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Tight-binding model of adsorbate structures

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Tight-binding calculations are presented of the ground state energies of metal atoms absorbed on the surface of the same or similar metals. We consider rows and clusters of adsorbate, and find significant energy variations as a function of the number of the atoms. Results are presented for the (001) face both for fcc and bcc crystals. General results that are applicable for any elemental fcc or bcc crystal are obtained in the present paper. We include only *s*-wave tight-binding orbits in the nearest neighbor approximation.

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I. INTRODUCTION

Scanning tunneling microscopes routinely measure the geometrical structure of clusters of adsorbate atoms on crystal surfaces. It is often found that certain structures occur frequently, and obviously have the lowest energy. Of course, there are many possible situations: many crystals, many faces of the crystal, and many adsorbates. Here we present calculations of the ground state energy of rows of metal atom adsorbates on the faces of two crystal lattices: face-centered-cubic (fcc) and body-centered-cubic (bcc).

The monolayer adsorbed overlayer is a system with reduced dimensionality. It is found at the boundary between two media: the vacuum and a solid body. The interaction between adsorbed particles and substrate plays an important role in all surface phenomena. It affects virtually all properties of the adsorbates: their structure and thermal stability, migration of adsorbates along the surface, the pattern formation and surface diffusion of the clusters, etc. The physics of electrons in low-dimensional systems is a topic of considerable current interest. Experimental observations have been reported that show one-dimensional (1D) chain states on metal faces.[1] Several models have been offered to explain the 1D formation.[2] Here we address the following questions: are the lengths of the rows chosen randomly or are there energetically preferred lengths for rows? Ag atom chains with variable lengths have been observed on silicon surfaces. Some chains are as short as a single protrusion, while others incorporate four or five protrusions. The longest chain ever observed had 26 protrusions.[3] Here we present a calculation that tries to explain the observed length of the chains.

Much experimental and theoretical work on clusters is now exploring their properties as a function of the number of atoms involved.[4] According to nucleation theory[5] the cluster-size distribution of these aggregates would, however, be rather broad. However, the shell model predicts magic numbers for metal clusters. Recently, we have studied quantum size effects on the pattern formation for two-dimensional confinement islands on surface by using the free electron model.[6] In this calculation the contribution from the substrate was omitted, since quantum confinement plays the main role. The interesting results found in this calculation suggested the need for a more accurate theory. We feel a tight-binding model is a better theory for the calculation of a small number of adsorbates. In order to compare with our earlier calculations using the tight-binding model, we consider here only *s*-wave orbits. Later calculations will consider *p*- and *d*-wave binding.

Our present study is generally applicable for both elemental homoepitaxial adsorbates or growths on their fcc or bcc crystal substrates, as well as heteroepitaxial growths. We show that the rows do have preferred sizes and that the substrates play a crucial role on size selections both for fcc and for bcc isotropic crystals. The results are obtained by calculating the exact ground state energy in the tight-binding model. The method of doing this is described in the following section.

II. HAMILTONIAN AND GROUND STATE ENERGY

We write the Hamiltonian in the tight-binding form as

$$H = H_0 + V, \tag{1}$$

$$H_0 = \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) C_{\mathbf{k}}^{\dagger} C_{\mathbf{k}} + \sum_{p} C_p^{\dagger} C_p E(p), \tag{2}$$

$$V = \sum_{\mathbf{k}p} M_{\mathbf{k}p} [C_{\mathbf{k}}^{\dagger} C_p + \text{H.c.}], \tag{3}$$

where the label $\mathbf{k}$ denotes bulk states, while p denotes the band states of the adsorbates. They are connected by the matrix element $M_{\mathbf{k}p}$. We adopt the nearest neighbor model for the tight-binding Hamiltonian, which is taken to be an isotropic bonding in a cubic system. We assume the adsorbates are similar to the element of the substrate, and have the same first-neighbor overlap constant W_1. This model is the simplest possible theoretical system. We take the surfaces to be (100) for both fcc and bcc. We consider several cases: (i) the adsorbates are in a row so their eigenfunctions are one dimensional, (ii) they are $2 \times n$ arrangements, and (iii) a 3×3 square.

