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Theoretical study of single-atom extraction using STM

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Based on the discrete variational method with the local-density-functional approximation, we chose cluster models to simulate the extraction of a single Al atom from Al(111) sample surface by a scanning-tunneling microscopy W tip with and without external bias voltages. Our cluster calculations, which can deal with the detailed geometry of the sample and the tip (especially with an active site), can provide useful and relatively reliable results: (1) The ''chemical interactions'' between the sample and the tip play an important role in single-atom extraction processes; e.g., an Al atom can be extracted as the tip-sample separation becomes 10 a.u. (5.3 Å) without any external fields. (2) The polarity and the value of the external bias (near the threshold) are other important factors; e.g., at the tip-sample separation 12 a.u., an Al atom can be extracted with the threshold field (0.6 V/Å, positive bias to the sample), and the extracted Al atom can be put back with a negative bias to the sample. (3) The W atom on the tip cannot be extracted. [S0163-1829(99)03323-8]

I. INTRODUCTION

Scanning tunneling microscopy[1] (STM) has provided a revolutionary method for obtaining information on surfaces of metals and semiconductors with atomic resolution in real space. STM has been used not only for observing surface properties but also for manipulating a single atom[2–4] or cluster[3,4] on a surface.

Modification of semiconductor surfaces is of particular interest for the fabrication of nanometer-scale quantum devices.[4] It was shown that a single Si atom can be extracted from the Si(111)-7×7 surface,[3–8] and the extracted Si atom can be redeposited onto the surface,[3,5–8] by applying a voltage pulse between the tip and the sample in appropriate polarities. Recently, Pang and co-workers[9,10] have achieved that Si atoms can be removed from a Si(111)-7×7 sample surface by the use of high tunneling current with low bias method. There are some other experimental works on the modification of metal surfaces.[11–13] Rabe and Buchholz[11] have shown that Ag atoms are extracted from Ag(111) surface by applying a positive voltage of 3∼7 V pulse to the Ag sample. This indicates that Ag atoms are extracted as ''positive ions.'' Chang and co-workers studied the Au (Refs. 12 and 13) and Pt (Ref. 13) atom transfer between the STM tips and samples and suggested that the Au can be more easily extracted as a ''negative ion,'' but the Pt favors ''positive-ion'' extraction (we will comment later). Another feature of the modifications on metal surfaces is that the processes are caused by field extraction and not by high temperatures[14] or current effects.[11]

Concerning the theoretical studies, most of the works are concentrated on the transfer of adsorbed atoms between two parallel-plate electrodes.[15–20] Ciraci *et al.*[15] calculated the interaction energy of an Al atom between two Al(001) slabs by the use of the self-consistent-field (SCF) pseudopotential method. Their results show that the double wells in the interaction energy collapses into a single minimum when the separation between two slabs is shorter than 2.5 interlayer spacings (about 5.0 Å). Lang using a jellium model calculated the transfer of an adatom Si (Ref. 16) and Al (Ref. 17) between two closely spaced electrodes. His results show that most of the activation barrier lowering that permits a measurable transfer rate at room temperature is a chemical effect due to the proximity of the electrodes, but the electric bias provides an additional barrier lowering and a directional driving force. Furthermore, the atom acquires a distance-dependent charge no larger than several tenths of a unit charge $|e|$. Later, Koetter *et al.*[18,19] calculated the interaction energy and forces between tunneling tips composed of an adsorbed W or Al atom on W(110) and Al(111) planes to simulate single-atom extraction processes between a W tip and an Al sample by use of a parametrized Hartree-Fock theory. Their results show that the Al atom will be spontaneously transferred from the Al surface to the W surface, if the ''W tip'' is brought close enough to the Al sample (about 6 Å) even without any external electric field. Recently, using *ab initio* density cluster techniques, Akpati *et al.*[20] investigated the effects of external homogeneous electric fields (without tip) on the chemical bond between an adatom H or Al and a Si(111) surface. Their results show that both the Si-H and Si-Al bonds are weakened and broken at high fields, irrespective of their polarity, but the effect of the field

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is much stronger when the field direction is the same as that of the bond dipole. Based on the jellium model, Hirose and Tsukada used the recursion transfer-matrix method to calculate the electronic structures of the Na bielectrode system[21] and the Al tip with the Si surface system.[22,23] The activation barriers for the extraction of a single atom decrease with the applied bias voltages.

In the studies with two parallel-plate electrode models as mentioned above, the detailed geometric structures of the tip and the sample could not be taken into account, so that the relative position of the top atom of the tips to the sample surfaces could not be treated as in real STM systems (especially for the tip with an active site), and only the homogeneous electric field were used to simulate the external bias. In this paper, we report our theoretical results of extraction of a single Al atom in the Al(111) surface (i.e., not an adsorbed one) by a widely adopted STM W tip. Based on the discrete variational method with the local-density-functional approximation (DVM-LDA),[24,25] we adopt a ''cluster model'' (Refs. 26 and 27) to simulate physical systems of an Al(111) surface and a STM W tip with tip-sample separations S and applied bias voltages (including the cases without any external electric field) as represented in Sec. II and III. In our cluster model, the detailed geometric structures of the tip and the sample are taken into account. Effects of the STM W tip and external fields can be elucidated clearly in the atomic scale. We focus on single-atom extraction processes with near-threshold external fields. Our results indicate:

(1) The ''chemical interactions'' between the tip and the sample, which are close related with the tip-sample separation and the relative position of the tip to the sample, play an important role in the atom extraction processes. A single Al atom cannot be extracted from the Al(111) surface only by the action of the W tip without an external electric field, until the tip approaches the sample within 10 a.u. (5.3 Å) because of ''activation barrier lowering'' through chemical interaction between the tip and the sample.

