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Effects of an electric field in atomic manipulations

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Some recent scanning-tunneling-microscopy (STM) experiments on atomic-scale manipulation of material surfaces are explained in terms of high-temperature field evaporation, directional walks in an applied field gradient, and the formation of liquid-metal cone, etc. The evaporation fields for metals and the charge states of ions formed by an electric field in the STM configuration are shown to depend on the tip-to-sample distance. The possibility of field evaporating as negative ions is also considered. We find this possibility exists especially for alkali metals and adsorbed atoms of large electron affinity and noble gases. Favorable physical conditions for atomic manipulations are also discussed. In addition, a method for creating a thermally stable top surface layer with an atomic pattern of embedded foreign atoms of one's design, using electric-field manipulations and atomic replacement, is described.

I. INTRODUCTION

One of the subjects of great current interest in scanning-tunneling-microscopy (STM) research is nanolithography and the manipulation of atoms and molecules on solid surfaces.[1,2] It is now possible to slide and position single Xe atoms on a nickel surface by using the tip-atom interaction,[3] to manipulate adsorbed atoms and molecules to diffuse toward the probing tip by applying voltage pulses to the tip,[4] to impress or deposit molecules and mounts of atoms on a surface[5] or to remove them from the surface by applying voltage pulses,[6] etc. These and other atomic-scale manipulation experiments[7] open up additional possibilities of designing man-made materials and molecules on the atomic scale. Most of the interpretations presented are, however, rudimentary. In this report, I will present some explanations for the various phenomena observed in these STM experiments, and also suggest additional methods of atomic manipulation with the STM.

II. FIELD EVAPORATION IN THE STM CONFIGURATION

A. General discussion of the tip-atom-sample interaction

Field evaporation was used by Gomer to explain the sudden change of tunneling behavior observed in many early STM experiments.[8] The biasing voltage used in a typical STM experiment appears to be too low to produce a sufficiently high electric field for field-evaporating surface atoms. An alternative explanation is that tip changes by a transfer of atoms between the tip and the sample by a tip-atom-sample interaction or diffusion of surface atoms or chemisorbed atoms occur during the scanning. Field evaporation was also thought to be responsible for transferring mounts of Au tip atoms to a sample surface.[5(a)] Field evaporation, or field desorption, is a basic physical process in field-ion microscopy (FIM).[9] While our understanding of this phenomenon is by no means complete, simple theoretical models are available for explaining many experimental observations in FIM with a considerable degree of success. The "evaporation fields" of most metals can now be calculated to an accuracy of better than ±10% using these surprisingly simple models, and the charge states of the most abundant ion species derived from these models also agree with field-ion mass spectroscopic observations. It is therefore worthwhile to extend these theoretical models of field evaporation appropriate for the simple isolated tip geometry of the FIM to the tip-sample configuration of the STM. To facilitate our subsequent discussions, let us consider first how an adatom on the tip surface interacts with both the tip and the sample in the STM.

For simplicity, we will assume that the tip consists of a facet parallel to the sample surface. The facet size is large compared to the range of the atom-surface interaction and the tip-sample distance. Therefore the tip can be approximated by a flat surface. This assumption is not essential, but it simplifies our discussion of the basic interactions in the tip-atom-sample system. When the tip-sample distance d is comparatively large, the tip-atom interaction potential energy curve U_{at} and that of the atom-sample interaction U_{as} do not overlap significantly as shown in Fig. 1(a). Near room temperature, the binding energy of the atom with the tip Λ_t is too strong for the chemisorbed adatom to be thermally activated to the potential well of the atom-sample interaction. However, when the tip-sample distance d is shortened, U_{at} and U_{as} start to overlap. Now the total potential-energy curve of the atom interacting with both the tip and the sample, $U_a = U_{at} + U_{as}$, shows a hump of height Q_0 from the tip side and $Q_0' = Q_0 + (\Lambda_s - \Lambda_t)$ from the sample. At room temperature where most STM experiments were performed, the rate of transfer of the atom from the tip side to the sample side $\kappa = \nu \exp(-Q_0/kT)$ becomes 1 s^{-1} if Q_0 is reduced to about 0.772 eV when ν is taken to be $\sim 10^{13}$ s^{-1}. An atom at the sample side can also be

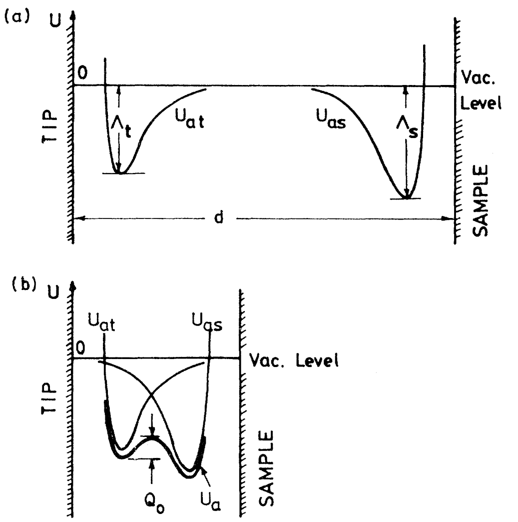

FIG. 1. When the tip to sample distance d is large, the atom-tip and atom-sample interactions U_{at} and U_{as} do not overlap significantly as shown in (a). When d is small, the two start to overlap and U_a, which is the sum of U_{at} and U_{as}, exhibits a double-well structure having a small activation barrier. The atom can either be transferred from the tip to the sample or from the sample to the tip, as shown in (b).

