathbf{R}_1,\mathbf{R}_2) = -\sum_{\lambda,\mu} V'_{1,\lambda}[\mathbf{R}_1]\underline{\chi}_{\lambda\mu}V'_{2,\mu}[\mathbf{R}_2] \; . \tag{3}$$

Here $\xi = 1,2$ refers to the two adatoms, and λ,μ combine the site index and the Cartesian component. E_{relax} is the energy gain upon the adsorption of an isolated adatom due to the relaxation of the substrate atoms, and E_{INT} is the indirect interaction energy between two adatoms. V' is the force that an adatom exerts on the substrate atoms and is evaluated at their positions in the absence of adatoms, and χ is the surface susceptibility. In practical calculations we do not know in detail how the adatom changes the substrate force constants, and thus we take χ to be that for the clean substrate, $\chi = (W'')^{-1}$ where the derivatives with respect to the substrate coordinates are evaluated at the equilibrium positions of the clean substrate.

In the present work we study the technologically important problem of O adatoms on the Si(100) surface. For the vibrational properties of this surface in the absence of adatoms we use the same approach that we used previously.[3] It is based on a Keating model for the forces between the substrate atoms,

$$V = \frac{2}{a^2}\left\{ \sum_{\text{bonds}} \alpha(\mathbf{r}_{ss'}\cdot\mathbf{r}_{ss'} - \mathbf{r}^{(0)}_{ss'}\cdot\mathbf{r}^{(0)}_{ss'})^2 + \sum_{\substack{\text{bond}\\ \text{pairs}}} \beta(\mathbf{r}_{ss'}\cdot\mathbf{r}_{ss''} - \mathbf{r}^{(0)}_{ss'}\cdot\mathbf{r}^{(0)}_{ss''})^2 \right\} . \tag{4}$$

Here α is a bond-stretching force constant, β includes the effects of both angle bending and bond stretching, and $\mathbf{r}_{ss'}$ is the separation between atoms at sites s and s′.

The (1×1) geometry of the unreconstructed Si(100) surface is shown in Fig. 1. The clean Si(100) surface is known to reconstruct into a 2×1 pattern by the formation of dimer bonds in the $[01\bar{1}]$ direction between neighboring pairs of surface atoms.[4,5] We have studied the vibrational response functions of both the (1×1) unreconstructed and (2×1) dimer reconstructed clean surfaces.[6,7] The vibrational spectral density of the unreconstructed surface in the $[01\bar{1}]$ direction has a large feature at low frequency corresponding to the tendency of the surface to reconstruct by forming dimer bonds in this direction, but the reconstructed surface does not have such a low-frequency feature. Physically we expect the correlation function χ of the surface in the presence of adatoms at

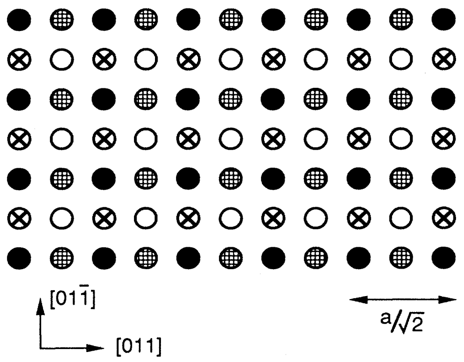

FIG. 1. Geometry of the unreconstructed Si(100) surface. ●, atoms on the surface layer; ◍, atoms in the second layer, ○, atoms in the third layer; and ⊗, atoms in the fourth layer.

low coverage to behave in a manner similar to that of the reconstructed surface and in particular to lack the soft response of the unreconstructed surface. In our earlier work[3] we introduced and discussed a model of the lattice dynamics of the Si(100) surface which is appropriate for the study of adatom-adatom interactions on this surface. In this model we maintain the (1×1) symmetry of the unreconstructed surface, and we place a bond with a central force $\alpha_d = \alpha/6$ between the Si surface dimer atoms. We have found[3] that for all α_d of this order or larger the vibrational spectral densities are qualitatively similar to those of the reconstructed surface.