(2) The polarity and the value of the external bias are other important factors to manipulate a single atom in the STM with external electric fields near the threshold. A single Al atom can be extracted from the Al(111) surface by applying a least-positive 4 V bias to the Al sample as the tip-sample separation is fixed at 12 a.u. (the corresponding threshold of the electric field is about 0.6 V/Å), and the extracted Al atom can be put back on the Al(111) surface by changing the polarity of the applied bias. In the high-field cases, the chemical bonds between atoms should be broken, and a cluster of atoms might be extracted, irrespective of the polarity of the bias as pointed out by Akpati *et al.*[20].

(3) The extracted Al atom acquires a height-dependent net positive charge irrespective of polarity of the bias (near the threshold) when the Al atom is extracted from Al (111) surface. The net charge is only a few tenths of a unit charge $|e|$, so the extracted atom cannot be considered an isolated bare ion. Therefore, the field evaporation models[4,5,7,12,13] based on the bare ion treatment should be modified.

(4) It is impossible to remove the W atom from the W tip, because of a much larger activation barrier (about 5.5 eV).

The discussions in detail are presented in Sec. IV.

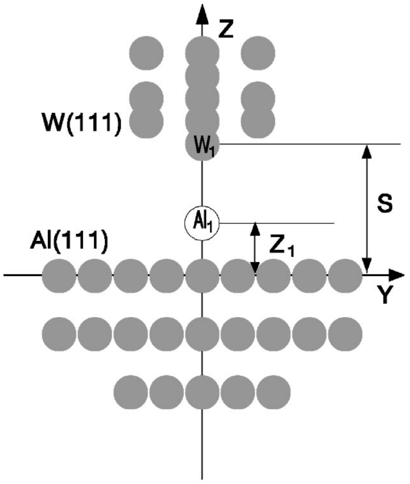

FIG. 1. The cluster model projected on the YZ plane. The solid circles represent the tip and sample atoms, the open circle represent the extracted atom Al_1. The distance between the top atom W_1 of the tip and the Al(111) surface is assumed as tip-sample separation S, the height of the extracted Al_1 atom above the Al(111) surface is assumed as Z_1.

II. COMPUTATION METHOD AND CLUSTER MODEL

The cluster model as shown in Fig. 1 was used to simulate the Al(111) surface and W tip. In order to diminish the effect of boundary of the cluster in simulations, five shells of Al atoms (a total of 43 Al atoms) from the surface center atom (labeled as Al_1) was chosen to simulate the sample; five layers of W(111) (a total of 11 W atoms) was chosen to simulate the tip. The low-energy electron diffraction (LEED) experimental results show that the Al(111) is hardly relaxed,[28] so the relaxation of Al(111) surface is ignored in our present study. The configuration of the system was constructed in such a way that the tip-top W atom (labeled as W_1) was located above the center atom Al_1 of the sample Al(111) surface with a tip-sample separation S. Note that the tip-sample separation S here is the absolute distance from the nucleus of the top atom W_1 of the tip to the Al(111) surface, but the tip-sample separation S' defined from the electric contact point,[3–8,12,13] in the STM experiments may have a displacement, e.g., $S \approx S' + 2.5$ Å for the W tip and the Al sample. The bias voltage V_s is applied to the sample with respect to the tip. During the extraction process, the Al_1 atom is moved upward out of the Al surface by a height Z_1.

The discrete variational method[24,25] with the appropriate cluster model has been used successfully to study the electronic structure of chemisorption on metal surfaces[29] and the grain boundary in intermetallic compounds,[30] the self-diffusion mechanisms on metallic fcc $\{001\}$ surfaces,[31] and the geometric structure of Na clusters.[32] We adopt a modern version of the DVM,[25] which is an all-electron calculation with the innermost atomic core orbitals frozen as an option and only a typical minimal basis set required. In our DVM calculation, the static potential produced by the external bias is introduced as an external potential in the local-density approximation. Furthermore, the external static potential should be matched with appropriate boundary conditions of the tip and the sample and can be obtained at each integration mesh point according to electrostatics. In cluster calculations, the energy level of the highest occupied molecular orbital (HOMO) corresponds to the Fermi level in the bulk according to Fermi statics. In such a system that is composed of two relative separated subsystems, i.e., the tip and the sample, their HOMOs are independent if their separation is large enough without mutual interactions. However, a single HOMO of the whole system can be automatically determined in our SCF calculations of the cluster if the tip and the sample are close enough with mutual interactions. If the separation between the tip and the sample is large enough, the HOMO's of the tip or the sample will be shifted respectively according to the external bias, because the external fields are applied with the appropriate boundary conditions as mentioned above. The total energy E_T of the system can be given by