thermally activated over to the tip surface, although with a lower rate of $\kappa' = \nu \exp(-Q_0'/kT)$. Thus, by simply bringing the tip and the sample sufficiently close to one another, an atom or molecule can be transferred either from the tip to the sample or from the sample to the tip, though at a different rate. The probability of finding the atom on the tip side and that on the sample are $\exp(Q_0')/[\exp(Q_0)+\exp(Q_0')]$ and $\exp(Q_0)/[\exp(Q_0)+\exp(Q_0')]$, respectively. It is obvious that by stopping the probing tip at a desired site of the sample surface and then properly pushing the tip to approach the sample temporarily, an atom or a molecule can be transferred either from the tip to the sample or from the sample to the tip according to these probabilities. If Λ_t and Λ_s are comparable in magnitude, an atom or molecule can be impressed from the tip to the sample surface or be removed from the sample surface to the tip with nearly equal probability. This explains the observation of Foster, Frommer, and Arnett.[5(b)] It also suggests that one can deposit atoms from the tip to the surface in a controlled manner using the STM, provided that Λ_t is smaller than Λ_s, or to remove an atom from the sample surface to the tip if Λ_s is smaller than Λ_t. Unfortunately, a continuous transfer of atoms is difficult since it is very difficult to create an adatom repeatedly at the tip surface for transferring to the desired locations of the sample surface. One solution may be the use of high-temperature field evaporation and a field-gradient-induced surface diffusion of atoms from the tip shank to the tip apex, as will be discussed.

B. Field evaporation in the STM configuration

We will consider only the case where both the tip and the sample are metals, even though similar arguments can be developed along the same line for other systems. There are two well-accepted theoretical models of field evaporation of metals which are known as the charge-exchange (CE) model[10] and the image-hump (IH) model.[11] Details of these models can be found in the literature.[9] For our purpose here we will adopt these models in their simplest forms so that essential physics can be more easily understood. In the CE model under FIM geometry, shown in Fig. 2(a), the activation energy of field evaporation is given by $U_i(F)$ or U_a at z_c, which is the intersection point of the atomic curve U_a and the ionic curve $U_i(F)$ in the applied field F, minus U_a at the equilibrium position of the atoms. The ionic curve $U_i(F)$ is related to $U_i(0)$, the ionic potential in zero field, by $U_i(F) = U_i(0) - neFz$, where $U_i(0)$ is given by

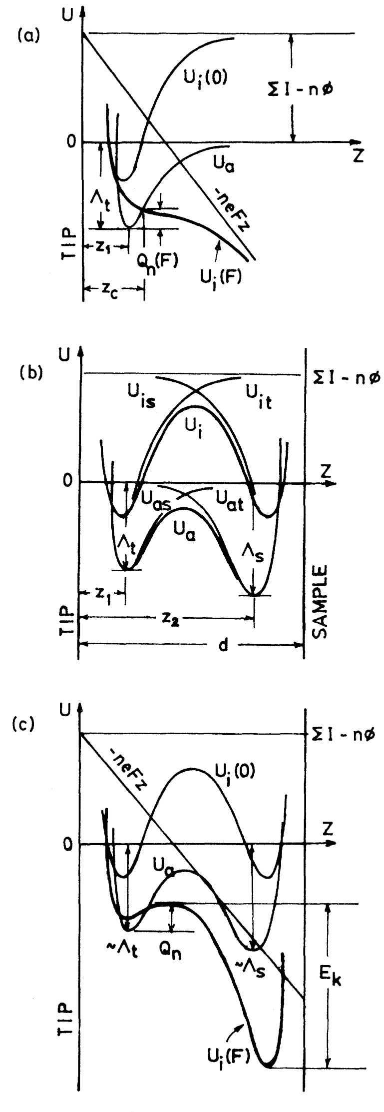

FIG. 2. (a) A potential-energy diagram for field evaporation of metals in an isolated tip geometry of the FIM. (b) Ionic and atomic potentials in the STM configuration in the absence of an applied field. (c) Ionic and atomic potentials in the STM configuration when a positive field F is applied to the tip.

$-n^2e^2/4z+U_{\text{rep}}+\sum_{i=1}^{n}I_i-n\phi$. The first term is the image potential, the second term is the repulsive potential of the ion-surface interaction, and the last two terms account for the energy needed to produce an ion far away from the surface in the absence of an applied field which requires $\sum_{i=1}^{n}I_i$, the total ionization energy of the atom to the $n+$ charge state, minus $n\phi$, where ϕ is the work function of the surface. This is because n electrons are returned to the surface at the Fermi level, thereby regaining an energy of $n\phi$. Similar to that discussed in the preceding paragraph, in the STM configuration, when the tip-sample distance d is shortened, both the atomic potential curve and the ionic potential curve are changed. In the absence of an applied field, the atomic and ionic curves are simply the sum of U_{as} and U_{at} and that of U_{is} and U_{it}, respectively, as shown in Fig. 2(b). When a positive electric field is applied to the tip, $-neFz$ is added to the ionic potential, and these potential curves are modified as schematically shown in Fig. 2(c). As a result of the applied electric field, the potential barrier a tip atom has to activate over to reach the sample is greatly reduced. On the other hand, the potential barrier an atom at the sample surface has to activate over to reach the tip surface is greately increased. Field evaporation as positive ions thus can occur only from the positive electrode to the negative electrode, not the other way around, and vice versa.

