Atomic Emission from a Gold Scanning-Tunneling-Microscope Tip

H. J. Mamin, P. H. Guethner, and D. Rugar
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
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We have demonstrated that a gold scanning-tunneling-microscope tip can be used as a miniature solid-state emission source for directly depositing nanometer-size gold structures. The emission mechanism is believed to be field evaporation of tip atoms, which is enhanced by the close proximity of the substrate. The technique has been used in air on Au(111) surfaces to write several thousand features with no apparent degradation of the tip's ability to emit atoms.

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Field evaporation, first discovered by Müller in 1941, is the process whereby atoms are ionized and ejected from a surface due to the action of a high electric field.[1] Typical field-evaporation experiments use sharp metallic tips subjected to potentials on the order of kilovolts. In this paper, we explore field evaporation in a very different regime, where the field-evaporation tip is part of a scanning tunneling microscope and is positioned within nanometers of a substrate. Because the gap between the tip and substrate is so small, high-field strength may be achieved with substantially lower voltage than with an isolated tip. Furthermore, the close proximity of the two surfaces causes overlap of the atomic potentials, which can lead to a lowering of the energy barrier for field evaporation. We have found that when using gold as the tip material, reliable atomic emission from the tip is achieved and that this emission can be used for direct deposition of nanometer-size gold structures.

Field evaporation in the context of scanning tunneling microscopy (STM) has received relatively little attention thus far. Gomer suggested that field evaporation of atoms off the tip may account for the spontaneous changes in tunneling behavior commonly observed in STM.[2] Bell, Rao, and Swanson demonstrated ion emission from a liquid-metal source with voltages as low as 200 V when the source was spaced on the order of 100 nm from the substrate.[3] It is probably not practical to position liquid-metal-ion sources much closer than this distance, however, because of the attractive forces from the substrate which act on the liquid.

In this work, we used solid-state emitters and obtained our best results using gold as the tip material. Gold has two advantages. First, it is known to have a lower threshold for field evaporation compared to refractory metals (commonly used for STM tips). Second, it is an excellent material for experiments performed in air, since it does not oxidize. The gold tips were prepared from 250-μm-diam gold wire by electrochemical etching in concentrated hydrochloric acid (1.5–2 V dc).

Gold was typically used for the substrate as well, because it is inert and because one can easily prepare flat surfaces. The substrates were made from 500-μm gold wire melted in an oxyacetylene torch to give gold balls with (111)-oriented facets.[4] Preliminary work has also been done on platinum substrates prepared in the same way, and similar behavior as with the gold substrates has been seen. The samples were placed on a homemade STM built around a tube scanner. Imaging was typically performed with a steady-state voltage of 100 mV and a constant current of 0.1 nA. To cause gold emission, voltage pulses were applied while the tip was within tunneling range. The pulses were sufficiently short (typically a few hundred nanoseconds or less) that the servo loop