$$E_T=\sum_i n_i\varepsilon_i-\frac{1}{2}\int \rho(\mathbf{r})V_C d\mathbf{r}+\int \rho(\mathbf{r})[\varepsilon_{\mathrm{xc}}(\mathbf{r})-\mu_{\mathrm{xc}}(\mathbf{r})]d\mathbf{r}+\frac{1}{2}\sum_{\mu,\nu}{}'\frac{Z_\mu Z_\nu}{R_{\mu\nu}}+\sum_\mu Z_\mu V_{\mathrm{ext}}(R_\mu), \quad (1)$$

where i labels single electron functions with eigenvalues ε_i and occupation n_i, $\rho(\mathbf{r})$ is the electron density, V_C is the Coulomb potential due to the electrons, μ_{xc} is an exchange-correlation potential and $\varepsilon_{\mathrm{xc}}$ is the corresponding energy density per electron, Z is the nuclear charge, and V_{ext} is the external electrostatic potential. An important point to be stressed is that the DVM can compute the cluster total energy and the reference total atomic energy on the same integration mesh points, so that the binding energy E_b of the cluster, which is the integral of their difference, should be reliable numerically.[25,31,32] As a test of the accuracy of DVM with cluster model, the lattice constants of bulk Al and W was calculated by choosing almost the same size cluster model. The calculated results is 4.10 and 3.03 Å for Al and W, respectively, and the error is within 4.2% in comparing with the experimental data [the lattice constant for Al is $a_{\mathrm{Al}}=4.05$ Å and for W $a_{\mathrm{W}}=3.16$ Å (Ref. 33)].

The relative variation of the energy of the system in the procedure of an atom extraction can be described by the calculation of binding energy E_b. Based on the binding energy E_b, we define an escape energy E_{esc} as

$$E_{\mathrm{esc}}=E_b(Z_1)-E_b(0), \quad (2)$$

where the $E_b(0)$ and $E_b(Z_1)$ are the binding energies of the system when the Al_1 atom is located at the equilibrium position on the Al(111) surface and at the height of Z_1 from the Al(111) surface, respectively. The positive (or negative) of E_{esc} means that the system adsorbs (or releases) energy when the Al_1 atom is extracted from the sample surface to the height Z_1.

III. RESULTS

A. The escape energy without external bias

In order to analyze the effect of the tip on the extraction, we calculate the variation of escape energy when the extracted atom Al_1 is pulled to different heights at fixed separations ($S=\infty$, 12, 11, 10, and 9 a.u.), without external electric field. The results are shown in Fig. 2.

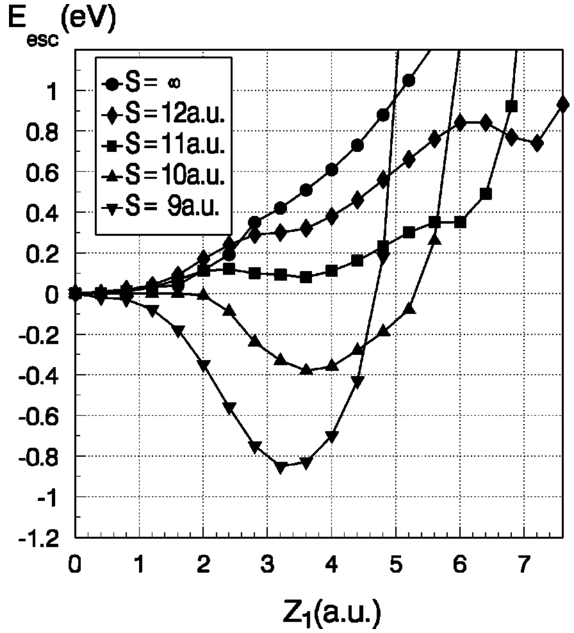

FIG. 2. The escape energies E_{esc} as a function of the height Z_1 of the extracted atom Al_1 above the sample surface for cases of $S=\infty$, 12, 11, 10, and 9 a.u.

Without W tip ($S=\infty$), the E_{esc} increases almost monotonously with the increase of Z_1, but there is a turning point at $Z_1^p=2.8$ a.u., at which the slope of the E_{esc} curve is decreased. It is owing to the polarization interaction between the extracted atom Al_1 and the Al(111) surface dipole layer (this will be discussed in detail in Sec. III C). Without W tip, the energy barrier of the extraction of a single Al atom from the clean Al(111) surface is about 3.98 eV.

With a W tip above the Al(111) surface, the variation of E_{esc} with respect to Z_1 is similar to the case of $S=\infty$ (except for the region near the W tip), as the separation S between them is larger than about 12 a.u.. However, there is a shallow potential well, when the Al_1 atom approaches the W tip. With $S=12$ a.u., the bottom of the potential well is at the height $Z_1\approx 7.2$ a.u., and the distance between Al_1 and the top atom W_1 of the tip is about 4.8 a.u. In this region, a strong bond is formed between Al_1 and W_1. In this case the activation barrier for the extraction is about 0.82 eV. Bring up the tip to shorter separations, the activation barrier is lowered. If the separation S is short enough ($S\leqslant 10$ a.u.), the activation barrier disappears, and a stable potential well is formed in the region between tip and the sample surface. It indicates that the Al_1 atom will be transferred from the Al(111) surface toward the W tip, even without external electric field. At the bottom of the potential well, the attractive interaction between the Al_1 and W_1 is very strong, and at the same time, the attractive polarization interaction between the Al(111) surface dipole layer and Al_1 is also strong. These two interactions couple each other and lower the energy of the system very much. The vanishing of the activation barrier is just the result of the coupling of these two interactions.