An interesting question is how the evaporation field of a metal changes from the FIM geometry to the STM configuration, and how this field varies with the tip-sample distance d in the latter case. In field-ion microscopy, the low-temperature evaporation fields of metals are taken to be the fields to make $Q_n(F_{\text{ev}})=0$. They can be calculated by assuming that $U_{\text{rep}}(z_c)$ is negligible compared to the other terms in the CE model. As the repulsive force of the ion core should be a short-range force, this approximation is especially good if z_c is large, or if the field evaporation is done at a high temperature. The following equation gives very good agreement with experimental observations in field-ion microscopy:[12]

$$F_{\text{ev}}\simeq\frac{1}{nr_0}\left[\Lambda+\sum_{i=1}^{n}I_i-n\phi-\frac{n^2e^2}{4r_0}\right]=\frac{1}{nr_0}\left[\Lambda+\sum_{i=1}^{n}I_i-n\phi-\frac{3.6n^2}{r_0}\right]\ \text{V/Å}\ . \tag{1}$$

where r_0 is the atomic radius, taken to be the radius of ions in the 12-coordinated metal. In the IH model, one simply assumes that there exists a Schottky image hump which reduces the energy needed to produce an ion of charge state $n+$ by $(n^3e^3F)^{1/2}$. Thus the activation energy for field evaporation is given by $Q_n(F)=\Lambda+\sum_{i=1}^{n}I_i-n\phi-(n^3e^4F)^{1/2}$. Again, by taking $Q_n(F_{\text{ev}})=0$ in low-temperature field evaporation, one gets[13]

$$F_{\text{ev}}\simeq\frac{1}{n^3e^3}\left[\Lambda+\sum_{i=1}^{n}I_i-n\phi\right]^2=\frac{0.0692}{n^3}\left[\Lambda+\sum_{i=1}^{n}I_i-n\phi\right]^2\ \text{V/Å} \tag{2}$$

for the IH model. In these equations, energies are expressed in eV and distances in Å. These simple equations are very good for finding the charge states of the most abundant ions of metals which are the ion species with the lowest evaporation field among the species of different charge states. The evaporation fields calculated also agree with experimental values to better than ±10% for most metals. One can also make similar approximations and arrive at the following equations for calculating the evaporation fields of metals in the STM configuration at a temperature T and an evaporation rate κ:

$$F_{\text{ev}}^{\text{STM}}\simeq\frac{1}{nr_0}\left[\Lambda+\sum_{i=1}^{n}I_i-n\phi-\frac{3.6n^2}{r_0}-\frac{3.6n^2}{(d-r_0)}-kT\ln\left[\frac{\nu}{\kappa}\right]\right]\ \text{V/Å} \tag{3}$$

for the CE model, and

$$F_{\text{ev}}^{\text{STM}}\simeq\frac{0.0692}{n^3}\left[\Lambda+\sum_{i=1}^{n}I_i-n\phi-\frac{3.6n^2}{\left[d-\frac{1.90n^{1/2}}{F_{\text{ev}}^{1/2}}\right]}-kT\ln\left[\frac{\nu}{\kappa}\right]\right]^2\ \text{V/Å} \tag{4}$$

for the IH model. Here we do not assume $Q_n(F_{\text{ev}})=0$, but rather use $Q_n(F)=kT\ln(\nu/\kappa)$. In Fig. 3, the fields needed to field evaporate a few metals of interest to scanning tunneling microscopy at a rate of 1 s^{-1} at 300 K for various charge states as functions of the tip-sample distance d are shown. The evaporation field of Au as Au^+ is considerably lower than that as Au^{2+} at all tip-sample separations except when d is less than 4 Å. For W, the field needed to create $3+$ ions is the lowest, thus $3+$ is the expected charge states in field evaporation of W. Although not shown in this figure, for most metals, however, the most abundant ion species are the $2+$ ions, regardless of d. All the asymptotic values when d is large are in excellent agreement with FIM observations. It is remarkable that the CE model and the IH model give nearly identical results for nearly all metals for all charge states, despite the fact that Eqs. (1) and (2), and also (3) and (4), have completely different forms. A few exceptions are Au^+ and Ni^{2+}, etc. What seems to be unexpected is that the evaporation field is only slightly affected by the proximity of the tip and the sample in the STM. It reduces by only $\simeq 30\%$ at a very close separation of $d=6$ Å. Only when $d<4$ Å does the field reduces to less than one-half that appropriate for field-ion microscopy. At this distance, transfer of atoms by tip-atom-sample interaction should already be possible and the idea of field evaporation is somewhat obscured, but the field may still dictate the direction of the atom transfer.

