Fast nanoscale modification of Ag(111) using a scanning tunneling microscope

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Epitaxial Ag(111) films have been grown on mica. They exhibit flat terraces of a few 100 nm diameter, suitable for nanoscale modification with the scanning tunneling microscope (STM). Under ambient conditions, surface modifications of a few nanometers diameter were produced by raising the bias from below 1 V to a bias between 3 and 7 V for less than 50 ns. The steady-state current could be limited to 2 pA. This means that the modification is initiated while only a few electrons pass the tunneling junction, indicating that it is not a current effect. At positive sample bias, usually holes are formed, while at negative bias hillocks occur. In the case of hole formation, the current does not change significantly on a time scale of 10 μs. When hillocks are formed, the current may rise after the application of the voltage pulse. It was limited to 4 nA by the external circuitry and remains saturated until the tip is withdrawn on a time scale of milliseconds, i.e., the characteristic for the feedback loop control. Also in this case the modification is not caused by a current effect, since the limiting current would still allow nondestructive STM imaging. It is concluded that the modifications are caused by field evaporation of sample and tip material, respectively.

The ability of the scanning tunneling microscope (STM) to modify surfaces on the nanometer scale can be employed to investigate mechanical, thermal, and chemical processes occurring at interfaces, with obvious relevance for adhesion, tribology, and electrochemistry.[1–4] Moreover, it can give important insight into the processes occurring during STM operation. Finally, if the surface modifications can be made fast and reliable enough they may be of interest for high density information storage.

In practice, surface modifications with STM have been brought about by (1) driving the tip mechanically into the substrate, (2) raising the current, or (3) raising the bias voltage. Polycrystalline silver films have been modified by mechanical point contact formation under ultrahigh vacuum conditions,[5] and all three above-mentioned methods have been applied to various gold surfaces.[6–8] Of particular interest are the voltage-induced modifications, since spectroscopic STM experiments also employ bias-voltage variations. However, the bias-induced modifications are interpreted controversially in the literature. In particular, there is debate whether the hole formation on gold is attributable to intense local heating, similar to that observed at the anode spot in high-intensity electric arcs.[8,9] The goal of the present study was to better understand the processes underlying the voltage induced modification of noble metal surfaces, particularly Ag(111) under ambient conditions.[10]

A homebuilt STM[11] was operated under ambient conditions employing electrochemically etched Pt/Ir tips and a tunneling current between 2 pA and 2 nA. Voltage pulses of a duration of $\geqslant$20 ns were generated with a pulse generator (HP 8012B) and the current and z piezo response were recorded with a digital oscilloscope (Le Croy 9400). Silver films of 200 nm thickness were thermally evaporated onto green mica substrates (Mica Supplies, U.K.) at a substrate temperature during evaporation of 275 °C. Under these conditions Ag(111) terraces, several 100 nm in diameter and flat within $\leqslant$1 nm, can be prepared by epitaxial growth on mica.[12] Figure 1(a) shows the STM image of parts of two silver terraces on top of one large terrace spanning the whole image. The step heights are on the order of monolayers. It should be also noted that some small holes, a few nanometers in diameter and less than 1 nm deep, are present across the surface.

After recording the image of Fig. 1(a), the sample bias was raised four times for about 100 ns from +0.5 to +5 V, while scanning on a line across the surface. The subsequently recorded image exhibits a horizontal row of four holes, each about 10 nm in diameter and a few nanometers deep [Fig. 1(b)]. By contrast enhancement, it is shown that the produced holes are deeper than any of the naturally occurring holes, and therefore, can be easily distinguished from them [Fig. 1(c)]. It should be mentioned that occasionally also hillocks are formed; however, it appears that even then a hole is still present at the same time. Figure 2 exhibits a silver terrace with eleven marks produced in the same way as described above. In nine cases holes were formed, while in two cases a hillock is present, with at least one of them on top of a hole.