The row direction is taken to have the closest packing, as shown in Fig. 1. In Fig. 1, the view is looking down on the surface from above. The top layer of surface atoms are shown as circles, while the adsorbate atoms are squares. The

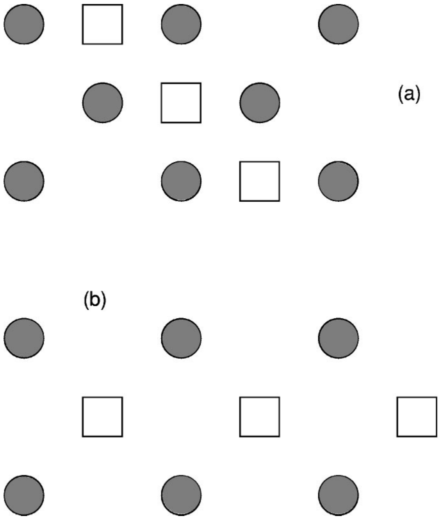

FIG. 1. Row growths on (a) fcc and (b) bcc surfaces. The circles represent surface atoms of the substrate, while squares denote adsorbed atoms.

adsorbate atoms are above the surface layer by a distance $a/2$ where a is the lattice constant of the cubic structure. Figure 1(a) is for fcc, while Fig. 1(b) is for bcc. In the case of fcc, the chains of adsorbate atoms run along the $(1,-1,0)$ direction, which permits them to have the same nearest neighbor distance as in the bulk. For the bcc, there is no direction of the chain which permits nearest neighbor overlaps at the same bond length as in the bulk, so they are drawn along the (100) direction. These two cases were chosen because they are different, and give different results. The matrix elements and eigenvalues for fcc are

$$\varepsilon(\mathbf{k}) = E_0 - W_1 \sum_{\boldsymbol{\delta}} \cos(\mathbf{k}\cdot\boldsymbol{\delta}), \tag{4}$$

$$= E_0 - 4W_1[\cos(k_x/2)\cos(k_y/2) + \cos(k_x/2)\cos(k_z/2) + \cos(k_y/2)\cos(k_z/2)], \tag{5}$$

$$E(p) = E_{00} - 2W_1 \cos(p), \tag{6}$$

$$M_{\mathbf{k}p} = W_1 \sum_{\alpha,\delta} \sin(p\alpha)\psi_k(R_\alpha + \delta), \tag{7}$$

$$= 2W_1 \sqrt{\frac{2}{(n+1)V_s}}[\cos(k_x/2) + \cos(k_y/2)] \times \sin(k_z/2)\Lambda(\mathbf{k},p), \tag{8}$$

$$\Lambda(\mathbf{k},p) = \sum_{\alpha=1}^{n} \sin(p\alpha)e^{i\mathbf{k}\cdot\mathbf{r}_\alpha} = \frac{\sin(p)}{2[\cos(m) - \cos(p)]}[1-(-1)^l e^{im(n+1)}], \tag{9}$$

$$m = \frac{1}{2}(k_x + k_y), \quad p = \frac{l\pi}{n+1}, \tag{10}$$

and for bcc are

$$\varepsilon(\mathbf{k}) = E_0 - W_1 \sum_{\boldsymbol{\delta}} \cos(\mathbf{k}\cdot\boldsymbol{\delta}), \tag{11}$$

$$= E_0 - 8W_1 \cos(k_x/2)\cos(k_y/2)\cos(k_z/2), \tag{12}$$

$$E(p) = E_{00}, \tag{13}$$

$$M_{\mathbf{k}p} = W_1 \sum_{\alpha,\delta} \sin(p\alpha)\psi_k(R_\alpha + \delta), \tag{14}$$

$$= 4W_1 \sqrt{\frac{2}{(n+1)V_s}}\cos(k_x/2)\cos(k_y/2) \times \sin(k_z/2)\Lambda(k_x,p), \tag{15}$$

$$\Lambda(k_x,p) = \sum_{\alpha=1}^{n} e^{ik_x\alpha}\sin(p\alpha) = \frac{\sin(p)[1-(-1)^l e^{ik_x(n+1)}]}{2[\cos(k_x) - \cos(p)]}, \tag{16}$$

