Field Evaporation between a Gold Tip and a Gold Surface in the Scanning Tunneling Microscope Configuration

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(Received 31 August 1993)

Mounds of gold atoms of horizontal size less than 200 Å and height < 20 Å, and pits of width < 50 Å and depth < 10 Å can be produced on a gold surface with nearly equal probabilities by applying voltage pulses to a gold tip in the scanning tunneling microscope. We study the effects of the polarity and the height of the applied voltage pulses, and those of the atmospheric environments. Our data show that field evaporation can occur both in positive and negative fields, but in ultrahigh vacuum, a tip can sustain itself only if it is in negative polarity.

PACS numbers: 79.70.+q, 61.16.Ch, 61.16.Fk, 68.45.Da

Through the development of atomic resolution microscopes, scientists can now routinely see the atomic structures of solid surfaces. Recently it has also been demonstrated that one can control and manipulate individual atoms on a surface [1–4]. Although atomic manipulation is a technique still in its early stage of development, it has already opened up a new horizon for creating artificial molecules and material structures of the atomic dimension. Whereas the technique is developing rapidly, our understanding of the physical processes involved in these manipulations is by no means complete. One of a few physical processes available for atomic and molecular manipulations is field evaporation [5–7], which is a basic physical process in field ion microscopy (FIM) [8]. Compared to intrinsic atomic interactions, or the so-called chemical effects, field evaporation may offer a better control of the direction and the rate of the atom transfer. Recently, Mamin and co-workers [6] observed a transfer of atoms from a gold tip to the sample surface in air and also considered the possibility of both positive and negative field evaporation of gold in the scanning tunneling microscope (STM). Kobayashi *et al.* [7] conclude from their experimental data that silicon can field evaporate in both negative and positive fields at nearly the same field strength. Tsong [9] extends field evaporation models of FIM to the STM configuration and concludes that for some elements, negative field evaporation may be favored. Miskovsky and co-workers [10,11] further show that gold and silicon favor negative field evaporation as $2-$ ions. Lang reports a first principle calculation of the atom transfer process for Si on a jellium surface. He concludes that due to the proximity of the tip and the sample in the STM, atoms never reach an integral ionic state during the transfer process [12]. A very recent report by Pascual *et al.* [13] considers another mechanism for the creation of gold mounds through the contact of the tip and the substrate. Although it is a subject of great current interest, few detailed experimental studies of field-induced transfer of gold atoms in STM are performed in UHV. Here, we report an STM study of the transfer of gold atoms between a gold sample and a gold tip in UHV and in air. We focus on the effects of positive and negative fields, and also on other factors affecting the repeatability of the atom-transfer process.

Our STM is a commercial one designed to work both in UHV and in air. For this study, we connect an external pulse generator to the tip. Voltage pulses of a few volts of either polarity and width 70 ns can be applied directly to the tip in a predesigned pattern of 48 locations using a computer program. For an easier interpretation of the experimental data, we use a symmetric system of a gold tip and a gold {111} surface. Our tips are prepared by electrochemical etching in an HCl solution. The gold sample is a 2 mm gold ball prepared by hydrogen flame melting of a pure gold wire at about 1000 °C [14]. Several optically flat facets are formed, one of which is then chosen for the study. The sample is not further subjected to degassing except that it is heated to 125 °C during the overnight vacuum bakeout of the system. The images shown in this Letter (Fig. 1) are taken under a pressure of less than 1×10^{-10} Torr with a tip bias of -40 mV and a constant tunneling current of 1 nA.

From earlier field ion microscope studies, it is now known that field evaporation in a reactive gas environment is extremely complicated, where field-induced chemical etchings of all sorts can occur for most metals at greatly reduced fields from the formation of compound ions such as metal-hydride and metal-hydroxide ions, etc. [8]. For the purpose of clarifying field evaporation in the STM configuration, we therefore perform the experiment in UHV conditions. Figure 1 shows some STM images of our experiment. By applying negative voltage pulses to the tip, we find that both pits and mounds are created on the sample surface, indicating that evaporation from both positive and negative fields can occur. Although the horizontal size of the mounds can reach 200 Å, their heights rarely exceed ~20 Å. Pits have a much smaller size of less than 50 Å with a depth of only a few Å. In many cases, one notices that within the 70 ns pulse duration, atoms are transferred both from the tip to the sample and from the sample to the tip, thus creating both a mound and a pit at nearly the same location. From the scanning direction (left to right), one also notices that negative and positive field evaporation occur in a random time se-

