Nanofabrication of Small Copper Clusters on Gold(111) Electrodes by a Scanning Tunneling Microscope

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The use of scanning tunneling microscopy in an electrochemical environment as a tool for the nanoscale modification of gold electrodes was demonstrated. Small copper clusters, typically two to four atomic layers in height, were precisely positioned on a gold(111) electrode by a process in which copper was first deposited onto the tip of the scanning tunneling microscope, which then acted as a reservoir from which copper could be transferred to the surface during an appropriate approach of the tip to the surface. Tip approach and position were controlled externally by a microprocessor unit, allowing the fabrication of various patterns, cluster arrays, and "conducting wires" in a very flexible and convenient manner.

Continuing miniaturization of electronic and mechanical devices has led in recent years to an interest in the generation of nanometer-sized structures on surfaces. The invention of scanning probe techniques, particularly scanning tunneling microscopy (STM) (*1*), has made it possible to modify surfaces at the nanometer scale and to manipulate even single atoms with the STM tip (*2*). In a pioneering study, Becker *et al.* reported in 1987 an atomic-scale modification of Ge(111) with an ultrahigh vacuum (UHV) STM (*3*). The most striking examples of nanoscale modification have been given by Eigler *et al.*, who arranged individual Xe atoms on a Ni(110) surface (*4*) and constructed quantum corrals from single atoms by means of an STM tip (*5*). These experiments were done in UHV with an STM operating at low temperatures (4 K). Others have used field evaporation of tip atoms under STM conditions by applying relatively large voltage pulses to generate nanometer-sized metal clusters, for example, using an Au tip in air to decorate Au(111) surfaces with small Au clusters (*6*, *7*).

The use of STM in an electrochemical environment has triggered the development of new methods for the nanostructuring of electrode surfaces. Penner and co-workers were among the first to use electrochemical STM for nanoscale modification of electrode surfaces by depositing small metal clusters at preselected sites on highly oriented pyrolytic graphite (*8*, *9*). Surface defects that were generated with the STM tip then acted as nucleation centers for the metal deposition reaction (*8*, *9*). In situ atomic force microscopy has also been used to locally enhance electrochemical metal deposition by creating surface defects, for example, in a passivating overlayer on Cu surfaces (*10*). Ullmann *et al.* reported on a method of electrochemical nanoscale modification (*11*, *12*), namely, the formation of Cu clusters on an Au(111) surface during an appropriate approach of the STM tip as a result of the transfer of Cu predeposited onto the STM tip, without damaging the substrate surface. We report a modified technique, based on the tip-induced metal deposition described in (*11*, *12*), for the production of clusters and cluster ensembles with high speed and precision. We have developed a microprocessing unit that allows a very controlled tip approach and hence reproducible generation of various patterns and cluster arrays in a flexible and convenient manner. This procedure can be considered a step toward the automatic fabrication of nanostructures on electrode surfaces.

We performed STM studies using either the electrochemical version of a Nanoscope E (Digital Instruments, Santa Barbara, California) or a PicoSPM (Molecular Imaging Corporation, Tempe, Arizona). All images shown in this report were obtained in the constant-current mode. The electrolyte used throughout this study was 0.05 M H_2SO_4 + 1 mM $CuSO_4$, prepared from H_2SO_4 (Merck, suprapure), CuO (Merck, puriss. p.a.), and Milli-Q water (Millipore). Counter and reference electrodes were made of Au and Cu wires, respectively. All potentials were measured and are quoted against the Cu/Cu^{2+} reference electrode. Technical details are given in (*13*).

In earlier reports we demonstrated that Au surfaces can be modified on a nanometer scale by tip-induced deposition of Cu clusters (*11*, *12*). The Cu was first deposited on the tip and then transferred from the tip to the substrate by an appropriate tip approach. In our earlier experiments, we applied a potential step to the sample during which the tunneling voltage U_T changed its sign, that is, U_T passed through zero. In such a case, the feedback circuit forced the tip to approach the surface in order to maintain a constant tunnel current. By choosing appropriate damping parameters for the internal feedback, a tip crash could be avoided so that Cu clusters could be deposited without damaging the electrode surface. In this case, the potential step was not applied for electrochemical reasons (for example, discharge of Cu^{2+} ions), but rather was used to force the feedback circuit to react and to move the tip toward the surface.