When the tip approaches the sample closely, for example the tip-sample separation $S=10$ a.u., the interaction between the top atom W_1 and the sample surface is very strong. Is it possible for the W_1 atom to escape from the tip and transfer to the sample surface? In order to answer this question, the

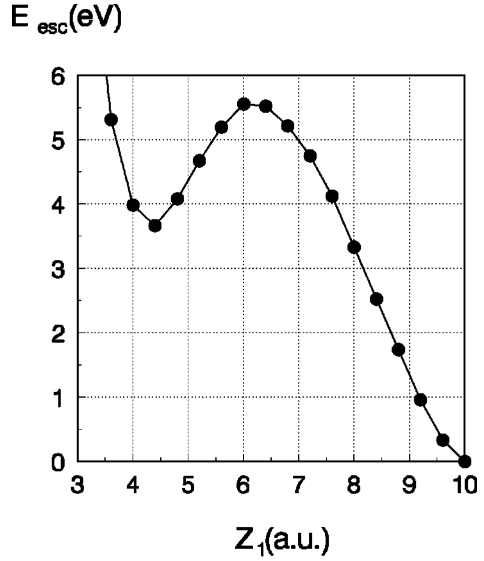

FIG. 3. The escape energies E_{esc} of W_1 atom as a function of the height Z_1 of W_1 above the sample surface. The Al_1 atom is kept at its original equilibrium site on the Al(111) surface, but the W_1 atom is removed from the tip.

variation of the escape energy of W_1 atom with respect to the separation (also labeled as Z_1) between the W_1 atom and the Al surface is calculated. The result is shown in Fig. 3. It can be concluded that the W_1 atom cannot be removed from the tip, even though the tip-sample separation is very small ($S = 10$ a.u.), because the activation barrier for the W_1 extraction is very high (about 5.5 eV). That is the reason why tungsten should be used as STM tip material in order to manipulate the Al surface atoms.

B. The effects of external bias on the escape energy

Having examined the effect of the tip on the extraction of an atom from the sample surface, we study the effect of external electric field on the extraction. As the first step, we study the effect of polarity of the external field on the escape energy E_{esc} when the separation S is fixed at 10 a.u. (this case is the critical point for the extraction of the Al atom without external field). The calculated results are shown in Fig. 4. It can be found that the external field makes the extraction of the Al_1 atom from Al(111) surface easier when 2 V bias voltage is applied to the sample; but more difficult when 2 V bias voltage is applied to the tip (the activation barrier is raised to 0.5 eV). This phenomena may be interpreted in terms of the Al_1 atom with a net positive charge when it escapes from the Al(111) surface. In a metal system, the electrons are shared among atoms; it is very difficult to determine how many electrons belong to a certain atom. In our calculation, the Mulliken population analysis is used to analyze the electron population on each atomic orbital, and the net charge for each atom can be obtained approximately. Of course, this analysis procedure is very crude, and the data can only give us an approximate tendency. The electron population results indicate that the Al_1 atom acquires a net positive charge when the Al_1 atom escapes from Al(111) surface even without external field. The net charge, which the Al_1 atom acquires when it escapes from the sample surface, is always positive whether the 2 V voltage is applied to the sample ($V_s = 2$ V) or to the tip ($V_s = -2$ V). Its value is only several tenths of a unit charge $|e|$ and varies with the height Z_1 of the Al_1 atom. It was also found in the transfer of a Si and an Al adatom between two closely spaced electrodes.[16,17] In STM, unlike in the field-ion microscopy (FIM), the amount of the net charge acquired by the extracted atom is very small. The extracted atom cannot be considered as an isolated bare ion. These field evaporation models[4,5,7,12,13] based on the bare ion treatment should be modified for the case in the STM atom extraction.

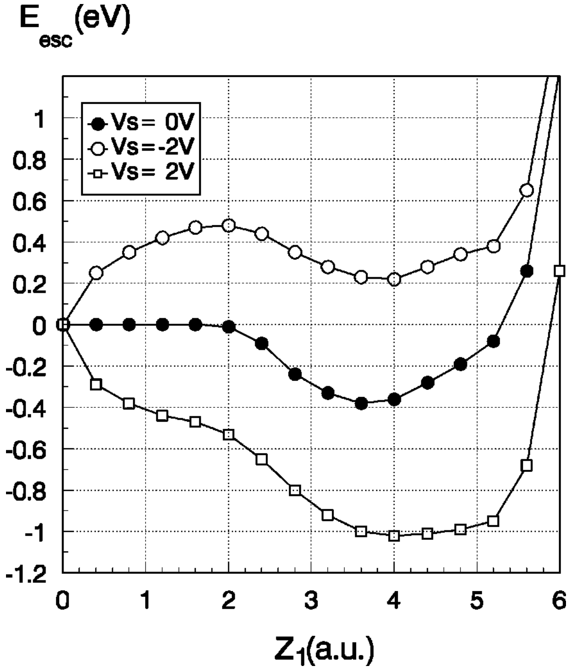

FIG. 4. The escape energies E_{esc} as a function of the height Z_1 of the extracted atom Al_1 above the sample surface, when a positive 2 V bias is applied to the sample ($V_s = 2$ V) and to the tip ($V_s = -2$ V). The tip-sample separation $S = 10$ a.u.