The location and bonding of O adatoms on the Si(100) surface at low coverage has received considerable attention in the literature but is not yet completely understood.[8-16] In recent work[16] based on *ab initio* electronic calculations it has been argued that atomic O is more stable in the first-layer bridging positions between two surface dimer atoms and that this location accounts for electron-energy-loss-spectroscopy (EELS) data on this system. In the present work we will study O adatoms in these bridging positions between surface dimers. We will be interested primarily in the qualitative features of the spatial dependences of the adatom-adatom interaction.

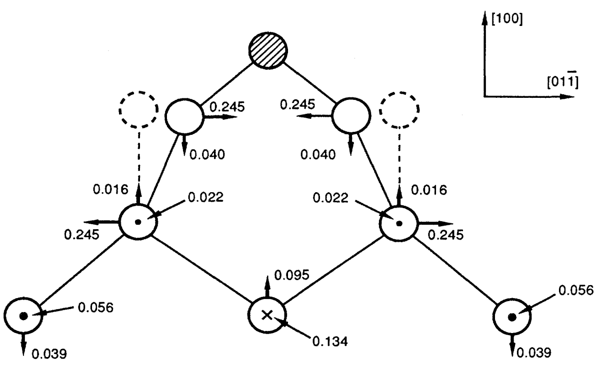

FIG. 2. Forces due to the O adatom (cross-hatched circle) on the atoms of the surface layers. The units are eV/Å. Dashed circles indicate the positions of the Si dimer atoms in the unreconstructed (1×1) geometry of the clean surface.

We have obtained a model for the interaction of the O adatoms with rigid Si substrate based on recent cluster

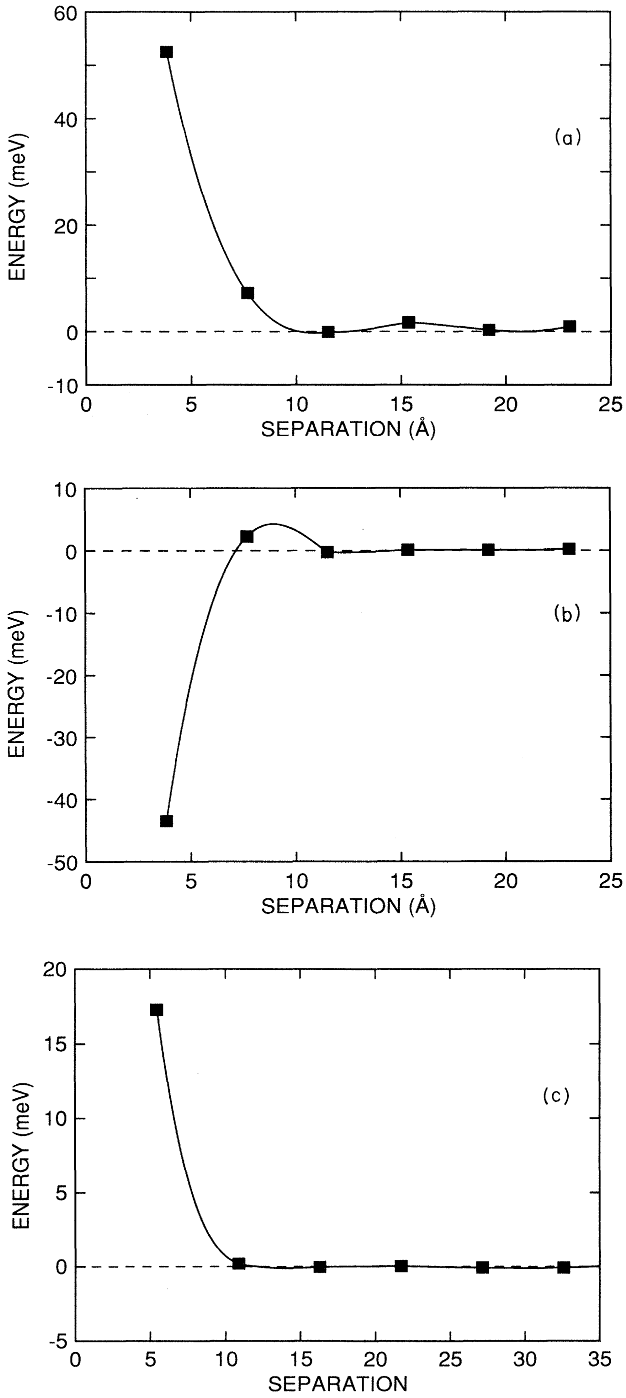

FIG. 3. Energy of interaction between O adatoms vs separation. (a) Adatom separation along the [01$\bar{1}$] direction. (b) Adatom separation along the [011] direction. (c) Adatom separation along the [010] direction.