where V_s is the volume of substrate. There are n adsorbate atoms in a chain along the directions shown in Fig. 1(a) for fcc and Fig. 1(b) for bcc. We have assumed that the adsorbates are on a (001) face of an fcc or bcc crystal, so that every adsorbate atom has four neighbors on the host crystal, which are at the points $(\pm 1,0,-1)/2$ and $(0,\pm 1,-1)/2$ for fcc, or $(\pm 1,\pm 1,-1)/2$ for bcc. There is no dispersion in $E(p)$ for bcc since the adsorbates are not first neighbors in the assumed arrangement. For bcc adsorbates do not overlap each other, but only the substrate. The adsorbed chain of n atoms has wave vectors $p = \pi l/(n+1)$, $l = 1,2,\ldots,n$. The wave vectors $\mathbf{k}$ are assumed to be continuous, and the Brillouin zone has the usual shape for an fcc or bcc crystal. In Eq. (15) the factor of $\sin(k_z/2)$ arises from the substrate wave function. For a one-dimensional chain in the tight-binding approximation, the wave function at site j is proportional to $\sin(kj)$. We assume this form applies to the substrate wave function at the surface, which gives $\sin(k_z/2)$, since the layer spacing is $a/2$.

Since the Hamiltonian has a bilinear form, one can write an exact expression for the change in the ground state energy caused by the interaction of the adsorbed row with the substrate. We use the formalism in Chapter 3 of Ref. 7. The off-diagonal self-energy of the adsorbate states is defined as

$$\Sigma_{pp'}(ip_n) = \sum_{\mathbf{k}} \frac{M^*_{\mathbf{k}p}M_{\mathbf{k}p'}}{ip_n - \varepsilon(\mathbf{k})}, \tag{17}$$

$$G(p) = \frac{1}{ip_n - E(p)}. \tag{18}$$

The Green's function for the p-state is defined above. The integrals over wave vector were done over the correct Brillouin zone for the appropriate crystal. The expansion for the ground state energy yields the series

$$\Omega = \Omega_0 + \delta\Omega, \tag{19}$$

$$\beta\Omega_0=-\sum_{\mathbf{k}\sigma}\ln[1+e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}]-\sum_{p}\ln[1+e^{-\beta(E(p)-\mu)}], \tag{20}$$

$$\delta\Omega=\frac{2}{\beta}\sum_{p}\left[G(p)\Sigma_{pp}+\tfrac{1}{2}\sum_{p'}G(p)\Sigma_{pp'}G(p')\Sigma_{p'p}+\cdots\right], \tag{21}$$

$$=-\frac{2}{\beta}\sum_{ip_n}\ln\det|\delta_{pp'}-G(p)\Sigma_{p,p'}|. \tag{22}$$

The summation of the series to the log of a determinent is derived in Ref. 8. The dimension of the determinent equals the number of atoms in the adsorbed chain. For a chain of *n*-atoms the formula is

$$=-\frac{2}{\beta}\sum_{ip_n}\ln\begin{vmatrix}1-G(1)\Sigma_{11} & -G(1)\Sigma_{12} & \cdots & -G(1)\Sigma_{1n}\\ -G(2)\Sigma_{21} & 1-G(2)\Sigma_{22} & \cdots & -G(2)\Sigma_{2n}\\ \vdots & \vdots & \ddots & \vdots\\ -G(n)\Sigma_{n1} & -G(n)\Sigma_{n2} & \cdots & 1-G(n)\Sigma_{nn}\end{vmatrix} \tag{23}$$

$$=-\frac{2}{\beta}\sum_{ip_n}\ln[f(ip_n)]. \tag{24}$$

The evaluation of the thermodynamic potential involves the summation of the above expression over all values of ip_n. This can be converted to a continuous integral along the real axis,

$$\delta\Omega=2\int\frac{d\varepsilon}{2\pi i}n_F(\varepsilon)\mathrm{Im}\left[\ln\left(\frac{f(\varepsilon+i\eta)}{f(\varepsilon-i\eta)}\right)\right], \tag{25}$$

$$=2\int_{-\infty}^{\varepsilon_f}d\varepsilon\frac{\phi(\varepsilon)}{\pi}, \tag{26}$$

$$\tan(\phi)=\frac{\mathrm{Im}(f)}{\mathrm{Re}(f)}, \tag{27}$$

where ε_f is the Fermi level which is the top of the band when filled. For the half-filled bands, the Fermi level is at E_0 for bcc and at E_0+W_1 for fcc. These equations were derived for the case that the adatoms are in a row, and the index *p* denoted the band state of the adsorbed atom. However, the same general expressions apply for any arrangement of adsorbate atoms. In this latter case, we can make the indices *p* denote atoms location, while $G(p)$ is the single site Green's function.