As the second step, we calculate the effect of the external field on the escape energy E_{esc} when the separation S is increased to 12 a.u. In this case, the activation barrier is about 0.82 eV, and the Al_1 atom cannot be extracted from the Al(111) surface without external field. When a bias voltage is applied to the sample, the activation barrier is lowered (see Fig. 5). When 2 V bias voltage ($V_s = 2$ V) is applied to the sample, the energy barrier is still about 0.2 eV; the Al_1 atom cannot be transferred from the sample to the tip if the temperature is low. When the bias voltage is increased to 4 V, the activation barrier disappears. From the E_{esc} curve, it can be found that the potential well is deeper when the Al_1 approaches the W tip ($Z_1 = 7.2$ a.u. and the distance to the W_1 atom is 4.8 a.u.) than the well in the region near the Al(111) surface. As a result, the Al_1 atom can be extracted from the Al(111) surface and transferred to the W tip with the action of higher external field. The corresponding threshold of the electric field for the Al atom extraction from the Al(111) surface toward the W tip is about 0.6 V/Å as the tip-sample separation is 12 a.u. (6.3 Å). Note that the definition of the tip-sample separation S here is different from that defined in the experiments.[3,4,6,9,12] The case of $S = 12$ a.u. (6.3 Å) here is as the case of $S' \approx 3.8$ Å in the

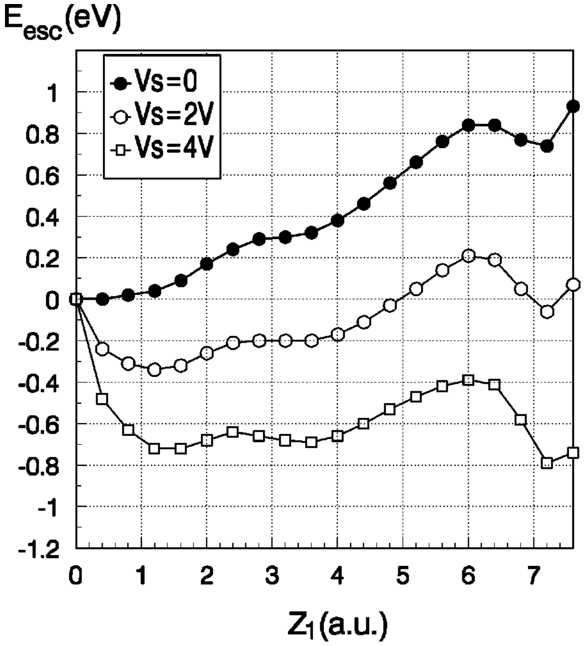

FIG. 5. The escape energies E_{esc} as a function of the height Z_1 of the extracted atom Al_1 above the sample surface, when a positive bias $V_s = 2$ V and $V_s = 4$ V is applied to the sample, respectively. The tip-sample separation $S = 12$ a.u.

experiments. The value of the threshold of the electric field is about 1.05 V/Å if we use the definition of tip-sample separation S' in the experiments. Our cluster model calculation results are in good agreement with the experiments[3,4,6,9,12] and consistent with the other theoretical results.[17]

C. The charge distribution

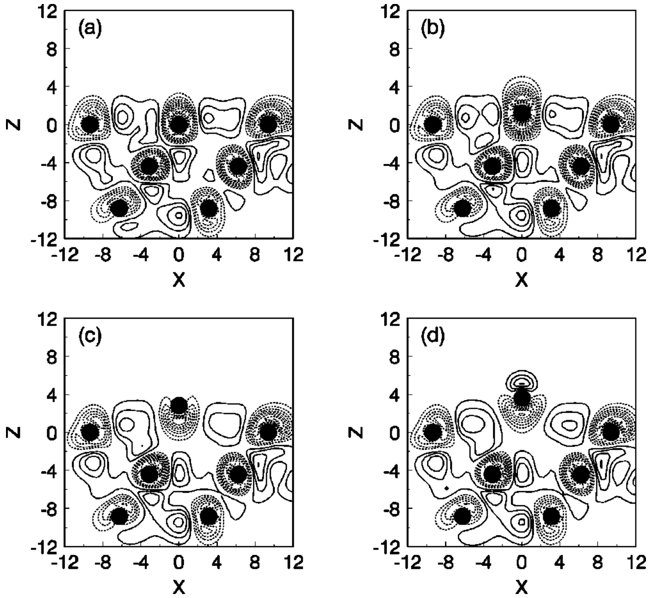

FIG. 6. The electron-density difference of the system when the Al_1 atom escapes from Al(111) surface to the different heights. (a), (b), (c), and (d) are corresponding to the cases of $Z_1 = 0.0$, 1.2, 2.8, and 3.6 a.u., respectively. The tip-sample separation $S = \infty$, i.e., without W tip. The solid and dotted lines represent the increase and decrease of electrons comparing to the free reference atom. The contour spacings are $0.001e\ (\mathrm{a.u.})^{-3}$.