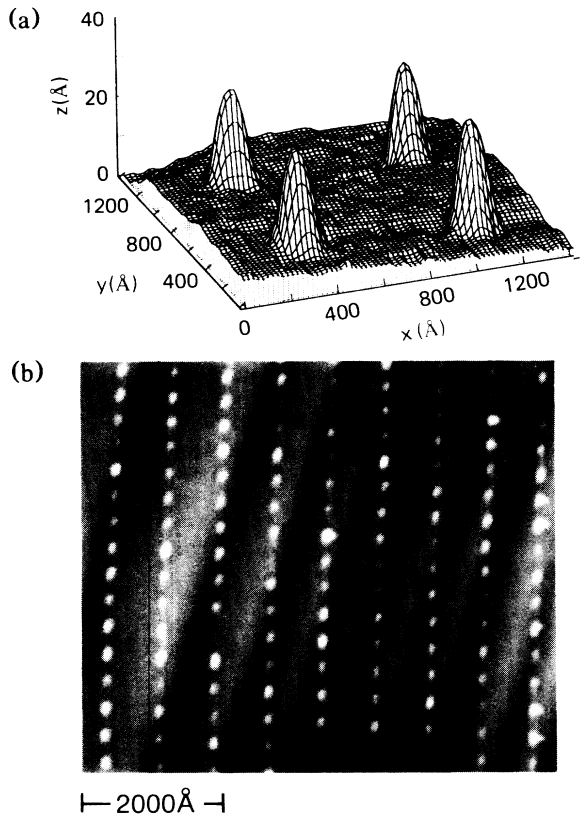

FIG. 1. (a) Gold mounds made by applying voltages pulses between gold tip and sample. Pulse width was 600 nsec and voltage was +3.6 V to surface (tip grounded). (b) Array of ~150 mounds made with 4.2-V, 300-nsec pulses on a stepped gold surface.

did not need to be disengaged during the pulsing. All imaging was performed in air.

The effect of applying a voltage pulse to the tip is the creation of a small mound on the substrate surface, as shown in Fig. 1(a). Each mound was formed at the desired location by a single 600-nsec pulse of +3.6 V applied to the sample. The mounds are typically 100–200 Å across at the base and 20–30 Å high, although they can be as small as 50 Å across. The emission process is both reproducible and fast. Figure 1(b) shows an array of roughly 150 mounds which was written with 300-nsec pulses on a stepped gold surface. Mounds have been written reproducibly with even shorter pulses, down to 10 nsec, the shortest pulse which we were able to apply. Overall, the tips are remarkably stable. We have subjected individual tips to several thousand pulses and have observed no loss in the tip's ability to emit, although some tip changes were occasionally observed.

The probability for emission displayed a sharp threshold with pulse height, as shown in Fig. 2. Within a fraction of a volt, the writing probability went from zero to essentially 100%. The threshold value was somewhat tip dependent and was usually between 3.5 and 4 V. Pulses of both positive and negative polarity created mounds on the surface, but had slightly different behavior. The threshold voltage with the tip negative was generally a few tenths of a volt higher than with the tip positive.

We have further explored how the writing threshold voltage changes when the tunneling conditions are changed. The tip was first brought into tunneling range at a set bias voltage and current. The threshold voltage was then measured as a function of the tunneling conditions just prior to writing. Bias voltage was varied over the range of 0.1–1 V, and tunnel current was varied from 0.1 to 1 nA. The threshold voltages are plotted against the gap impedance in Fig. 3. The data fall on one straight line, indicating that the threshold voltage depends only on the gap impedance in this range.

The tunneling impedance increases exponentially with the separation, so that the horizontal scale in Fig. 3 represents the tip-surface separation. This linear dependence of threshold voltage on separation is therefore evidence that emission occurs when the applied field reaches a certain critical value. It is difficult to assign a distance scale to the horizontal axis, since the conversion requires knowledge of the tunneling barrier height. An apparent barrier height of roughly 0.5 eV was obtained by measuring the tunnel current as a function of the voltage to the z piezoelectric drive. This value, which was measured in air, probably underestimates the true tunneling barrier, however, because the change in tip-sample separation is overestimated due to elastic deformation effects.[5] The gap impedance depends on the actual tip-sample separation, so it is more appropriate to use the actual barrier height, which will be closer to the work function of the metal. If we use the value of 4.3 eV, corresponding to the work function of clean gold,[6] we get an upper limit on the slope of the threshold voltage versus separation curve of 0.4 V/Å, which is an indication of the critical field.

