Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/S151-06
Chinese Physics
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LOCAL ELECTROCHEMICAL DEPOSITION OF METAL ISLANDS MECHANICALLY INDUCED WITH THE TIP OF AN ATOMIC FORCE MICROSCOPE*

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(Received 2 December 2000; revised manuscript received 27 March 2001)

The investigation of electrochemical processes on the nanometer scale is of great scientific as well as technological interest. Here we study the electrodeposition of copper on a polycrystalline gold surface, and demonstrate that copper deposition can be locally induced by mechanical activation with the tip of an atomic force microscope (AFM). Whereas at higher values of the deposition voltage (>100mV), a solid copper film can grow on the gold surface without tip activation, at lower voltages (approx. 30–60mV), copper deposition only occurs at the position where the surface is activated by the AFM tip due to scanning in mechanical contact with the sample. With this mechano-electrochemical "writing" process, which can be performed at ambient conditions, the controlled local deposition of metallic islands is possible, at applied force loads of the order of 10nN. Both the size-dependence of the locally induced structures on the deposition time and the reversibility of the local deposition process are studied. Depending on the deposition parameters, individual copper islands between 50nm and 200nm in size were deposited at predefined locations on the gold surface. The investigations open perspectives for the controlled mechano-electrochemical writing of more complex nanostructures with the AFM tip.

Keywords: electrochemistry, nanostructuring, atomic force microscopy (AFM, SFM), copper deposition
PACC: 8280F, 6146, 6116P, 8115G

I. INTRODUCTION

Scanning probe microscopes such as the atomic force microscope (AFM) and the scanning tunneling microscope (STM) are not only valuable instruments for imaging surfaces. They also allow the controlled modification of surfaces on the nanometer scale and even on the atomic scale. Numerous examples of surface modification with scanning probe tips are found in literature. With the STM, individual atoms[1,2] and molecules[3,4] were manipulated and arranged in a controlled manner. Atomic-scale switching processes were induced locally on layered semiconductors even at room temperature and under ambient conditions.[5,6] AFM was used for nano-plowing.[7,8] Recently, we showed that the forces acting between AFM tip and sample surface can be used to break chemical bonds within the sample mechanically.[9–11] This not only allows the controlled structuring of solids lattice constant by lattice constant,[11] but also opens perspectives for mechanically inducing chemical reactions with the AFM tip.

In the field of selective local electrodeposition, numerous experiments have been performed by different groups, using either a scanning electrochemical microscope (SECM) or an electrochemical STM. In most cases, a conductive tip and the sample are kept within the electrolyte, and voltage pulses are applied between tip and sample.[12–19] To increase the reproducibility, the spatial selectivity and the resolution of the local deposition process, different procedures were developed, including the deposition of metals on the STM tip with subsequent mechanical transfer to the sample[15,16] or the application of complex voltage pulse sequences.[17,18].

Few attempts, however, have been made so far to use the tip of an AFM for the controlled local electrodeposition. First experiments by LaGraff and Gewirth[20,21] indicate that the influence of a scanning tip can both reduce or enhance copper electrodeposition on copper single crystals, presumably depending on the applied force between tip and sample. While these experiments demonstrate the relevance of tip-sample interaction on the electrodeposition process, the underlying mechanisms are not yet clear.

*Project supported by the Deutsche Forschungsgemeinschaft within Sonderforschungsbereich 195.

Here, it is demonstrated that the local electrodeposition of copper can be induced selectively at a predefined location with the tip of an AFM with no detectable deposition in the surrounding area. It is shown that this process can be performed even on polycrystalline gold films and in ambient environmental conditions. Questions of reproducibility and reversibility of the structuring process are studied, and the underlying mechanisms are discussed.

II. EXPERIMENTAL

For the experiments, a home-built electrochemical AFM system with a conventional beam deflection detection system was used (Fig.1). The AFM system includes the electrochemical cell, a computer controlled potentiostat and an electrochemistry software package for the control of the potentiostat. Two different V-shaped silicon nitride cantilevers of lengths 220μm and 140μm with attached pyramidal tips were used for the experiments, which have nominal force constants of 0.03N/m and 0.1N/m, respectively. The same cantilevers were used for both surface modification and subsequent imaging of the resulting deposited structures. In all experiments reported below, normal forces of approx. 10nN were applied between tip and sample.