In order to discuss the procedure of atom extraction in detail, the electron redistributions are obtained based on microscopic SCF calculations in LDA. The electron-density difference is obtained by subtracting the electron density of the free atoms at the superpositions from that of the cluster system, so that the electron redistribution when the Al_1 atom locates at different heights can be seen clearly. First, let us see the changes of the electron-density difference when the Al_1 atom escapes from the Al(111) surface to the different heights: $Z_1 = 0.0$, 1.2, 2.8, and 3.6 a.u. without the W tip as shown in Fig. 6. When Al_1 locates at the equilibrium site on the Al(111) surface, i.e., $Z_1 = 0.0$ a.u., the electron density near the nuclei is decreased and that in the intermediate region among the atoms is increased. The electrons are shared among the neighbor atoms, and metallic bonds are formed in the Al cluster. When the Al_1 atom escapes from the sample surface, the changes of electron density around the Al_1 atom take place. When the height $Z_1 < 2.8$ a.u. [as shown in Fig. 6(b)], the electron distribution around Al_1 resembles the electron distribution around Al_1 in the surface as shown in Fig. 6(a). On the other hand, when $Z_1 > 2.8$ a.u. [as shown in Fig. 6(d)], the electron distribution is much different from the distributions as in the cases of $Z_1 < 2.8$ a.u. The electrons are accumulated above the Al_1 nucleus, but electrons are lost under the Al_1 nucleus, and a dipole is manifested. It is the joining point at $Z_1 = 2.8$ a.u., where the electron distributions [as shown in Fig. 6(c)] just begin to be polarized. The charge polarization around the Al_1 atom is caused by the polarized charge distribution, i.e., the dipole layer around the Al(111) surface. In order to show the surface dipole layer more clearly, the electron density (not the electron-density difference) around the Al(111) surface is also calculated based on the LDA as shown in Fig. 7. Along the direction perpendicular to the surface, the electron density exponentially decays when it departs from the Al surface. As a result, a ‘‘dipole layer’’ around the Al surface is formed, if we take into account the positive charge of nuclei and the negative charge of electrons. We now return to the escape energy curves (see Fig. 2) presented in Sec. III A. The slope of the escape energy E_{esc} with the height Z_1 is decreased when $Z_1 > 2.8$ a.u., because the attractive interaction between the dipole around the Al_1 atom and the ‘‘dipole layer’’ around the Al(111) surface decreases the energy of the whole system. As a result, a turning point occurs at the height of Z_1

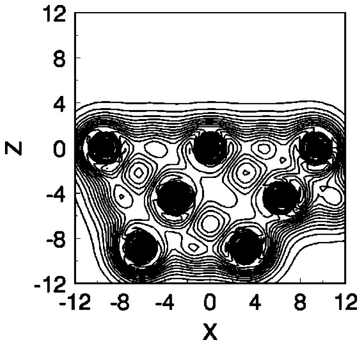

FIG. 7. The electron density of the pure Al(111) surface. The contour spacings are $0.002e\ (\mathrm{a.u.})^{-3}$. A surface dipole layer is clearly manifested.

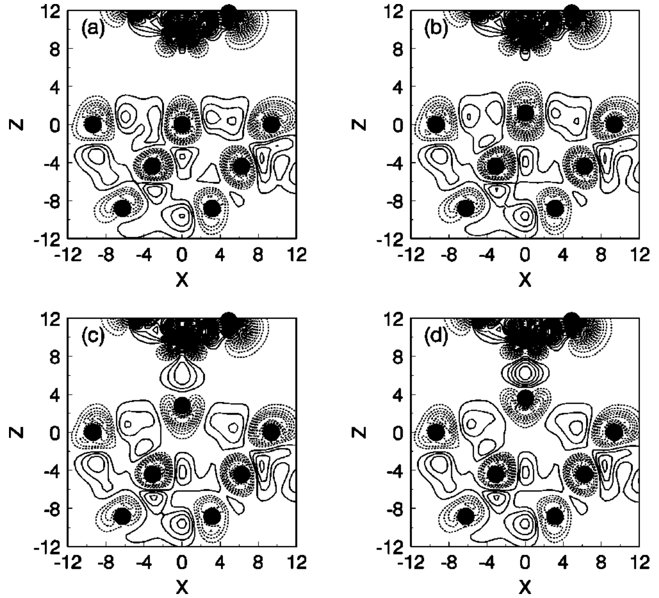

FIG. 8. The electron-density difference of the system when the Al_1 atom is extracted from Al(111) surface to the different heights. (a), (b), (c), and (d) are corresponding to the cases of $Z_1 = 0.0$, 1.2, 2.8, and 3.6 a.u., respectively. The tip-sample separation $S = 10$ a.u. The solid and dotted lines represent the increase and decrease of electrons comparing to the free reference atom. The contour spacings are $0.001e\ (\mathrm{a.u.})^{-3}$.