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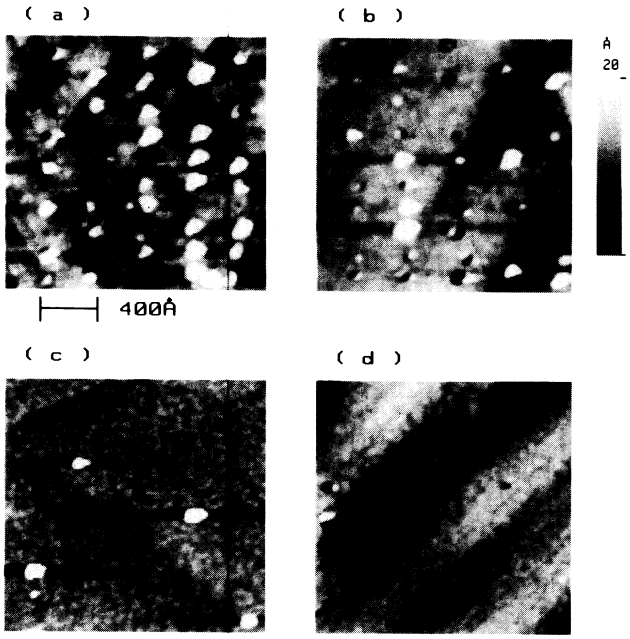


FIG. 1. Generation of mounds and pits by applying the same voltage pulse at 48 preselected positions in a frame for four different pulse voltages at a constant tip-sample distance. (a) -3.9 V, (b) -3.5 V, (c) -3.3 V, and (d) -3.2 V. All the pulses have the same duration, 70 ns.

quence; thus a mound can be either on the right- or the left-hand side of a pit and sometimes they are at the same spot. The numbers of mounds and pits created are nearly identical, indicating that the critical fields for evaporating in negative and positive fields are nearly identical.

With regard to the formation of mounds, Pascual *et al.* [13] have proposed a mechanism involving the formation of a contacting neck between the tip and the sample after the application of a voltage pulse in the air. In our UHV experiment this can happen occasionally as shown in Fig. 2. In this figure, the tail on the right-hand side of some mounds is the result of the breaking of the neck. Even though neck formation can be used to explain the formation of mounds, it cannot be used to explain the formation of pits. We believe that in the initial stage, field evaporation is responsible for transferring atoms between the tip and the sample. Of course, if the amount of atoms transferred is too large, a neck may be formed between them. In our analysis, we exclude such data to avoid the uncertainty of determining the evaporation rate.

The apparent percentage of forming either a mound or a pit is $\sim 100\%$ at a -3.9 V pulse height for a given tip, and reduces to nearly zero around a -3.2 V pulse height as shown in Fig. 3. This percentage is calculated based on accumulated data of over 100 points at each pulse voltage. In counting the number of created features, i.e., mounds and pits, we set a size limit of ~ 10 atoms in order to identify them without ambiguity. At those places where both a mound and a pit appear, we arbitrarily assign $\frac{1}{2}$ to each. As can be seen from this figure, within the statistical uncertainties of the data, the apparent percentages of the mound and pit formations are equal. We can also define a "critical voltage" where the probability of creating a feature by field evaporation is nearly 100% for a tip which has reached a steady state. For this system it is ~ 3.6 V although it depends slightly on individual tips. In field evaporation as well as other thermally activated atom-transfer processes, the rate is given by $\kappa = \nu \exp(-Q/kT)$, where Q is the activation energy and ν is the frequency factor which is about 10^{13} s^{-1}. At room temperature, the threshold field is when the activation barrier has reduced to ~ 0.288 eV or less, which we estimate as follows. The tip to surface distance is calculated to be 6.4 ± 1.0 Å by taking the work function of a clean gold surface, 4.3 eV, to be the tunneling barrier and assuming a value of 0.02 Ω^{-1} as the conductance at con-

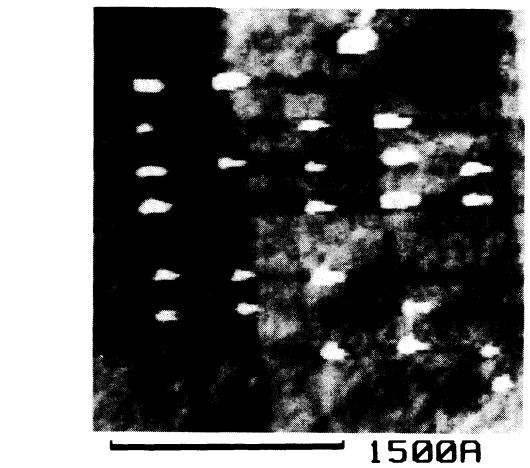


FIG. 2. STM image showing tail-like images for some of the mounds. They are formed by breaking of the necks formed between the tip and the sample by an excess field-induced transfer of atoms between them.