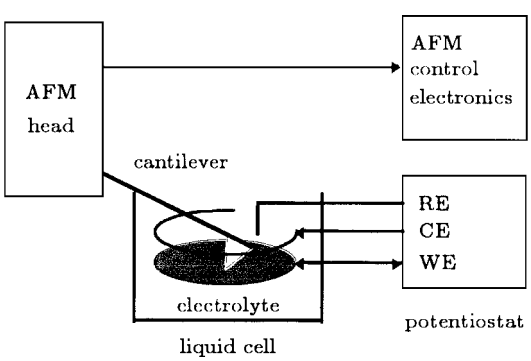


Fig.1. Schematic diagram of the electrochemical atomic force microscope setup, including the electrochemical cell with Cu reference (RE) and counter electrode (CE) and an evaporated Au substrate as working electrode (WE).

All AFM images shown in this article were taken by contact-mode AFM in the deflection mode. Both forward and backward scan were performed with the same scanning velocity. The images shown below represent unfiltered data. They were taken in the forward scanning direction, i.e. while scanning the tip from left to right relative to the sample. Scan rates of 1 line per second in the case of Fig.2 and 4 lines per second in the case of Fig.4 were used. The AFM images are given in a linear gray-scale, increasing brightness corresponding to increasing height. The experiments were performed at room temperature and in ambient environmental conditions, i.e. the electrolyte was exposed to ambient air during the experiments. All images were taken in situ within the electrolyte.

Gold films (thickness 50nm) on glass substrates, which were obtained by thermal evaporation, served as working electrodes for the electrodeposition. Prior to evaporation, the glass substrates were cleaned by sonication first in acetone and subsequently in ethanol. To increase adhesion of the gold film to the substrate, a Cr layer (thickness 4nm) was evaporation deposited before evaporation of gold. The substrate was kept at room temperature during the evaporation process. The base pressure in the evaporation chamber was approx. 10^{-6} mbar. Film thickness was measured with a quartz microbalance.

Two 0.25mm diameter copper wires (Goodfellow) served as reference and counter electrodes, respectively. The electrolytes consisted of aqueous solutions of 50mM H_2SO_4 (suprapure, Merck) with 1 mM $CuSO_4$ (p.a., Merck). All potentials were measured against the Cu/Cu^{2+} reference electrode. The deposition experiments were made at an overpotential of –300mV in the case of the copper island film and –60mV in the case of the local tip activated deposition (see Fig.3).

III. RESULTS

A. Copper island film growth

The growth of copper films from a $CuSO_4$ solution (concentrations: see above) was studied in situ within the electrochemical cell of the AFM. Figure 2 shows AFM images of one and the same 5μm×5μm scanning area before deposition (Fig.2(a)) and after deposition for three different deposition times (Fig.2(b)–(d)). Near the center of the scanning area, a hillock is visible in the gold substrate which serves as a position label to make sure that in the four images of Fig.2, the same sample area was imaged. To avoid artifacts due to the AFM scanning process, the AFM tip was not scanning during the copper deposition process in the deposition experiments shown in Fig.2.