In the technique of controlled tip approach for tip-induced Cu deposition that we report here, we applied an externally generated voltage pulse directly to the *z*-piezo, which leads to a corresponding movement of the STM tip in the *z* direction. A "signal access module" break-out-box (Digital Instruments, Santa Barbara, California) is connected between the controller and the STM. The controller is responsible for generating, among other things, the voltages for the *x*-, *y*-, and *z*-piezos to move the STM tip. By modifying the *x*- and *y*-piezo signals, it is possible to move the tip across the surface by external control. In order to

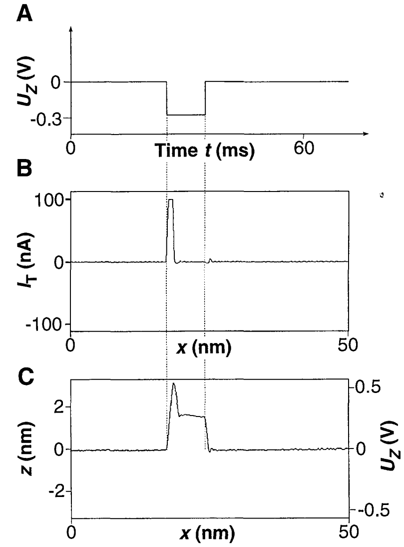

Fig. 1. The imposition of an external voltage pulse U_z on the *z*-piezo (**A**) causes a change in the tunnel current I_T (**B**) and a tip movement in the *z* direction (**C**). The voltage pulse height $\Delta U_z = 0.28$ V causes an approach of $\Delta z = 1.2$ nm. Pulse duration was $\Delta t = 10$ ms. The Au(111) electrode was in 0.05 M H_2SO_4 + 1 mM $CuSO_4$. Sample potential $E_{sample} = +10$ mV versus Cu/Cu^{2+}; tip potential $E_{tip} = -30$ mV; tunneling current $I_T = 2$ nA. In (B), it is shown that after about 3 ms the feedback circuit causes the tip to retract in order that the tunneling current regain its predetermined value of $I_T = 2$ nA (constant-current mode). The reverse step of the *z* pulse causes the STM tip to retract from the surface by 1.2 nm. The corresponding decrease in current, however, is hardly seen on the linear scale in (B).

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form a pattern, the required coordinates of the cluster positions are calculated and sent to the microprocessor, which generates the corresponding control voltages for the x- and y-piezos, thereby moving the tip from one desired cluster position to the next. The coordinates can be stored in a computer file, thus automating the whole patterning process.

An external voltage pulse on the z-piezo results in simultaneous responses of tip height and tunnel current (Fig. 1). On the forward step of the z pulse, the tunnel current exhibits a sudden drastic increase up to saturation within the first millisecond (Fig. 1B), showing that the STM tip approached the surface. The height scan illustrates the formation of a Cu cluster (Fig. 1C). These results demonstrate that the tip approach due to an additional voltage pulse on the z-piezo leads to the deposition of a Cu cluster, provided that this approach is close enough.

We suggest the following mechanism of material transfer (Fig. 2). First, Cu is deposited on the tip if the tip potential is held at values that are slightly negative compared with those of the Cu/Cu^{2+} reference electrode, typically at about −30 mV versus Cu/Cu^{2+}. Then the Cu-covered tip is forced by an external voltage pulse to approach the surface momentarily for a transfer of material from the tip to the substrate. This will leave a small Cu cluster on the Au surface, while the retracted tip will be loaded again with Cu from solution. Various theoretical models have been proposed to describe the material transfer process (*14*–*16*). For instance, at a certain tip-to-sample separation [for example, for a Ni tip and an Au surface or an Au tip and a Ni surface at about 4.2 Å (*16*)], a so-called "jump-to-contact" can occur that leads to a "connecting neck" between the tip and the sample. After retraction of the tip, the neck breaks and a cluster is left on the substrate. Recently, Kuipers *et al.* have reported experimental evidence for W tips and Pb surfaces in UHV, which is consistent with this mechanism of material transfer (*17*). They suggested that this behavior is a consequence of surface diffusion, as the "jump-to-contact" ability increases with increasing temperature.