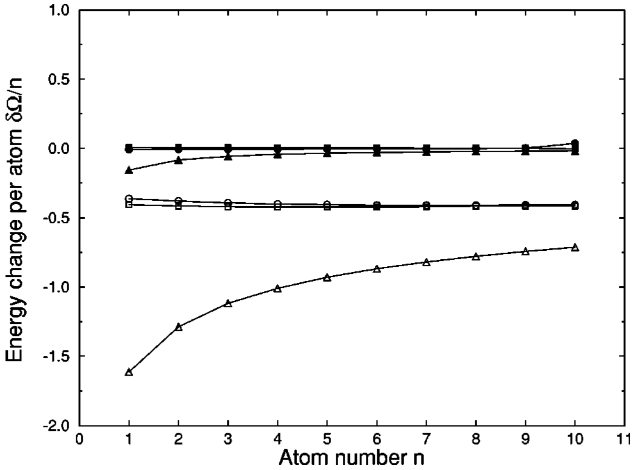

FIG. 2. The energy change $\delta\Omega/n$ due to the interaction between 1D growth row and substrate as a function of the number of row atoms for (a) filled band and (b) half-filled band bcc. Values of E_{00} are denoted by -4 (circles), -8 (triangles), and -12 (squares). Closed dots are for full substrate bands, while open dots are for half-filled substrate bands.

III. RESULTS AND DISCUSSION

The above formulas are used to calculate the ground state energy of 1D adsorbate systems. For both fcc or for bcc crystals, we obtain the variations of energy $\delta\Omega$ with the number *n* of 1D and 2D adsorbed atoms from $n=1$ to $n=10$. It turned out to be more useful to plot $\delta\Omega/n$ in order to see whether minima occurred for any value of *n* other than 1. The 1D results are shown in Figs. 2 and 3 for bcc and fcc systems. The 2D arrangements on fcc are shown in Fig. 4. In each case, closed dots are for the substrate having a filled band, while open dots are for the substrate having a half-

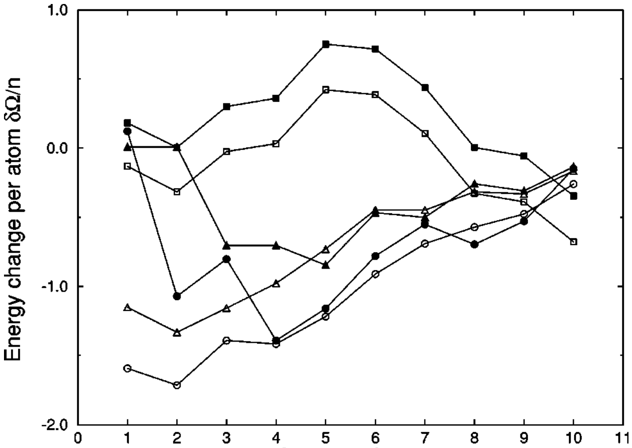

FIG. 3. The same as Fig. 2, but for fcc. Values of E_{00} are denoted by -6 (circles), -8 (triangles), and -12 (squares).