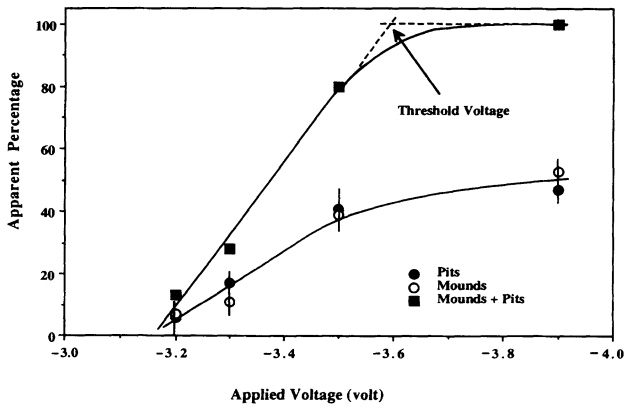


FIG. 3. Apparent percentage of mounds and pits formed as a function of the applied voltage of the pulses.

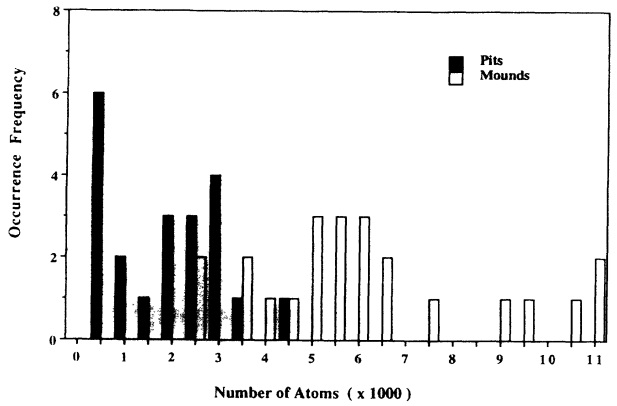


FIG. 4. Size distribution of mounds and pits in terms of the number of atoms for the pulse height of -3.9 V.

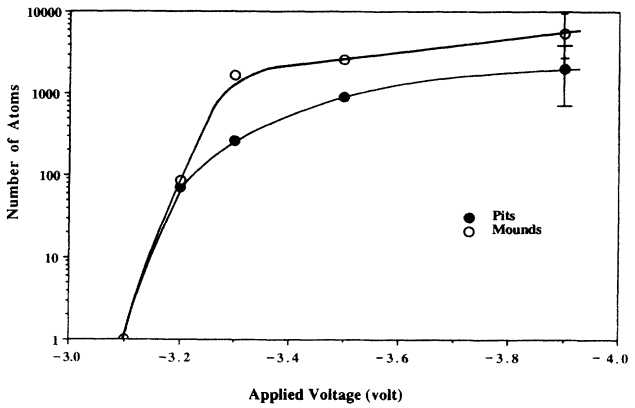


FIG. 5. The size of mounds and pits as a function of the height of the applied voltage pulses.

tact [15]. The threshold field so determined is ~ 0.6 V/Å. This value is slightly higher than that obtained for the same system in air [6] but is still considerably smaller than a calculated value of ~ 0.9 V/Å [10]. That calculation is valid only for large gap distances and is not directly applicable to our experimental conditions. However, the possibility of negative field evaporation is confirmed. Unfortunately, there is no first principle calculation for this system to compare with our experiment.

In vacuum, field evaporation with the tip negative is quite reproducible even though the sizes of the mounds and pits created vary over a wide range. In other words, the gold tip can sustain itself. When positive pulses are applied to a tip, mounds can be created on the surface, but then the tip will be quickly destroyed, or the tip cannot sustain itself. It appears therefore that positive field evaporation needs a field slightly lower than negative field evaporation for Au. In air, the situation is quite different. Au mounds can be deposited on the surface by applying either positive or negative pulses to the tip with a much better reproducibility and size fluctuations as found earlier by Mamin and co-workers [6]. However, we find that in addition to mounds, pits can also be created frequently.