To illustrate microprocessor-controlled tip-induced metal deposition, we deposited 12 Cu clusters on an Au(111) surface in a circular array (Fig. 3A). The Cu clusters are sitting not directly on the Au surface but on a (1 × 1) Cu monolayer formed by underpotential deposition of Cu on Au(111) (*18*) at this sample potential (E = +10 mV versus Cu/Cu^{2+}). At this potential, bulk Cu deposition from solution is thermodynamically impossible. The individual Cu clusters are about 0.8 nm high (Fig. 3B), corresponding to four atomic layers of Cu, and show a full width at half maximum (FWHM) of about 3.5 nm. The latter value, however, most likely reflects the lateral resolution of the STM rather than the actual width of the clusters. Although the sample potential was slightly more positive than the corresponding Nernst potential for Cu deposition (E = +10 mV versus Cu/Cu^{2+}), the clusters were remarkably stable, even at more positive potentials (*12*). Only when the sample potential was raised to about +300 mV versus Cu/Cu^{2+} did all Cu clusters dissolve, usually leaving an undamaged Au surface. This increased stability is most likely because of tip shielding.

With the microprocessor unit we found it possible to readily generate patterns on even a larger scale. An array consisting of 400 single Cu clusters (20 clusters by 20 clusters) on an area 245 nm by 275 nm (Fig. 4) was fabricated in less than 90 s. We were able to achieve this relatively fast patterning process by allowing the tip to approach the surface while it was scanning over the surface as in the usual imaging mode. It was necessary to apply the additional voltage pulses on the z-piezo for the tip approach at the right moments; these times were calculated by an additional circuit that can detect the beginning and end of a scan line. In principle, such an array could be produced also as a programmed pattern as in the case

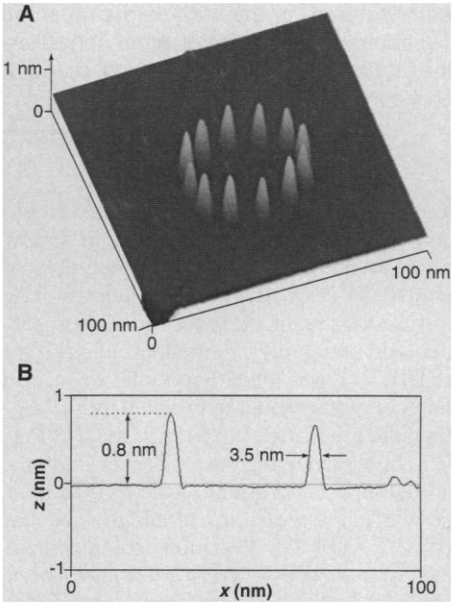

Fig. 3. (**A**) STM image of 12 Cu clusters on an Au(111) electrode in 0.05 M H_2SO_4 + 1 mM $CuSO_4$. E_{sample} = +10 mV; E_{tip} = −50 mV; I_T = 2 nA. The clusters were generated by 12 programmed approaches of the tip to the surface caused by external voltage pulses to the z-piezo. Tip displacement Δz = 1.6 nm; pulse duration Δt = 10 ms. (**B**) Cross section through the center of the circle (diameter, 41 nm), showing the height and FWHM of the Cu clusters.