The above result suggests that the gold transfer is field induced. One possible mechanism is ionization and subsequent field evaporation of atoms in the tip.[2] Figures 4(a) and 4(b) show schematically how the application of an electric field can make it energetically favorable for an ion to be emitted from the metal. Figure 4(a) shows the binding energy Q_0, the energy to remove an ion from the metal in the absence of an electric field. Application of an electric field lowers the energy outside the metal and creates a potential-energy barrier, known as the

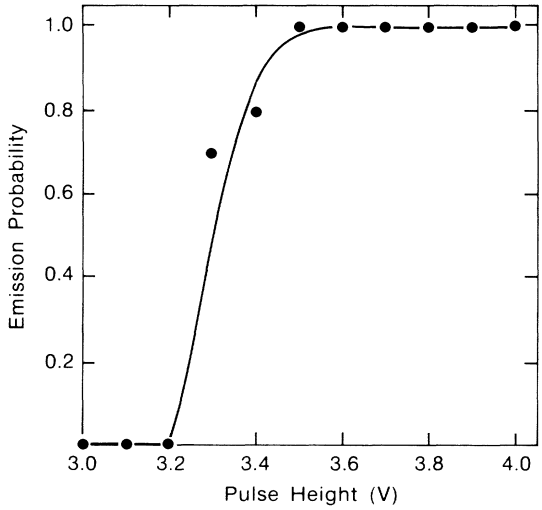

FIG. 2. Probability of tip emission as a function of pulse voltage. The plot shows the results from roughly 100 trials (10 at each voltage). A sharp threshold is seen at about 3.4 V.

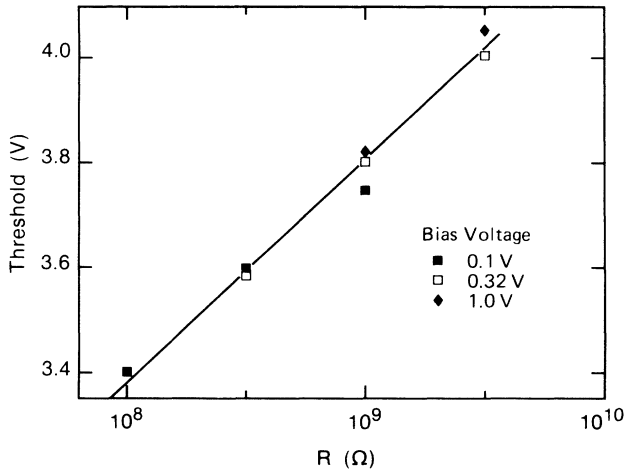

FIG. 3. Voltage threshold for writing as a function of tunneling gap impedance, plotted on a logarithmic scale. Each point is derived from a threshold curve such as that shown in Fig. 2. The linear behavior is evidence of a threshold field.

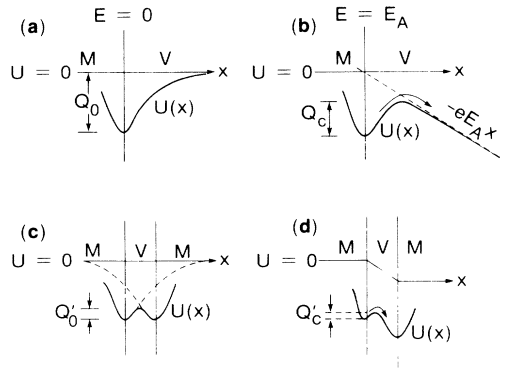

FIG. 4. Simplified energy diagrams for an ion at a metal-vacuum interface. (a) Single metal-vacuum (M-V) interface with no applied field. The depth of the well is Q_0. (b) Single interface with applied field E_A. The ion can lower its energy by leaving the metal, provided it can overcome the barrier of height Q_c. (c) Metal-vacuum-metal structure with two like metals and no applied field. The barrier height Q_0' is significantly reduced compared to Q_0. (d) Same structure with an applied field. Q_c' is also reduced compared to Q_c.