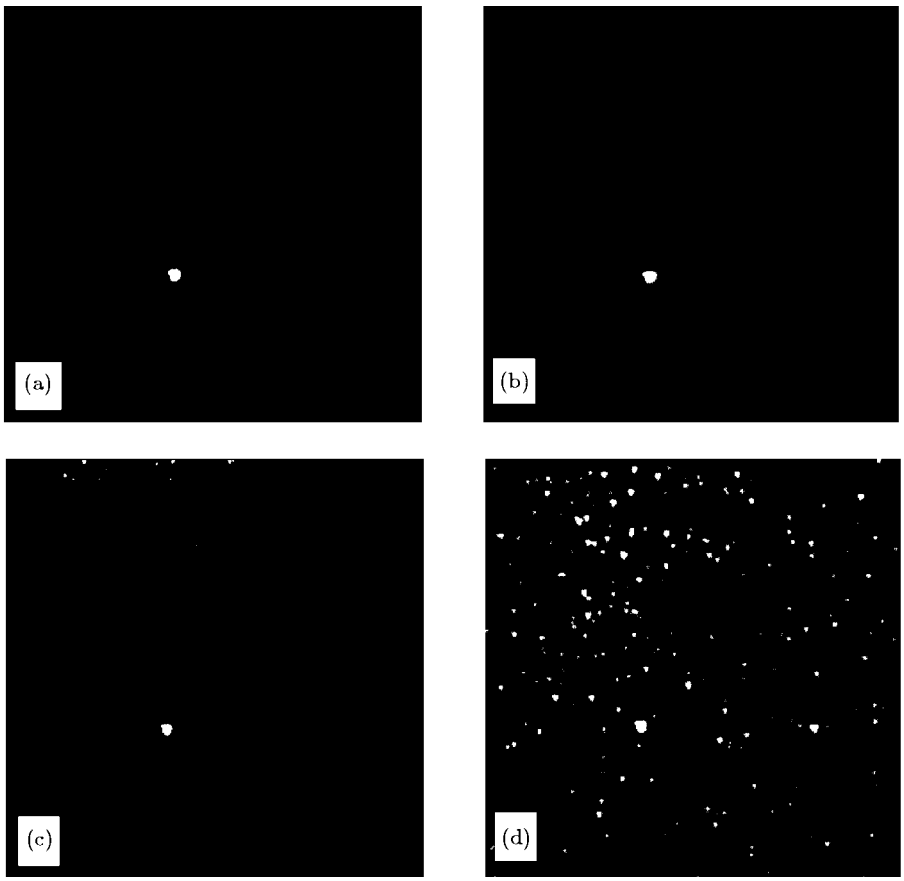


Fig.2. In situ AFM images of Cu deposition on a polycrystalline Au substrate in dependance of the deposition time (a) 0s, (b) 8s, (c) 10s, (d) 15s. Deposition potential: –300mV, scan size: 5μm×5μm.

After the AFM image of the as-prepared surface (Fig.2(a)) was taken, the scanning process was stopped and the potential of the sample surface relative to the copper reference electrode was changed from 0V to a value of –300mV for a period of 8s and then again set to approx. 0V. Subsequently, the image of Fig.2(b) was obtained, which again exhibits the bright spot of the hillock within the gold substrate. In contrast to the as-prepared sample surface of Fig.2(a), however, small copper islands with typical diameters between 30nm and 80nm are observed in the upper part of the image, leading to a partial coverage of the gold surface. The fact that island growth did not occur homogeneously over the entire scanning area, but preferably in the upper part of the image may be due to local gradients in concentrations within the electrochemical cell. After applying a voltage of +300mV for 20s, these islands are completely dissolved. After dissolution, the potential was again set to the deposition voltage of –300mV for 10 s and then set back to 0V again. Subsequent AFM imaging lead to the image of Fig.2(c), which shows a significantly higher area density of copper islands on the surface, the upper third of the scanning area being almost completely covered with copper. After complete dissolution of the deposited copper layer (+300mV, 20s), a third deposition experiment was performed, using a deposition time of 15 s at –300mV. The result of subsequent AFM imaging is given in Fig.2(d). The surface is almost completely covered with copper islands with typical sizes between 40nm and 200nm. Again, deposition was completely reversible.

The experiments allowed a direct study of copper island nucleation and film growth on polycrystalline gold substrates in situ within the electrochemical cell of the AFM. Both average island size and surface roughness of the copper films are significantly higher than that of the gold substrate.

B. AFM tip-induced growth of individual copper islands at predefined positions

Figure 3 shows a cyclic voltammogram taken within the electrochemical cell of the AFM. Varying the deposition potential, we find that copper deposi-

tion can be observed in the overpotential range below –100mV. In the regime of the overpotential between –60mV and –30mV, no copper deposition was found while the AFM tip was not scanning. However, if the tip was scanning at forces of the order of 10nN, deposition of copper could be observed within the scanning area. By choosing small scanning areas during copper deposition within this potential range, individual copper islands could be grown selectively at predefined locations.

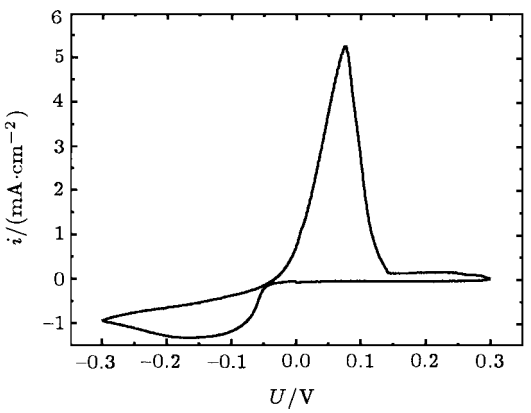


Fig.3. Typical cyclic voltammogram of the system Au/0.05M H_2SO_4 + 1mM $CuSO_4$ in the electrochemical cell of the AFM. The potential is measured against a Cu reference electrode. Voltage sweep rate: 5.9mV/s.