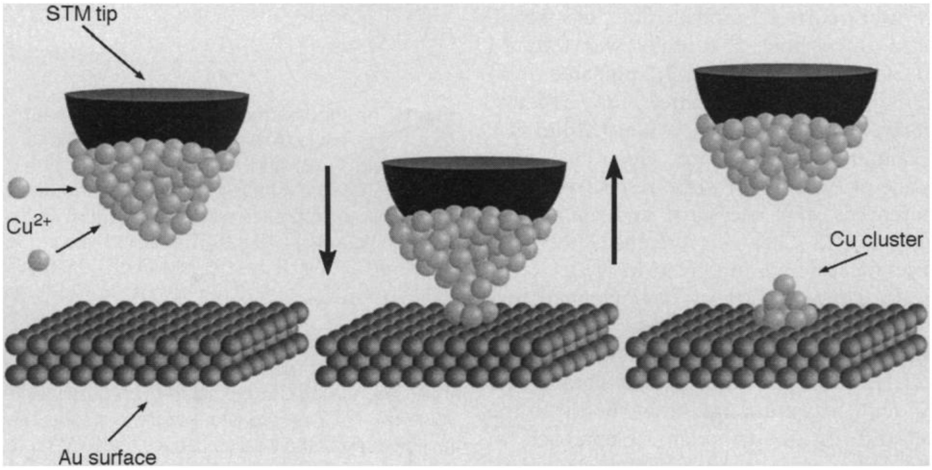

Fig. 2. Schematic diagram of the suggested mechanism of material transfer from a Cu-covered STM tip to the Au substrate, caused by an appropriate tip approach.

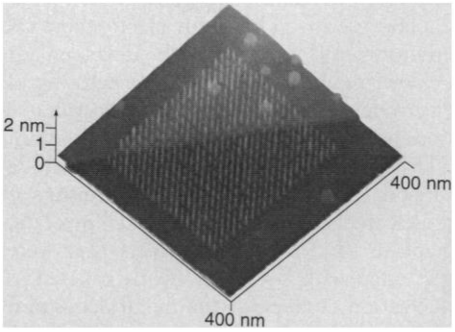

Fig. 4. STM image of an array of 400 Cu clusters on Au(111) in 0.05 M H_2SO_4 + 1 mM $CuSO_4$, covering an area 245 nm by 275 nm. E_{sample} = +10 mV; E_{tip} = −30 mV; I_T = 2 nA. The Cu clusters were generated by 400 single voltage pulses on the z-piezo while the tip was scanning over the surface. Tip approach Δz = 0.8 nm; pulse duration Δt = 2.5 ms.

of the circle shown in Fig. 3A. However, because the tip would have to be moved from one cluster position to the next, controlled by the microprocessor, this method would be much slower (approximately by a factor of 10) than cluster production during scanning. Although 400 Cu clusters were produced during a very short time, there was no indication of Cu depletion at the tip as all clusters are nearly identical in size (height $h = 0.6$ nm, FWHM = 3.5 nm). This result suggests that the Cu reservoir at the tip is continuously refilled as a result of permanent Cu deposition from solution (tip potential $E_{tip} = -30$ mV versus Cu/Cu^{2+}).

Continuous structures can also be generated with microprocessor-controlled cluster formation by placing the Cu clusters very close together so that they can contact each other. For example, we have produced nanometer-sized "conducting wires" with a FWHM of 3 to 4 nm and a length of several hundred nanometers on Au(111) (*19*).

In addition to precisely positioning individual Cu clusters with identical heights, it is also possible with this system to vary the size of the deposited clusters in a controlled manner within certain limits. This can be done by varying the extent of the tip approach with the external *z* pulse, which controls the amount of Cu transferred from the tip to the Au surface (Fig. 5, A and B). In general, the cluster height increases with increasing *z*-pulse height, but, above a tip displacement of $\Delta z \approx 1.2$ nm, the cluster height did not increase further and holes appeared in the surface instead. This result suggests that the tip displacement became too large and the tip struck the substrate.