"Schottky saddle,"[7] over which the ion may escape. One can obtain an expression for Q_c the height of the barrier, by considering the simplest possible model in which the potential energy of an ion outside the metal is given solely by the superposition of the applied potential and the image potential to the metal. For this case, the potential $U(x)$ is given outside the metal by[8-10]

$$U(x) = -(Ne)^2/4x - NeE_A x \quad \text{for } x > 0, \tag{1}$$

where E_A is the applied field and $-(Ne)^2/4x$ is the image potential. The barrier height is then easily found to be

$$Q_c = Q_0 - (Ne)^{3/2} E_A^{1/2}. \tag{2}$$

This is the well-known expression derived by Müller; it is also obtained by Gomer for the case of direct ionic evaporation.[8,9]

For a positive ion, $Q_0 = \Lambda + \sum_n I_n - N\phi$, where Λ is the heat of evaporation of a neutral atom, $\sum_n I_n$ is the total ionization potential, and ϕ is the electronic work function. For a negative ion, $Q_0 = \Lambda + N\phi - \sum_n A_n$, where $\sum_n A_n$ is the total electron affinity.[10] Q_0 is typically on the order of 5-10 eV. For the case of gold, $\Lambda = 3.8$ eV, $\phi = 4.3$ eV, $I_1 = 9.22$ eV, and $A_1 = 2.3$ eV, so that $Q_0 = 8.7$ eV for a singly charged positive ion and $Q_0 = 5.8$ eV for a singly charged negative ion.[6,11,12] Thermally activated evaporation occurs when Q_c is of the order of a few times $k_B T$. This simple model then predicts threshold fields of 2-7 V/Å for $Q_c = 5$-10 eV. These values are of the same order of magnitude as observed in the field-ion microscope (FIM). In gold, emission of singly and doubly charged positive ions is observed at fields of about 3.5 V/Å.[13]

The threshold fields that we have inferred from our measurements are substantially lower than these values. The above treatment as well as the field-ion-microscope measurements all refer to isolated tips, however. When two surfaces are placed in close proximity, the barrier for evaporation may be lowered as the atomic potentials begin to overlap, as suggested by Figs. 4(c) and 4(d). The image potential due to the second surface also contributes to this lowering. This effect is analogous to the lowering of the effective barrier height for electron tunneling calculated by Lang for two surfaces in close proximity.[14] To estimate the effect of the second electrode, we consider a model analogous to that given above: We treat the one-dimensional problem and use the classical image potentials. We also add a potential to account for the additional chemical binding of an ion to the metal. For electrodes located at $x = 0$ and $x = d$, the image potential can be written approximately as

$$U_{\text{im}}(x) = -\frac{e^2}{d}\left[(\ln 2 - 1) + \left(\frac{x - d/2}{d}\right)^2 + \frac{d^2}{d^2 - 4(x - d/2)^2}\right], \quad 0 < x < d, \tag{3}$$

as discussed by Binnig *et al.*[15] The nonabrupt nature of the electrode edge as well as screening effects can be accounted for by defining d to be the distance between the image planes, which may be offset slightly from the electrode surface.[10,15] We take the ion binding energy to the surface to be of the form

$$U_{\text{be}}(x) = Q_0 e^{-\kappa x}, \quad \kappa = 1\ \text{Å}^{-1}, \quad x > 0. \tag{4}$$

This ansatz is chosen for simplicity, but it is justified by the fact that the exchange-correlation potential has this form, with $\kappa \sim 1$ Å^{-1},[14] and because it is consistent with previously calculated metal-metal binding energies, again for $\kappa \sim 1$ Å^{-1}.[16]

In this simple model, the total potential $U(x)$ felt by an ion in the gap is given by

$$U(x) = U_{\text{im}}(x) - Q_0(e^{-\kappa x} + e^{-\kappa(d-x)}) - NeE_A x, \quad 0 < x < d, \tag{5}$$

For $d = 5$ Å we find that Q_0', the height of the barrier for $E_A = 0$, is given by $Q_0' = Q_0 - U(x = d/2) = 0.85 Q_0 - 2$ eV. Thus the barrier is significantly reduced. The magnitude of the change is model and gap dependent, but the effect is always some reduction in barrier height. This model predicts critical fields in the range of 1-3 V/Å for $Q_0 = 5$-10 eV, or about a factor of 2 less than expected for the case of the isolated tip. This simple picture does not fully explain the low threshold fields that we have observed. Neither does it attempt realistically to take into account the exchange, correlation, and screening effects which must be considered at smaller distances.[10,14] More theoretical efforts would be desirable to address these issues in the context of field evaporation. Qualitatively, though, we see that one might expect significant reduction in the barrier height and critical field when there are two surfaces in close proximity.