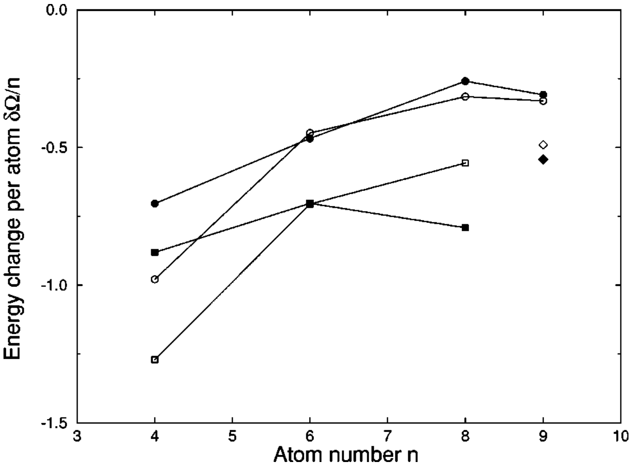

FIG. 4. Comparing square clusters with row energies on the fcc surface. Circles denote 1D rows, while squares are $2\times m$ structures. The diamonds denote a 3×3 square array. Open dots are half-filled bands in the substrate, and closed dots are completely filled bands in the substrates.

filled band. These graphs plot the quantity $\delta\Omega/n$ in units of W_1. The shapes of the curves in Figs. 2 and 3 are thereby universal. They do not change even if we change the elemental parameters E_0 or W_1. The parameter W_1 sets the energy scale, but does not influence the shape.

In calculating these curves, we set $E_0=-8W_1$ for the substrate metal. The adsorbate constant is labeled E_{00}. If $E_{00}=-8$ then the adsorbed atom is the same as the substrate atom. We also calculated cases where $E_{00}=-4$ and -12 in units of W_1. These are cases where the adsorbed atom is a different element than the substrate host.

For the bcc case, the results for $E_{00}=-4$ gives the same results as the case that $E_{00}=-12$. This result is a consequence of particle-hole symmetry for half-filled bands. The bcc lattice is bipartite, and the density of states is symmetric for electrons and holes. The slight difference shown in the figures between the results for $E_{00}=-4,-12$, shown by circles and squares, is due to numerical errors. The curves should coincide. For bcc the results for the filled bands show that there is no adsorbate binding energy at all. Keep in mind when viewing these results that we are plotting $\delta\Omega/n$, which does not include the energy E_{00}, but only the changes in energy from the hopping. For the half-filled case, the bcc binding energy seems to go as $\delta\Omega_n=nE_1$. In this case, each atom has its own binding energy, and there is no benefit from lining up in a row. We find no tendency to form a linear array. Our theory includes the indirect interactions between the adsorbates through the substrate, but these interactions seem to have little effect on the answer for the cases of $E_{00}=-4,-12$. On the other hand, for $E_{00}=E_0$, as shown by triangles, the binding energy of $n=2$ adsorbates is less than twice the energy for 1. In this case the atoms have an energy penalty for lining up in a row.

The results for fcc are very different. This lattice is not bipartite and lacks particle-hole symmetry. Indeed, the density of states is extremely asymmetric. Results are shown for $E_{00}=-6$ (circles), -8 (triangles), and -12 (squares). For the half-filled case for all three values of E_{00} there is a tendency to form short rows, since the binding with $n=2$ is lower than two times $\delta\Omega_1$. However, there is an energy penalty for longer rows. For filled bands with fcc the $\delta\Omega$ for $E_{00}=-12$ is positive, while those of $E_{00}=-6,-8$ are negative. There is a tendency to form rows of $n=4,5$ for the latter two cases.

Finally, in Fig. 4 is shown the result for small clusters on an fcc lattice. The circles show 1D chains, while the squares and diamonds show clusters. The cases of $n=4,6,8$ compare 1D rows of n atoms with clusters of the same number of atoms: 2×2, 2×3, and 2×4. The results for $n=9$ compare a 1D row with a 3×3 square. The 1D rows always have higher values of $\delta\Omega/n$ so that the clusters are more likely to occur.

The significant variation of the energy with the number of row atoms shows that substrate play a crucial role on size selection and pattern formation of epitaxial growth. Our 1D results for fcc have shown that rows with four or five atoms are more likely formed than rows with other lengths, which is in agreement with the related observations of Ag atom chains on silicon surfaces.[3] We believe these findings can provide some understanding for relative existing observations on one-dimensional growth, adsorption, and surface reconstruction. The results for 2D clusters comparing with 1D rows present that substrates also contribute to the structural transition in size-selected clusters[2] and to the formation of 2D magic clusters.[4] Furthermore, the general application of these results should make it possible for future experimental studies to test the qualitative predictions made here.

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