total-energy calculations[17] in which the Si atoms to which an O is bonded were allowed to relax. The basic chemistry is that the Si—O bond is stronger than the Si—Si bond, and thus the O tends to break the Si—Si bond and form a Si—O—Si structure. In the present case we are interested in a situation in which the O bonds to the two dimer surface atoms via the lone pair orbitals of the dimer bond; this is the geometry studied in Ref. 16. The cluster total-energy calculations[17] show that the two Si atoms to which the O is bonded are approximately 0.69 Å closer to one another than in the unreconstructed (1×1) geometry of the clean surface (and 0.8 Å farther apart than in the dimer bond). The positions of the surface atoms in the clean (1×1) unreconstructed case and the case with the O adatom present are shown in Fig. 2. Here we use the values of the Si—O bond length used in the cluster calculations, which was obtained from the bulk value. The cluster calculations do not give information about relaxations of the other Si atoms of the substrate. We note that in semiconductors like Si the bond-stretching forces are much greater than the bond-bending forces[18] which implies that relaxations tend to involve mostly angle bending and little bond stretching.[4] Therefore, we use the bulk values for all Si—Si bond lengths and the bulk positions for all Si atoms in the second and deeper layers. In this way the forces from substrate interactions all arise only from the effects of angle bending and not bond stretching. The net effect is that the Si dimer atoms to which the O atoms are bonded are rotated toward one another from their (1×1) unreconstructed positions as shown in Fig. 2. The resulting forces V' due to the O adatom needed in the present formalism are those required to produce the above Si atom positions. They are given by

$$V'_{1,\lambda}+V'_{2,\lambda}=-\sum_{\mu} W''_{\lambda\mu}\,p_{\mu}\ , \tag{5}$$

where $\{p_\mu\}$ are the substrate atom positions. It is found that there are forces between the adatom and seventeen of the substrate atoms. These forces are given in Fig. 2.

We have carried out detailed calculations of the relaxation energy and adatom-adatom interaction energies for this system. Details of the calculational method have been given earlier.[3,7] For an isolated O adatom on the surface dimer position the relaxation energy is -133 meV, which represents a gain in the adsorption energy. The adatom-adatom interaction energies are shown in Figs. 3(a)–3(c). For separations along the $[01\bar{1}]$ direction the interaction is repulsive at the nearest separations and decreases rapidly for larger separations. For separations along the [011] direction the interaction is attractive at nearest separations, weakly repulsive at the next lattice site, and decreases after that. The general behavior of the adatom-adatom interaction can be understood on simple, physical grounds. When an isolated O adatom is located at the dimer site, the two Si dimer bond atoms move together in the $[01\bar{1}]$ direction as indicated in Fig. 2. For nearest-neighbor separations of the O along $[01\bar{1}]$ the relaxations of the Si surface atom caused by the two neighboring O adatoms oppose one another, and thus there is a repulsion for near-neighbor atoms. On the other hand, this is not the case when the two O are nearest neighbors along the [011] direction, and we find that there is a significant attraction in this case.

Thus we see that the interactions between O adatoms on the Si(100) surface have nonmonotonic dependences on adatom separation, and have a strong dependence on the direction of the adatom separation along the surface. The latter may tend to make the atoms order along the [011] direction. These dependences result mainly from the positions of the adatoms with respect to the surface and not on the details of the interaction with the surface. For this reason we believe that qualitative features of the present results are not dependent on the details of the model used here for the interaction of the adatom with the surface. The same method can be used to study substrate relaxations and the interactions between adatoms in other surfaces geometries which may be of interest. In order to study such cases it will be helpful to know more about the interaction between the adatom and the surface.

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[*] Present address: Electrical, Computer and Systems Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12180.

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