Even at a constant height of the voltage pulses, the sizes of the mounds and pits created vary widely as shown in Fig. 4 for $V = -3.9$ V. The sizes of the pits formed are usually much smaller than the mounds, and their size distribution is also much narrower. Since the temperature of the sample is unlikely to be appreciably raised by the field emission current from the tip [16] produced by the voltage pulses around 0.6 V/Å, the distribution of pit sizes merely reflects the variation of the activation barrier Q at different positions as determined by the field variation. However, on the tip side the heating effect of the tip resulting from the field emission current cannot be neglected. The amount of atoms field evaporated from the tip surface will be a sensitive function of the tip shape, which progressively affects the field at the tip surface, the field emission current, the tip temperature, and ultimately the field evaporation rate. In addition, the possibility of a buildup contact in the gap [13] further introduces a fluctuating factor on the size of the mounds. Thus we find not only the size of the mounds fluctuates widely for a given tip, it also changes slightly from one tip to another.

The average sizes of the pits and mounds increase with the voltage of the pulses, or the applied field as shown in Fig. 5. Referring to the evaporation rate equation, the ordinate of this figure actually represents $\ln\kappa\tau$, or $\ln(\nu\tau) - Q/kT$; here τ is the width of the voltage pulses. The initial rapid rise in the evaporation rate as the field is raised is due to the effect of the field evaporation. Further increase in field will not raise the rate rapidly because of an atom-supply limited effect, similar to field ionization in FIM.

To be able to deposit atoms from the tip to the sample surface repeatedly, there must be a continuous supply of atoms to the tip apex so that the tip can sustain itself in its repeated consumption of atoms. In UHV, this sustaining is much more effective when the tip is in negative po-

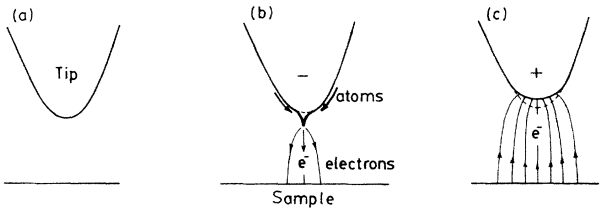


FIG. 6. Illustration of the effect of the heating by field-emitted electrons produced by the voltage pulse. (a) Tip shape before pulsing. (b) Tip shape after negative pulsing to the tip. Field electrons flow through the sharp section of the tip and heat up this section, thus inducing a field-gradient-promoted diffusion and hydrodynamic flow of atoms from the shank to the apex. (c) Tip shape after positive pulsing to the tip. Field electrons hit a larger area of the tip; thus they do not produce local heating of the tip. The gap between the tip and the sample is greatly exaggerated.

larity. This different behavior of the polarity can be understood if one realizes that when the tip is in negative polarity, field emission current, which is considerable at a field of ~ 0.6 V/Å and which flows through the sharpest apex section of the tip, can heat up the tip to induced surface diffusion [17] and even a hydrodynamic flow of gold atoms from the tip shank to the tip apex. This process is well known in liquid metal ion sources and the cusp-shaped tip is often referred as the Taylor cone [18]. This process has been utilized to sharpen a tip to single-atom sharpness [19]. It is produced by a field-gradient-induced directional walk of surface atoms [20]. For the positive tip polarity, electrons can be field emitted from the sample surface also. But, because of the momentum conservation, they will strike a much larger section of the tip, not enough to heat up the apex section of the tip to induce surface diffusion or hydrodynamic flow of atoms. Therefore the tip cannot sustain itself in repeated field evaporations. These points are illustrated in Fig. 6.

In conclusion, we have observed both positive and negative field evaporations under the STM configuration for the Au system in UHV. The threshold fields for these two processes are comparable but slightly favor the positive field. A value of ~ 0.6 V/Å is obtained for the threshold field. This field is large enough to produce a field emission current to heat up the sharp section of the tip when it is in negative polarity. A temperature and field-gradient-induced surface diffusion and hydrodynamic flow of atoms from the tip shank to the tip apex can sustain the repeated field evaporations of the tip. When the tip is in positive polarity, this cannot occur because the tip is quickly destroyed by positive field evaporation.

This work was supported by the National Science Council of the Republic of China under Grant No. NSC82-0208-M-001-117.

[1] D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990).

[2] L. J. Whitman, J. A. Stroscio, R. A. Dragoset, and R. J. Celotta, Science **251**, 1206 (1991).

[3] I. W. Lyo and P. Avouris, Science **253**, 173 (1991).

[4] J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991).

[5] R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, Nature (London) **325**, 419 (1991).

[6] H. J. Mamin, P. H. Guethner, and D. Rugar, Phys. Rev. Lett. **65**, 2418 (1990); H. J. Mamin, S. Chiang, H. Birk, P. H. Guethner, and D. Ruger, J. Vac. Sci. Technol. B **9**, 1398 (1991).

[7] A. Kobayashi, F. Grey, R. S. Williams, and M. Aono, Science **259**, 1724 (1993).