=2.8 a.u. in the escape energy curve. Our results of the charge distributions based on the microscopic calculations are consistent with the macroscopic ''dipole layer.''[34]

The electron-density difference in the cases with W tip at different separation S has also been calculated. Figure 8 shows the changes of this when $S = 10$ a.u. When the Al_1 atom locates at the original surface equilibrium site, there is no electron accumulation between the tip and the sample. However, when the Al_1 atom departs slightly from the sample surface, for example, $Z_1 = 1.2$ a.u., there is little accumulation of electrons between the tip and the sample. This indicates that there is attractive interaction between the top atom W_1 of the tip and the extracted atom Al_1, as the Al_1 atom departs slightly from the sample surface. The accumulation of electrons between the tip and the sample increases with the increasing of the height Z_1 of the extracted atom Al_1. When $Z_1 = 3.6$ a.u., strong bonds are formed between the W_1 and Al_1 atom, and the energy of the system is minimized. Comparing the changes of electron-density difference with the increasing of Z_1 in this case to that in the case of $S = \infty$, it can be found that the polarization of electron distribution around the extracted Al_1 atom occurs earlier, owing to the interaction of the W tip. The interaction between the dipole of the Al_1 atom and the dipole layer of the sample surface leads to the lowering of the energy of the system. This is the reason that the turning point in the escape energy curve (see Fig. 2) for $S = 10$ a.u. occurs at the lower position ($Z_1 \approx 2.0$ a.u.)

The effects of external bias on the electron distribution are also calculated. The results for the case of $S = 12$ a.u. are shown in Fig. 9. The most important is that the changes induced by the external electric field (when $V_s \leqslant 4$ V) are very small; they are in the order of one-tenth of the electron-density scale as in Figs. 6 and 8. But the changes are increased as the bias is enlarged. When the extracted Al_1 atom locates near the sample surface, for example, $Z_1 = 1.2$ a.u., comparing to the case without external field, the electron density in the region between the Al_1 atom and the neighbor Al atoms is increased, but that in the region above the Al_1 atom is decreased, if a positive bias is applied to the sample. When the Al_1 atom is extracted to a higher position, for example, $Z_1 = 6.0$ a.u., a vacancy is formed on the Al(111) surface. Comparing to the case without external field, the electron density in the vacancy and in the region under the Al_1 atom is increased, but that in the region above the Al_1 atom is also decreased, when a positive bias is applied to the sample. The reason is that the electrons are attracted by the positive bias and transferred from the upper part to the lower part of the Al_1 atom. However, the electron density in both the region above and below the Al_1 atom is decreased, when the Al_1 atom locates at the ''equilibrium'' site on the W tip (i.e., the separation between the Al_1 and the W_1 is about 4.8 a.u.). In this case, the Al_1 atom is already regarded to be associated with the W tip.

IV. CONCLUSION

Based on the discrete variational method with the local-density-functional approximation, we chose cluster models to simulate the extraction of a single Al atom from the Al(111) sample surface by a STM W tip with and without external bias voltages. In the cluster model, the detailed geometric structure of the tip and the sample can be taken into account, especially the tip with an active site. The external potential produced by the applied bias can be treated with appropriate boundary conditions of the tip and the sample. The HOMO of the cluster that corresponds to the Fermi level in the bulk can be automatically determined according to the Fermi statics. Therefore, the atom extraction process in a real STM manipulation can be simulated reliably with the DVM-LDA.

Based on the DVM-LDA, the extraction of a single Al atom from the Al(111) surface has been studied. The following conclusions have been obtained.

(i) The ''chemical interactions'' between the tip and the sample, which are close related with the tip-sample separation and the relative position of the tip to the sample, play an important role in the atom extraction processes. When the W tip approaches to the sample with the separation $S = 10$ a.u. (5.3 Å), the activation barrier lowering occurs through chemical interactions between the tip and the sample without any external electric fields; more specifically, the activation barrier for the Al atom extraction decreases from 3.98 eV (without tip) to zero as shown in Fig. 2. For various combinations of the tip and the sample, the chemical interactions at small separations are important for the single-atom manipulations and deserve further study, especially based on the present ''cluster model'' calculation of DVM-LDA.

(ii) The polarity and the value of the external bias are other important factors for the manipulations of a single atom in the STM with electric fields near the threshold. The extraction of a single Al atom is made easier if the sample is applied with positive bias, and it is made more difficult if the tip is applied with positive bias (as shown in Fig. 4). The