Another interesting point is that when d is very small, the charge state of the most abundant ion species tends to shift to the higher one, as seen in the case of Au. We are, however, not certain that these simple models remain valid at such a small d when the two models also start to deviate significantly. Also at $d = 6$ Å, the evaporation fields decrease by $\sim 20\%$ when the temperature is raised from 100 to 1000 K.

In an experiment by Li *et al.*,[6(b)] atoms on the sample surface are found to disappear by applying a negative voltage pulse to the STM tip. They explained this phenomenon to be produced by a heating-effect-induced explosive evaporation. However, a calculation indicates that the temperature rise is much too low to produce an explosive thermal evaporation.[14] One must recognize that in the STM configuration, because of the proximity of the tip and the sample, the field strength at the sample surface is not much lower than that at the tip surface. Thus it is possible that these atoms on the sample surface are field evaporated by the positive field at the surface, enhanced by the heating effect of the field-emitted electrons from the tip.

C. Field evaporation of negative ions

An interesting question is whether or not one can field evaporate or field desorb atoms from a surface as negative ions by applying a negative field to the surface. In an applied negative field, field electron emission will start around 0.3 V/Å. When the field reaches near 0.6 V/Å the field-emission current density will be large enough to melt tips of most metals by a resistive heating. In the STM configuration, these fields are further reduced by the tip-electron-sample interaction, or the two image potentials, similar to field evaporations. Thus, even though in principle atoms can be field evaporated as negative ions, if the evaporation field required exceeds a threshold field F_{th}, which should be less than 0.5–0.6 V/Å for most metals for a slender tip, this will not occur. This does not exclude field evaporation of negative ions from the sample surface or adsorbed atoms on a dull tip, however. As far as this author is aware, field evaporation of metals by

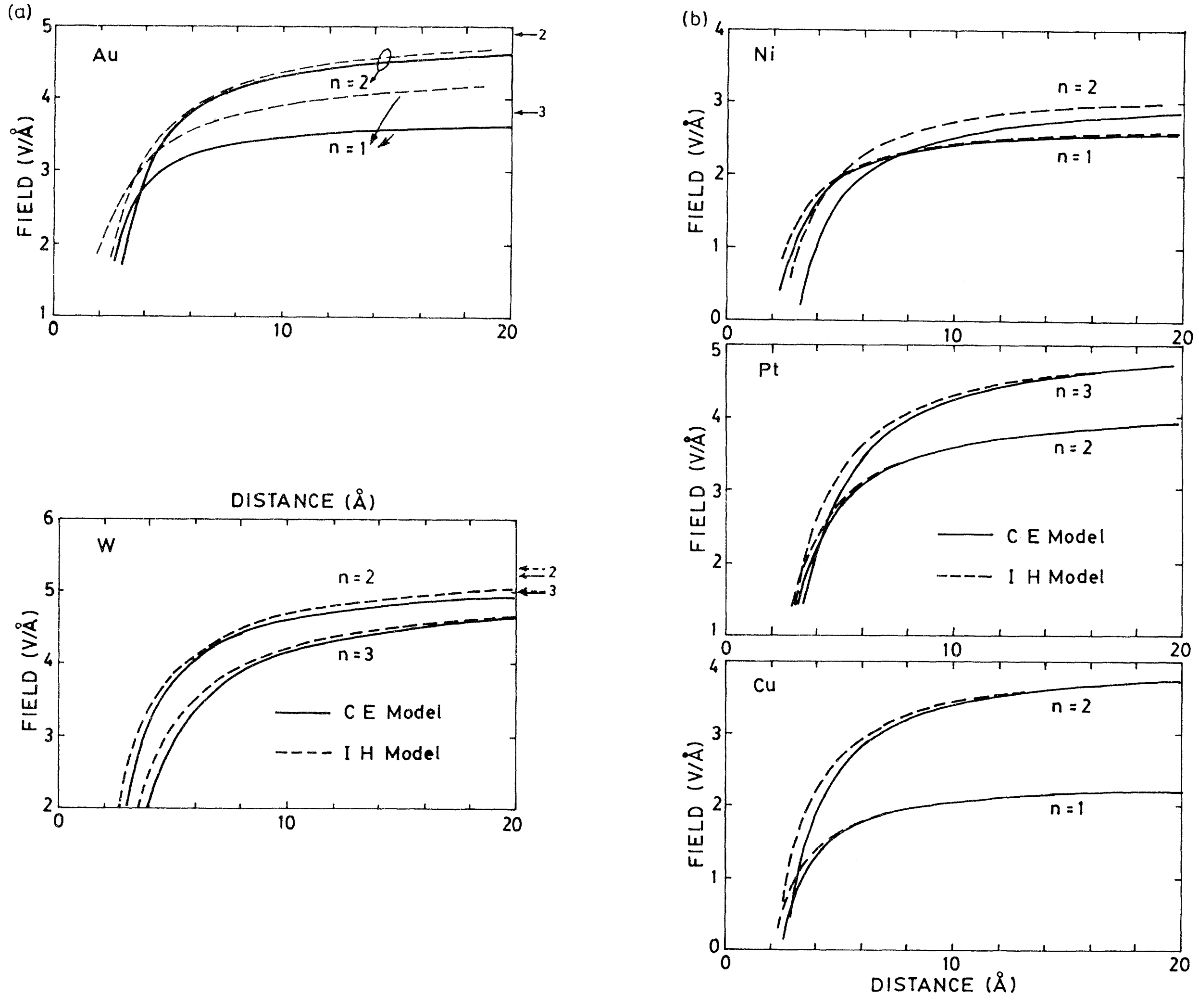

FIG. 3. (a) The fields needed to field evaporate Au as Au^{+} and Au^{2+} and W as W^{2+} and W^{3+} at a rate of 1 s^{-1} at 300 K as functions of the tip-sample distance d is the STM configuration. (b) Also for Ni, Pt, and Cu.