The observations described above are similar to what has been observed on gold.[6,7] In order to address the issue of local heating as the cause for the modification, the energy deposited during the formation of the holes was limited dramatically in the present study. It was found that a steady-state current of 2 pA and a bias pulse duration of less than 50 ns were sufficient to cause the holes. This implies that they can be initiated while only a few electrons pass the tunnel junction. Moreover, the current did not change significantly on a time scale of a few 10 μs, indicating that the hole formation cannot be attributed to a current effect. Instead, it is attributed to a field effect, namely field evaporation of the silver.

The electrical field strength required for field evapora-

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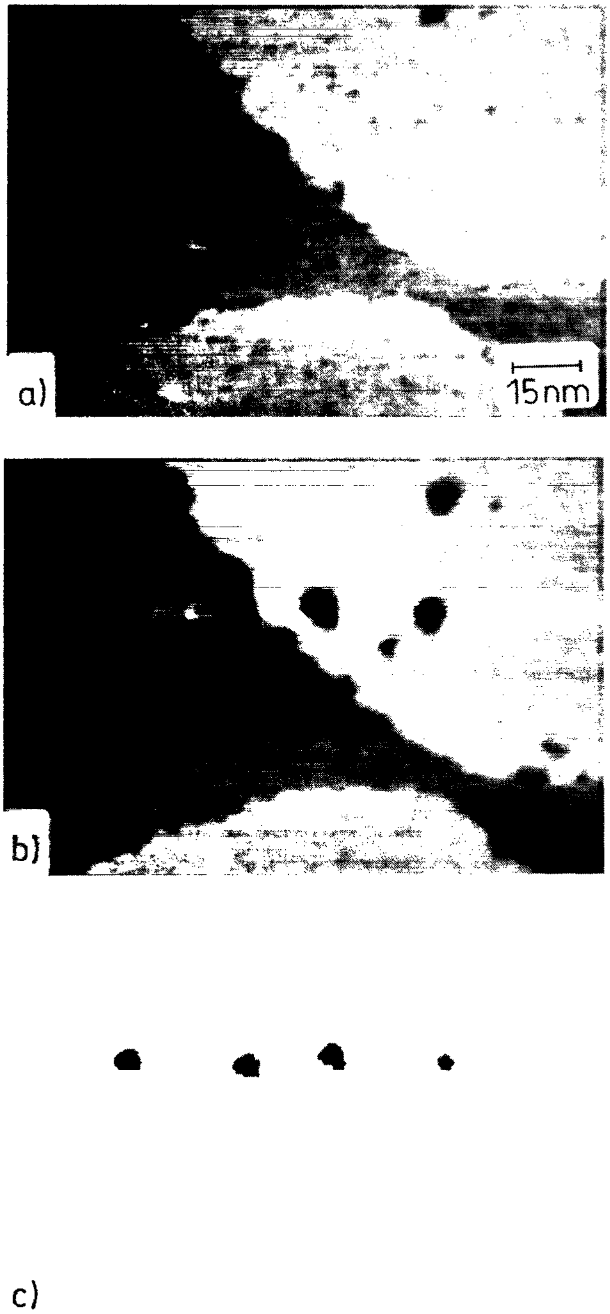

FIG. 1. STM images of Ag(111) on mica, (a) before and (b) after the formation of four holes in a horizontal row at positive sample bias. Step height between terraces and roughness on terraces is ≤1 nm. (c) Contrast enhancement demonstrates that the produced holes are deeper than the natural surface roughness. Image size: 130 nm × 90 nm.

tion is on the order of a few 10^{10} V/m, i.e., the order of the electrical field in the tunneling gap; moreover, metals are easily evaporated as positive ions.[13] The fact that reproducible STM images can be obtained at a steady-state bias of about + 1 V indicates that under these conditions the threshold for field evaporation is not exceeded. During the voltage pulses, however, the field is increased for a short time, and at positive sample bias the positive silver ions can be field evaporated.