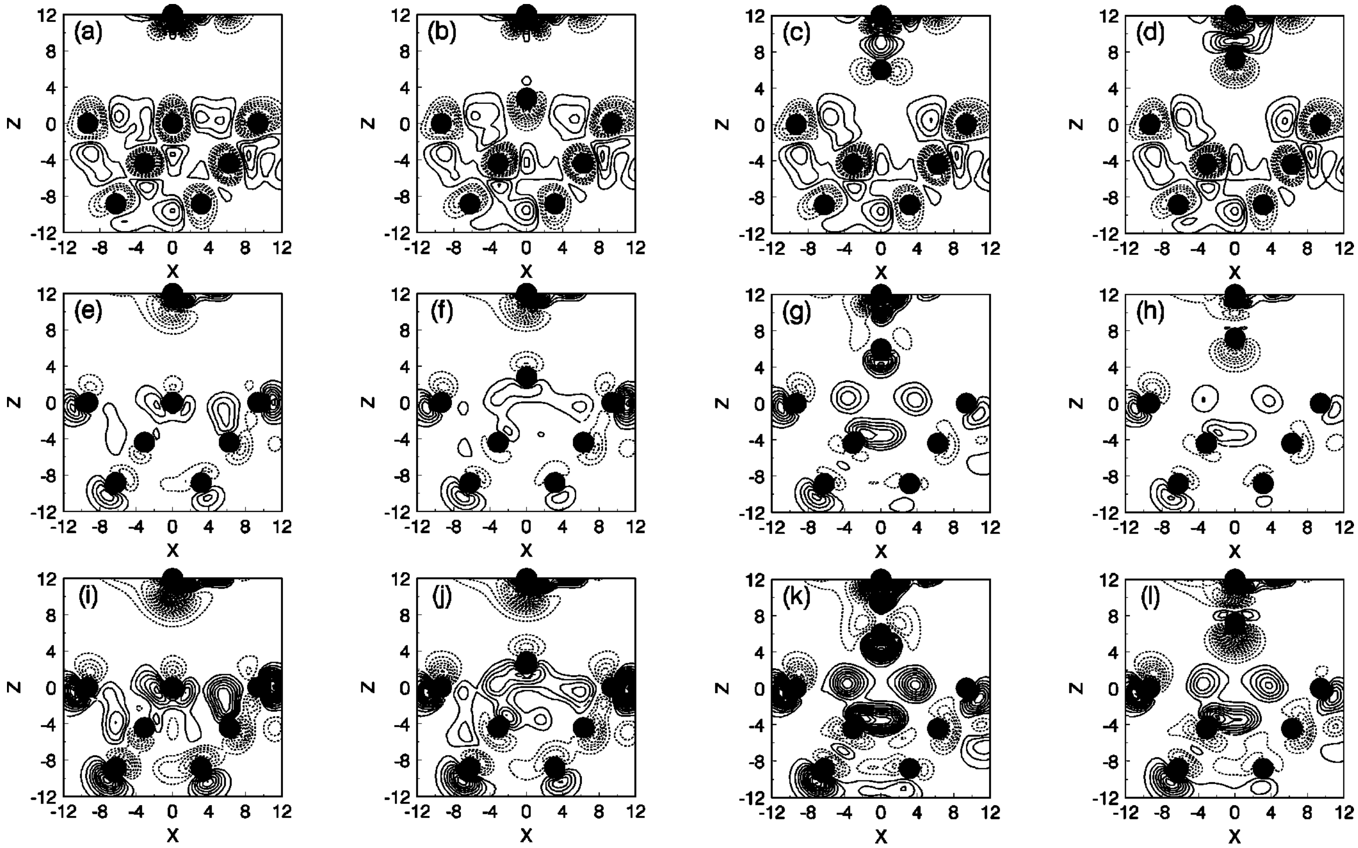

FIG. 9. The electron-density difference of the system [(a),(b),(c), and (d)] and the changes induced by the external bias [(e),(f),(g), and (h) for $V_s = 2$ V; (i),(j),(k), and (l) for $V_s = 4$ V] when the Al_1 atom is extracted from Al(111) surface to the heights: $Z_1 = 0.0$, 2.8, 6.0, and 7.2 a.u. The tip-sample separation $S = 12$ a.u. The solid and dotted lines represent the increase and decrease of electrons. The contour spacings are $0.001e$ (a.u.)$^{-3}$ for the electron-density difference, and $0.0001e$ (a.u.)$^{-3}$ for the changes induced by the external bias.

main reason is that the extracted Al atom acquires a net positive charge irrespective of polarity of the bias when the Al atom escapes from Al(111) surface. The net charge is only a few tenths of a unit charge $|e|$ and varies with the height Z_1 of the Al atom. Therefore, the extracted atom cannot be considered as an isolated bare ion. The field evaporation models[4,5,7,12,13] based on the bare ion treatment should be modified in the case of the STM atom extraction; especially, in the high-field cases, the chemical bonds between atoms are broken, and a cluster of atoms may be extracted. In this case, the polarity of external bias is not irrelevant for atom extraction as pointed out by Akpati *et al.*[20]

As the tip-sample separation S decreases, the threshold of electric field for the single Al atom extraction is decreased because of stronger ''chemical interactions'' involved. When the tip-sample separation S is fixed at 12 a.u. (6.3 Å), the Al atom cannot be extracted from the sample surface without external field. In order to extract out a single Al from the Al(111) surface, a positive least 4 V bias must be applied to the sample as shown in Fig. 5 (the corresponding threshold of the electric field about 0.6 V/Å). When the tip-sample separation S is decreased to 10 a.u., the threshold is decreased to zero (see Fig. 4). Furthermore, the extracted Al atom can be put back on the Al(111) surface by applying a positive bias to the tip (i.e., a negative bias on the sample). In addition, since our cluster model calculations can treat appropriately the geometries of the tip and the sample with external fields, lateral effects[7] of single-atom manipulations by the action of the external field can be studied and will be published elsewhere.

(iii) It is impossible to remove the W atom from the W tip in the system composed of the W tip and the Al sample, because of a much larger activation barrier (about 5.5 eV). It would deserve further studies to find out various tip-sample combinations systematically, especially based on the present cluster model of DVM-LDA.

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