a negative applied field has not been observed in FIM before. However, we will try to calculate the fields required for field evaporating metals in a negative field using similar models to see whether in the STM configuration, field evaporation of negative ions may become possible.

It will be clear from subsequent discussion that there is little chance that a multiply charged negative ion can be created by field evaporation since the second electron affinity of atoms should be very small or simply does not exist for many atoms. Thus our discussion will be confined to the field evaporation of singly charged negative ions. The method, however, can be easily generalized. To take an atom from a surface to free space requires an energy of Λ, the binding energy of the atom with the surface. To produce a negative ion, we take an electron from the Fermi level and attach it to the atom. This process requires an energy of $(\phi - E_{\rm aff})$, where ϕ is the work function of the surface and $E_{\rm aff}$ is the electron affinity of the atom. In other words, to produce a negative ion from a surface in the absence of an electric field, an energy of $(\Lambda + \phi - E_{\rm aff})$ is required. For comparison, the energy needed to produce a positive ion of $n+$ charge requires $(\Lambda + \sum_{i=1}^{n} I_i - n\phi)$. The ionic potential energy of a negative ion in a negative field is identical to that of a positive ion in a positive field; thus theoretical models for ordinary field evaporation can be adopted to field evaporation of negative ions. Now the CE model and the IH model can be directly applied to the present case if the $(\Lambda + \sum_{i=1}^{n} I_i - n\phi)$ term is replaced with the $(\Lambda + \phi - E_{\rm aff})$ term. The evaporation fields of materials as negative ions in both the FIM and STM configurations can be calculated from Eqs. (1)–(4) by such a replacement. In Fig. 4, we show the fields required to field evaporate Cu, Ag, Au, Zn, and Pb as $1-$ ions a a rate of 1 s^{-1} at 300 K in a negative field in the STM configuration. It is remarkable again that the two models give a nearly identical result for all these metals at all distances. Only when d is less than ~ 6 Å do the two models give a slightly different result. From these curves, it is quite clear that negative field evaporation is unlikely to occur for most metal tips since the fields required exceed $F_{\rm th}$ unless d is exceedingly small, less than 3 Å. At this distance, a transfer of atoms by direct atom-surface interaction should already be possible. Only for very-low-melting-point metals, such as Zn and Au, such a possibility exits if d is less than ~ 5 Å. Negative ions of alkali metals and chemisorbed atoms of large electron affinity such as Cl, Br, or I, and Zn, Au, as well as physisorbed atoms and molecules, however, can

TABLE I. Evaporation fields (300 K, 1 s^{-1}) in STM configuration ($d = 6$ Å).