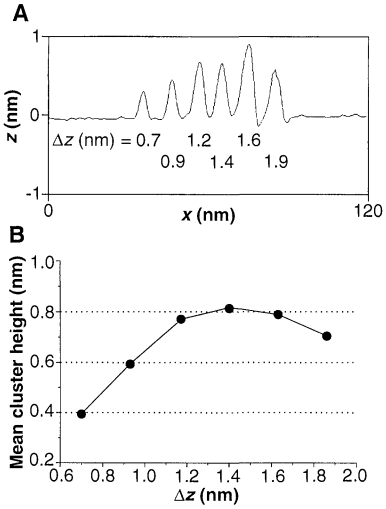

Fig. 5. (**A**) Cross section of six Cu clusters in a row on Au(111) in 0.05 M H_2SO_4 + 1 mM $CuSO_4$, which demonstrates the variation of cluster height with the *z*-pulse height. The corresponding tip displacement Δz is shown in the figure. Pulse duration of Δt = 10 ms; $E_{sample} = +10$ mV; $E_{tip} = -50$ mV; $I_T = 2$ nA. (**B**) Mean cluster height, as derived from 15 experiments, as a function of the tip displacement Δz used to generate the Cu clusters. The dotted lines indicate the height of a Cu monolayer. $E_{sample} = +10$ mV; $E_{tip} = -50$ mV; $I_T = 2$ nA.

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13. The potentials of tip and sample could be controlled independent of each other by means of a bipotentiostat. The tips used for modification and imaging were made from a Pt:Ir wire (80:20) by electrochemical etching and were subsequently coated with Apiezon wax to reduce the area in contact with the electrolyte, thus reducing the faradaic current at the tip to <0.1 nA. The working electrodes were evaporated Au films on Robax AF45 glass (Berliner Glas KG), which, after proper flame-annealing in an H_2-air flame, had (111) surfaces whose quality was similar to that of Au(111) single crystals.
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19. We are currently examining the possibility of the formation of such structures on semiconducting substrates, which would be of greater technological interest than deposition on metals (D. M. Kolb *et al.*, in preparation).
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Five-Coordinate Hydrogen: Neutron Diffraction Analysis of the Hydrido Cluster Complex $[H_2Rh_{13}(CO)_{24}]^{3-}$

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Pentacoordinate hydrogen atoms were identified by single-crystal neutron diffraction analysis of $[N(CH_3)_4]_3[H_2Rh_{13}(CO)_{24}]$. The hydrogen atoms are located in square pyramidal cavities of the Rh_{13} cluster, in positions almost coplanar with the Rh_4 faces on the surface of the cluster. They are slightly displaced inward, toward the central rhodium atom of the cluster, with average H–Rh(central) and H–Rh(surface) distances of 1.84(2) and 1.97(2) angstroms, respectively. This result shows that hydrogen, which normally forms only one bond, can be attached to five other atoms simultaneously in a large metal cluster.

In the late 1970s, it was shown by neutron diffraction (*1–3*) that H atoms could exist in the interstitial sites of metal cluster compounds such as $[HCo_6(CO)_{15}]^-$, $[HRu_6(CO)_{18}]^-$, $[HNi_{12}(CO)_{21}]^{3-}$, and $[H_2Ni_{12}(CO)_{21}]^{2-}$. The H atoms were found to be either six-coordinate (μ_6-H), located at the centers of metal octahedra (*1*, *2*), or in triply bridging positions (μ_3-H) on the interior faces of metal octahedral cavities (*3*). Here we report an example of pentacoordinate hydrogen (μ_5-H) found in the square pyramidal cavities of the cluster complex $[H_2Rh_{13}(CO)_{24}]^{3-}$.

The $[H_2Rh_{13}(CO)_{24}]^{3-}$ anion, first reported in 1975 (*4*), is a member of a family of clusters, $[H_xRh_{13}(CO)_{24}]^{(5-x)-}$ (x = 1 to 4), whose members are interconvertible by means of a series of acid-base equilibria (*4–9*). The Na salt of the title anion was prepared by refluxing a mixture of $Rh_4(CO)_{12}$ and NaOH in isopropanol under an atmosphere of H_2, followed by addition of Na_2CO_3 (*8*). It was

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