One would expect that, for a field-evaporation mechanism, the transfer will occur primarily from tip to substrate since the field is highest at the sharpest feature, usually the tip. This is what we generally observe for both positive- and negative-polarity pulses. These results would not be consistent with a current-induced mechanism such as electromigration, where one would expect the direction of transfer to reverse when the current is reversed. Another alternative possibility is that mound formation occurs as the result of mechanical contact between the tip and sample. Such contact might be initiated by the sudden increase in electrostatic force associated with the voltage pulse. We consider this scenario unlikely, however, due to the inertia of the tip and the very small mechanical impulse imparted by pulses as short as 10 nsec. Furthermore, there is no distortion or depletion of material visible in the area surrounding the mounds, as would be expected if the material were being pulled out of the substrate.

A field-evaporation mechanism may also explain some previously reported results on STM surface modification.[17-22] For example, when a refractory metal tip (such as tungsten) is used instead of a gold tip, we find that voltage pulses most often produce pits in the gold sample surface (instead of the mounds created when we use gold tips). This pitting effect has also been observed by others,[19,20] but was ascribed to an explosive evaporation caused by a temperature rise induced by the high current density.[20] Calculations, however, cast doubt on this hypothesis.[23] We believe that the pits are formed by local field evaporation of the gold substrate. Because the threshold for field evaporation is significantly lower in gold than in most refractory materials (3.5 V/Å in FIM experiments for gold versus 5.7 V/Å for tungsten[13]), a strong field is more likely to pull atoms out of the gold substrate surface than out of the tungsten tip. One would expect some of the gold removed from the substrate to be transferred to the tip. With repeated pulses the gold should at some point be evaporated off the tip back onto the surface, resulting in an occasional mound, which has been observed by us and by others.[20]

In conclusion, we have shown that a gold STM tip can be used as a source of evaporated atoms for deposition on a surface. The deposition process is fast, reproducible, and field induced. The technique can be used to make nanometer-size structures for possible eventual use in devices or for fundamental studies of the behavior of nanometer-size particles. The deposition mechanism is believed to be field-evaporation enhanced by the proximity of the substrate. Field evaporation would also explain a number of previously unexplained STM surface modification experiments.

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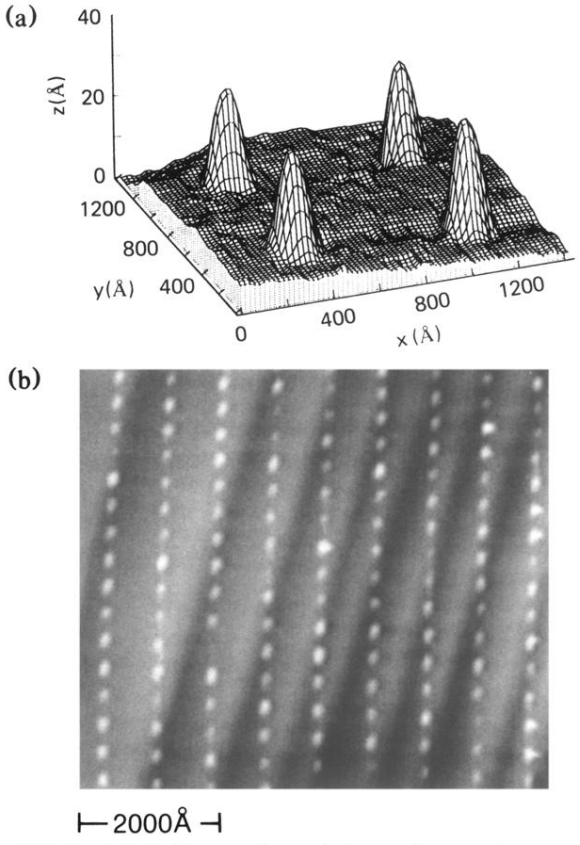

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