Element	Λ (eV)	ϕ (eV)	r_0 (Å)	I_1 (eV)	I_2 (eV)	I_3 (eV)	$E_{\rm eff}$ (eV)	F^{1+} (V/Å)	F^{2+} (V/Å)	F^{3+} (V/Å)	$\lvert F^{1-} \rvert$ (V/Å)	Ion species
Li	1.65	2.5	1.56	5.39	75.64	122.45	0.62	0.42	20.65	36.07	0	Li^{-}
Be	3.33	3.9	1.13	9.32	18.21	153.89	<0	3.59	2.92	40.40	3.13	B^{2+}
Na	1.13	2.3	1.91	5.14	47.29	71.64	0.55	0.23	9.72	16.17	0	Na^{-}
Al	3.34	4.1	1.43	5.99	18.83	28.45	0.46	0.81	2.09	3.22	2.90	Al^{+}
Fe	4.29	4.4	1.27	7.90	16.16	30.65	0.25	2.69	1.73	3.32	4.07	Fe^{2+}
Co	4.39	4.4	1.25	7.86	17.06	33.50	0.7	2.75	2.07	4.29	3.68	Co^{2+}
Ni	4.44	5.0	1.25	7.64	18.17	35.17	1.15	2.14	1.97	4.51	3.88	Ni^{2+}
Cu	3.50	4.6	1.25	7.73	20.29	36.83	1.23	1.78	2.80	5.61	2.46	Cu^{+}
Zn	1.35	3.8	1.39	9.34	17.96	39.72	0	1.98	2.44	6.20	1.01	Zn^{-}
Mo	6.81	4.2	1.40	7.10	16.15	27.16	1.0	3.99	2.67	3.25	5.89	Mo^{2+}
Rh	5.75	4.8	1.35	7.46	18.08	31.06	1.2	3.11	2.65	4.02	5.14	Rh^{2+}
Ag	2.96	4.6	1.45	7.57	21.49	34.83	1.3	1.30	3.09	5.24	2.21	Ag^{+}
In	2.60	(4)	1.66	5.79	18.87	28.03	0.3	0.37	1.96	3.20	2.53	In^{+}
Cs	0.83	(2)	2.73	3.89	25.1	35	0.47	0	2.82	4.43	0	Cs^{-}
Ta	8.09	4.2	1.47	7.89	16	22	0.6	5.28	3.35	2.59	7.67	Ta^{3+}
W	8.66	4.5	1.41	7.98	18	24	0.60	5.63	4.05	3.37	8.45	W^{3+}
Re	8.10	5.1	1.38	7.88	17	26	0.15	4.87	3.06	3.00	8.89	Re^{3+},Re^{2+}
Ir	6.93	5.3	1.36	9.1	17	27	1.6	4.81	2.93	3.08	6.44	Ir^{2+},Ir^{3+}
Pt	5.85	5.3	1.39	9.0	18.56	28	2.13	3.89	3.08	3.45	4.88	Pt^{2+}
Au	3.78	4.3	1.44	9.23	20.5	30	2.31	3.23	3.81	4.68	1.71	Au^{-}
Pb	2.04	4.1	1.75	7.42	15.03	31.94	1.1	0.96	1.12	3.28	1.36	Pb^{+}
C	7.37	(4)	0.92	11.26	24.34	47.87	1.27	10.04	8.54	13.22	4.79	C^{-}
Si	4.63	(4.2)	1.32	8.15	16.34	33.46	1.39	3.27	2.26	4.48	3.17	Si^{2+}
Ge	3.85	(4.2)	1.37	7.88	15.93	34.21	1.2	2.45	1.78	4.34	2.67	Ge^{2+}
He	~0	~4.5	1.1	24.6			<0	13.9			0	He^{-}
Ne	~0	~4.5	1.58	21.6			<0	8.4			0.6	Ne^{-}
Ar	~0	~4.5	1.88	15.8			<0	4.1			0.9	Ar^{-}
Kr	~0	~4.5	2.00	14.0			<0	3.0			1.0	Kr^{-}
Ke	~0	~4.5	2.17	12.1			<0	2.0			1.1	Xe^{-}

be produced by negative field evaporation. It also appears that evaporation of Na^- can occur by simply decreasing the tip-sample distance d and raising the temperature of the emitting surface without the need to even apply a negative field to the tip as can be seen in Fig. 4. For the sake of comparison, the fields needed to field evaporate Na as Na^+ at $1\ s^{-1}$ at 300 K as functions of d in the STM configuration are also shown. For Na, Zn, and Au, the fields needed to field evaporate as $1-$ions are lower than those of positive ions. In Table I, values of parameters used in these calculations are listed, and the most favorable ion species are also listed.

In general, the charge state of a field evaporating atom from the sample side (either -1 or $+1$ to $+3$) will be the one requiring the lowest field strength. For most metals, they are the positive charge states. Field evaporation from the tip side as negative ions is restricted to those requiring a field below ~ 0.6 V/Å since we have to worry about a tip melting. Field evaporation of flat samples and adsorbed atoms in STM is not subjected to this restriction. A general prediction will be difficult without the specifics of the system and the configuration.

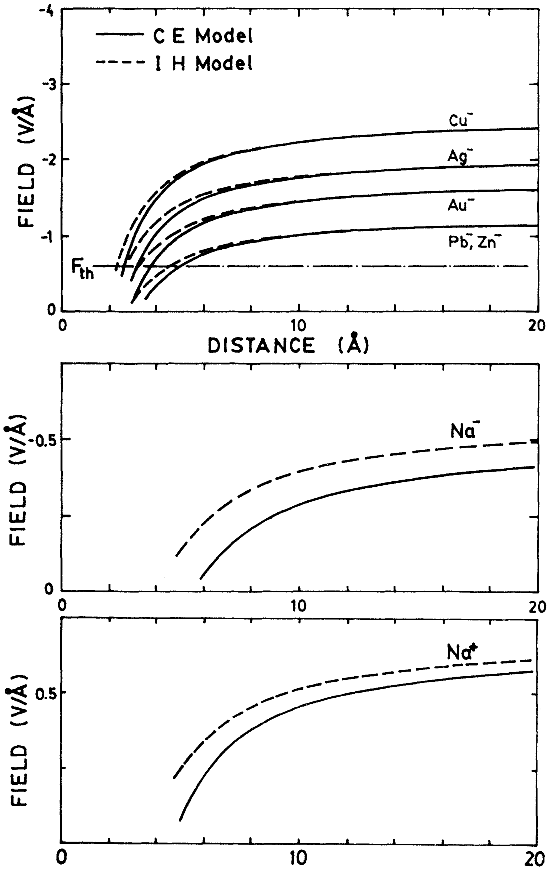

FIG. 4. The fields needed to field evaporate a few metals as singly charged negative ions at 300 K at a rate of $1\ s^{-1}$ as functions of the tip-sample distance in the STM configuration. The fields needed for Pb^- and Zn^- are too close together to draw separately. For comparison, fields for evaporation of Na as Na^+ are also shown.