At negative sample bias on the other hand, it should be

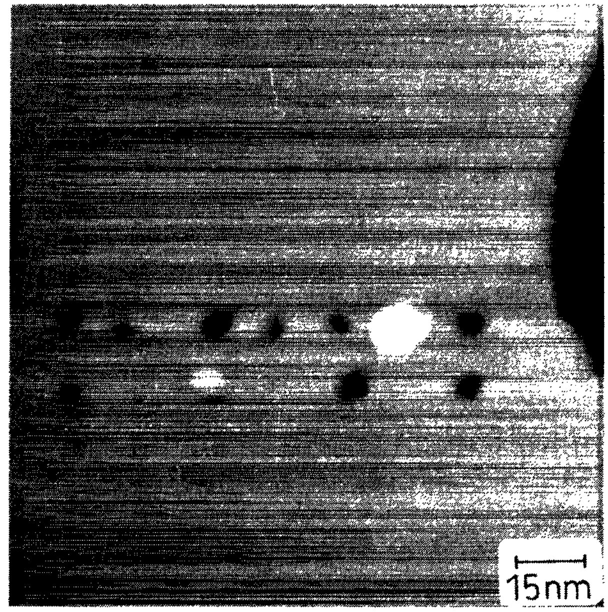

FIG. 2. STM images of Ag(111) on mica with eleven marks of about 10 nm diameter produced on two horizontal rows at positive sample bias. While generally a hole is formed, in two cases some material is transferred back to the surface, causing a hillock to be produced. Image size: 130 nm × 130 nm.

expected that tip material is field evaporated onto the sample. Figure 3 demonstrates that indeed hillocks are formed on the sample surface by voltage pulses at negative sample bias. In this case it has been observed that sometimes the current shoots up after the voltage pulse, indicating that a point contact has been formed. In order to also make sure that with the current in saturation for a few ms, the surface modification is not caused by a current-related thermal effect, the tunneling current was limited by external circuitry to 4 nA, i.e., a value which allows nondestructive STM imaging in the steady state.

Figure 4 summarizes the response of current and z piezo to the bias pulse for the case of negative sample bias (i.e., hillock formation), both (a) without and (b) with point contact. While without point contact the tip did move inward after the pulse, it had moved outward in the point contact case. This can be explained by the field evaporation from the tip in the case of no point contact, and a lengthening of the tip associated with breaking the contact mechanically by the piezo movement. In the case of hole formation at positive sample bias, the motion of the z piezo is not particularly pronounced.

Finally, the occasional occurrence of hillocks after positive sample bias pulses may be attributable to some tip instability after repeated silver transfer during several hole formations, indicating that the tip shape plays a role.

To conclude, thin epitaxial Ag(111) films on mica can be imaged reproducibly by STM under ambient conditions. They can be suitably flat for STM modification on the nanometer scale. Surface modifications of several nanometer diameter can be initiated by less than 50 ns voltage pulses. At positive sample bias, characteristic holes are