[8] E. W. Müller and T. T. Tsong, *Field Ion Microscopy, Principles and Applications* (Elsevier, New York, 1969); T. T. Tsong, *Atom-Probe Field Ion Microscopy* (Cambridge Univ. Press, New York, 1990).

[9] T. T. Tsong, Phys. Rev. B **44**, 13703 (1991).

[10] N. M. Miskovsky and T. T. Tsong, Phys. Rev. B **46**, 2640 (1992).

[11] N. M. Miskovsky, C. M. Wei, and T. T. Tsong, Phys. Rev. Lett. **69**, 2427 (1992).

[12] N. D. Lang, Phys. Rev. B **45**, 13599 (1992). Lang does not use the term "field evaporation" for the field-induced atom-transfer process in STM. We as well as many others use this term to signify the transfer of atoms by an applied field. The detailed mechanisms of field evaporation may be very sensitive to the tip to sample distance and many other factors. Lang's calculations are usually extended to a distance less than 10 bohrs. In many experiments, such as those by M. Aono's group, a distance over 10 Å is used. Under such conditions, models treated in Refs. [9–11] are appropriate.

[13] J. I. Pascual, J. Mendez, J. Gomez-Herrero, A. M. Baro, N. Garcia, and V. T. Binh, Phys. Rev. Lett. **71**, 1852 (1993).

[14] J. Schneir, R. Sonnenfeld, O. Marti, P. K. Hansma, J. E. Demuth, and R. J. Hamers, J. Appl. Phys. **63**, 717 (1988).

[15] G. Binnig, N. Garcia, H. Rohrer, J. M. Soler, and F. Flores, Phys. Rev. B **30**, 4816 (1984).

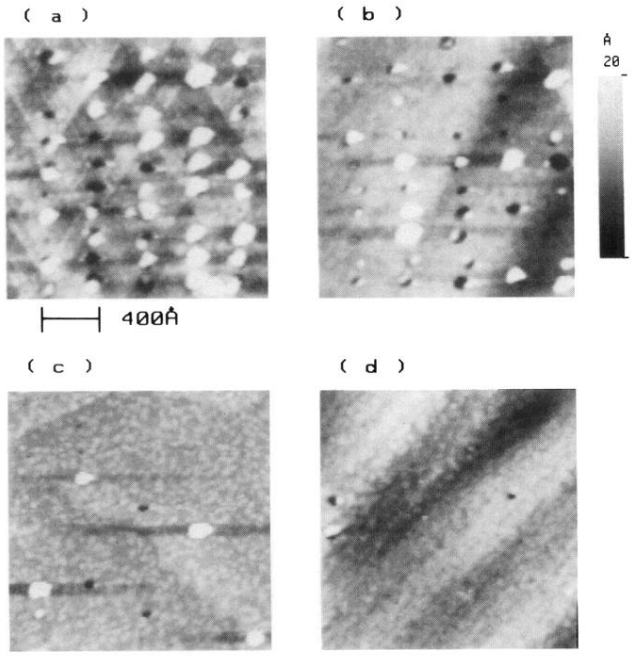
[16] P. F. Marella and R. F. Pease, Appl. Phys. Lett. **55**, 2366 (1989).

[17] E. V. Klimenko and A. G. Noumovets, Fiz. Tverd. Tela (Leningrad) **13**, 33 (1971) [Sov. Phys. Solid State **13**, 25 (1971)].

[18] See, for an example, p. 360 of Ref. [8] and G. I. Taylor, Proc. R. Soc. London A **280**, 283 (1964).

[19] V. T. Binh, S. T. Purcell, N. Garcia, and J. Doglioni, Phys. Rev. Lett. **69**, 2527 (1992).

[20] T. T. Tsong and R. J. Walko, Phys. Status Solidi A **12**, 111 (1972); T. T. Tsong and G. L. Kellogg, Phys. Rev. B **12**, 1343 (1975).



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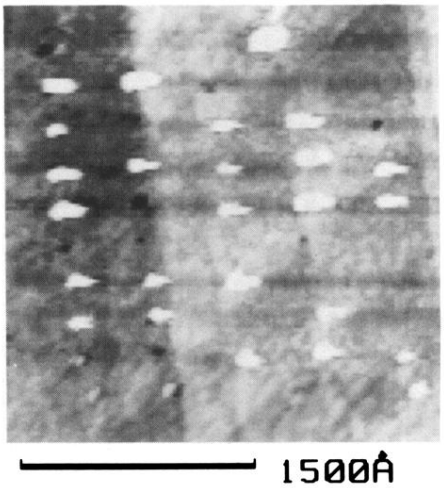

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