III. LIQUID-METAL CONE FORMATION

From the above discussions, we believe that the recent observation by Mamin, Guethner, and Rugar[5(a)] of a transfer of Au atoms from the tip to the sample by applying a voltage pulse, either positive or negative, to the sample is unlikely to be produced by field evaporation. The voltage used in the experiment, only a few volts, appears too low for field evaporation; especially when negative pulses are applied to the sample side. One possible explanation of this observation is that when a positive voltage pulse is applied to the sample, the tunneling current from the tip is suddenly greatly increased by the onset of field electron emission which produces a heat pulse to the tip by a joule heating. In a high electric field, regardless of whether it is a positive field or a negative field, atoms at the tip shank will diffuse to the tip apex by a field-gradient-induced surface diffusion.[15,16] If the temperature reaches near the melting point, a cusp-shaped liquid-metal cone, generally called the Taylor cone,[17] will be formed by either this diffusion or by a hydrodynamic flow of atoms, as illustrated in Fig. 5. Because of the proximity of the tip and the sample, this cusp-shaped cone will touch the sample surface. When the voltage pulse is over and the tip starts to cool down, the neck of the liquid-metal cone will be broken by surface tension, as shown in Fig. 5(c), leaving a amount of Au atoms on the sample surface. One can expect the first mount to be more difficult to produce if one starts from a dull tip. Once the tip settles into a steady-state cusp shape shown in Fig. 5(c), a reproducible result should be readily obtained. As the field at the sample surface is not very different from the tip surface due to their proximity, the same effect can occur by applying a negative voltage pulse to the sample. In this case, the tunneling electrons originate from the sample surface.

IV. FIELD-GRADIENT-INDUCED SURFACE DIFFUSION

The field-gradient-induced surface diffusion not only can be used to sharpen the tip and create a cusp-shaped cone; it can also be used to attract adsorbed atoms on the sample surface to the position directly under the probing tip as has been demonstrated by Whitman *et al.*[4] In fact, using this effect, the surface-induced dipole moment and the effective polarizability of adsorbed atoms has been measured quantitatively in FIM studies.[16] Figure 6 explains the basic mechanism of this phenomenon. In the absence of a voltage pulse, the field at the sample surface produced by the probing tip is too small to have an effect. Thus the adatom sees a horizontal but periodic surface potential as shown in the upper potential curve of Fig. 6. When a voltage pulse is applied to either the tip or the sample, a field with a large gradient will be created at the sample surface around the tip due to the asymmetry of the tip-sample configuration. As a result, the polarization energy $E_p(r) = -\boldsymbol{\mu}\cdot\mathbf{F} - \frac{1}{2}\alpha F^2$ is r dependent. When this energy is added to the periodic surface potential, the potential-energy curve becomes inclined toward the

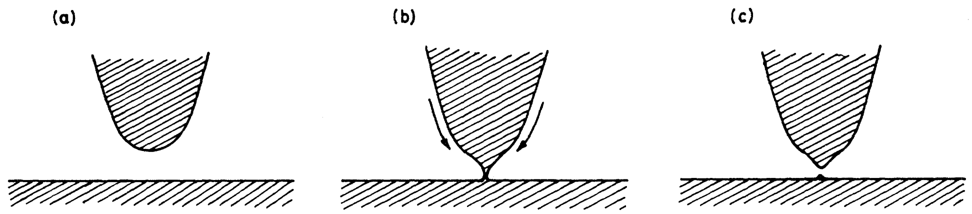

FIG. 5. Diagrams illustrating how piles of metal atoms can be deposited on a sample surface by applying either negative or positive voltage pulses to either the sample or the tip. When a high voltage pulse is applied, field electrons are emitted either from the tip or the sample according to the polarity of the pulse. This electron current will heat up or even melt the tip. Because of the field gradient existing at the tip surface, atoms will migrate from the tip shank to the tip apex either by a directional surface diffusion or by a hydrodynamic flow of atoms, resulted in the formation of a liquidlike-metal cone, which will touch the sample. When the pulse is over and the liquidlike-metal cone cools down, the neck is broken by surface tension leaving a mount of tip atoms on the sample surface.

center where the field is the highest, as shown in the lower potential curve of Fig. 6. Thus surface diffusion becomes directional, or adatoms always move from the outer region toward the tip. As the dominant term in $E_p(r)$ is the $\frac{1}{2}\alpha F^2$ term for most atoms, this effect can occur for either polarity of the voltage pulse. The directional walk is also a thermally activated process, although the activation energy of surface diffusion toward the center is now greatly reduced by the polarization energy, thus diffusion can start at a much lower temperature. In addition, when a voltage pulse is applied, the tunneling current is greatly increased with the addition of the field emission current which will heat the sample surface slightly, thus further promoting the occurrence of the directional surface diffusion.