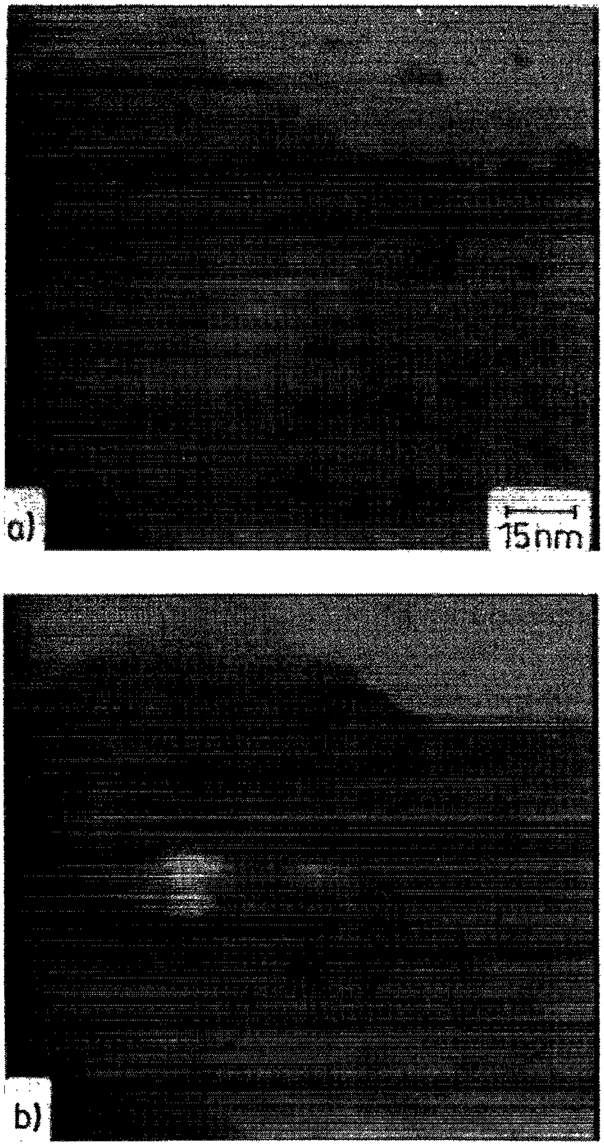

FIG. 3. STM image of Ag(111) on mica (a) before and (b) after the formation of a hillock at negative sample bias. Image size: 130 nm $\times$ 125 nm.

usually formed, while at negative bias, hillocks occur. As the underlying mechanism, current related thermal effects are excluded. Instead, the modifications are attributed to field evaporation of sample and tip material, respectively. While the formation of the hillocks can be associated with a point contact which is broken on the time scale of the feedback loop (ms), the hole formation can be fast ($\leqslant$50 ns).

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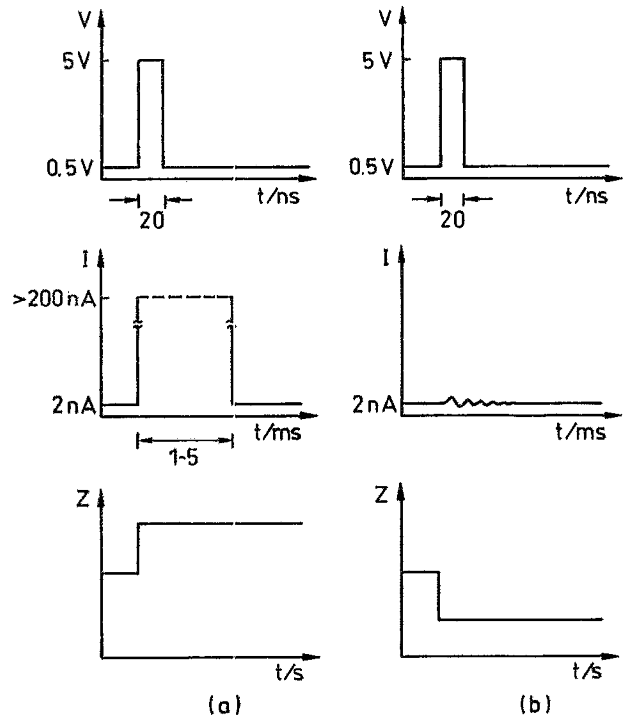

FIG. 4. Bias, current and z piezo position during surface modification by negative bias pulses applied with the STM. (a) without point contact formation and (b) with point contact formation.

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[10] This work has been presented at the STM'90/NANO I Conference in Baltimore, July 23–27, 1990, where also H. J. Mamin, P. H. Guethner, S. Chiang, and D. Rugar presented some related work on gold. As far as the basic conclusions go, i.e., field evaporation as mechanism for fast nanoscale modification, both studies are in good agreement.
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