V. ATOMIC DESIGN OF A THERMALLY STABLE TOP SURFACE LAYER

From the above discussions, we know that there are several methods of atomic manipulations one can use to design on atomic-scale surfaces of materials, namely a direct tip-atom-sample interaction, high-temperature

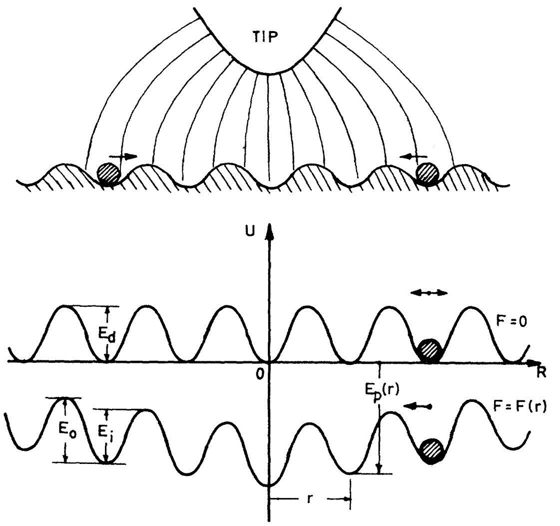

FIG. 6. Diagrams explaining why adsorbed atoms will migrate toward the tip by applying voltage pulses to the tip or to the sample. Regardless of the polarity of the voltage pulses, the adsorbed atoms will always migrate toward the center where the field is the highest. In the absence of a high voltage pulse, surface potential is periodic and horizontal as shown in the upper potential curve. Surface diffusion is in random directions. When a voltage pulse is applied, due to the nonuniformity of the field, the polarization energy is larger near the tip because of the higher field. As a result the surface potential is now inclined toward the center. Migration of adatoms is thus always toward the center.

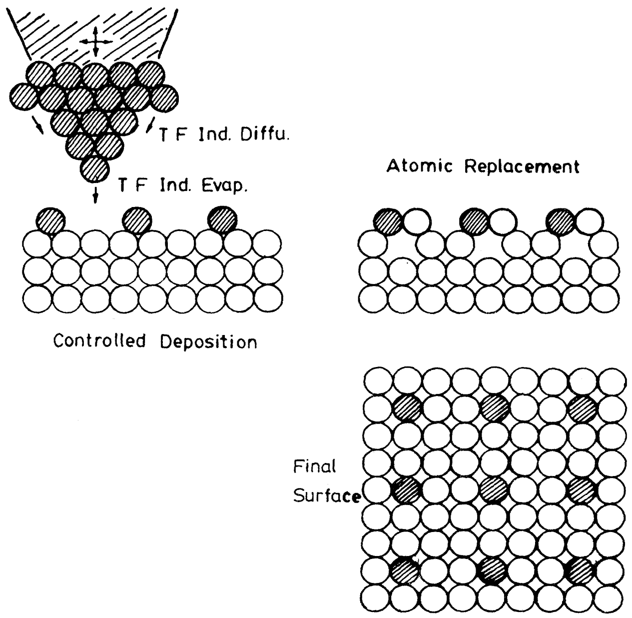

FIG. 7. Diagram describing how a thermally stable atomic pattern of substitutional foreign atoms of one's design can be created in the top surface layer by the electric-field effects and the atomic-replacement surface diffusion. First, atoms are deposited at the desired locations of the sample surface by high-temperature field evaporation. The same voltage pulses will induce a continuous supply of tip atoms from the shank to the apex by a temperature- and field-gradient-induced surface diffusion. Second, the sample surface is heated to induce an atomic-replacement surface diffusion. Third, the exchanged sample atoms are removed from the surface by a method described in the text.

field evaporation, field-gradient-induced surface diffusion, and field-emission-assisted liquid cone formation, etc. Using these atomic manipulations with the electric field in the STM, I would like now to suggest method for producing a thermally stable top surface layer with an atomic pattern of substitutional foreign atoms of one's design in it. Tip atoms can be deposited on the desired locations of the sample surface, one or a few at a time, by high-temperature field evaporation of the tip by applying voltage pulses to the tip, or the sample. The polarity of the pulses can be chosen according to Table I. During the deposition, the tip will be slightly heated by the tunneling electrons, mostly field-emitted electrons, from the sample. A temperature and field-gradient-induced surface diffusion will continue to supply atoms from the tip shank to the tip apex provided a proper experimental condition, i.e., by adjusting the tip-to-sample distance and the magnitude of the voltage pulses, can be found. Once a proper experimental condition is found and a desired pattern of tip atoms is deposited on the sample surface, the sample can be slightly heated to produce an atomic-replacement surface diffusion,[18] thereby the deposited tip atoms and the neighbor substrate atoms are exchanged. The atomic-replacement surface diffusion has been a subject of considerable interest and has been carefully established through recent field-ion-microscope experiments. It can occur for refractory metals at a temperature below ~300 K. Now the exchanged substrate atom will have to be removed from the surface by either the method described by Whitman *et al.*,[4] or by using another tip with a strong tip-atom interaction as has been described earlier. The atomic-replacement surface diffusion can occur below room temperature for refractory metals.[18] When the exchanged substrate atoms are carefully removed, the embedded foreign atoms will not move until the bulk diffusion temperature is reached, which is usually several hundred K. Thus the surface atomic pattern of substitutional foreign atoms so designed and created should be thermally stable up to several hundreds K. The procedures of this method are illustrated in Fig. 7. I believe that the atomic design of man-made materials and molecules can become a little easier by having a good understanding of the basic mechanisms of elementary atomic manipulation steps in the STM experiments as well as the energetics of various surface atomic processes.

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