Figure 4 shows the results of such a deposition experiment. The four images of Fig.4(a)–(d) show AFM topography images of the same 500nm×500nm area of the sample surface within the electrolyte. Figure 4(a) is the image of the as-prepared gold surface, imaged within the electrolyte. After taking this image, the scan size was reduced to 24nm×30nm, and the tip started to scan a trace of the shape of the number "8" within this area at a rate of 50 cycles per second for a period of 2 seconds. During this time, the sample potential was set to a value of –60mV. After this deposition time interval, the scanning of the "8" was stopped and the sample potential was set back to 0V. Subsequently, the scanning area was increased to 500nm×500nm again, and the AFM image of Fig.4(b) was obtained. It shows that due to the scan activated deposition process, a pair of coalescent copper islands had grown at the position where the AFM tip was scanning.

After dissolution of the deposited copper island at a sample potential of +300mV, copper was deposited in the same way as described above for Fig.4(b), except for the use of a longer deposition time of 3 seconds. As a result, a larger copper island had grown, again at the position where the tip was scanning during deposition (Fig.4(c)). After subsequent dissolution, a third deposition experiment was performed, applying a deposition time of 4 seconds (Fig.4(d)).

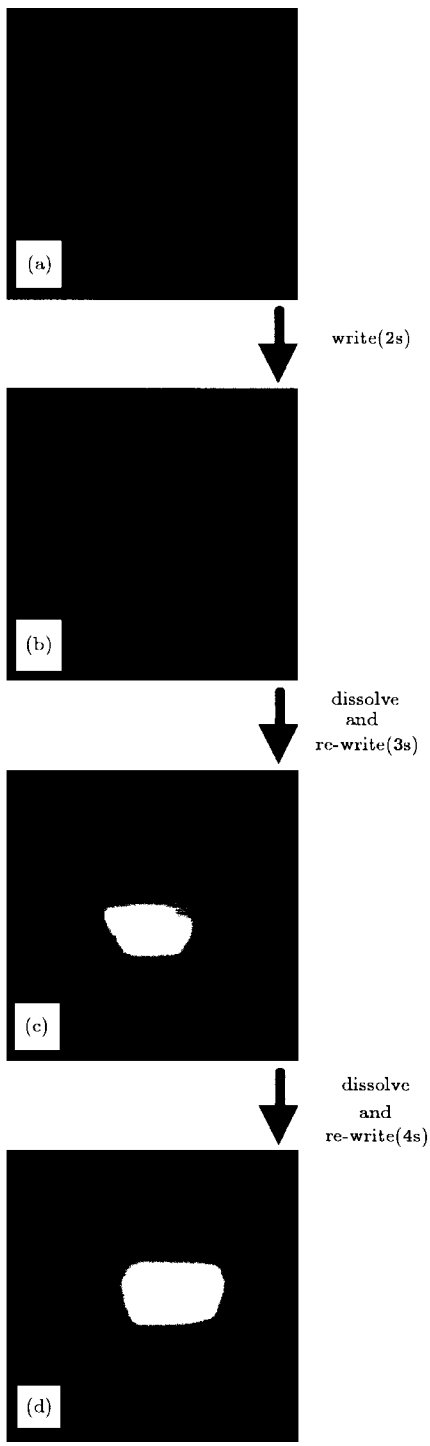


Fig.4. AFM tip induced electrodeposition of Cu islands on a polycrystalline Au substrate. The AFM images (a)–(d) show the same area of the sample surface (a) before deposition, (b) after tip induced Cu deposition (deposition time: 2s), (c) after Cu dissolution and subsequent deposition (deposition time: 3s), (d) after Cu dissolution and subsequent deposition (deposition time: 4s). Deposition potential: –60mV, scan size: 500nm×500nm.

Figures 4(a)–(d) are displayed using the same height scale, illustrating the increase of both size and height of the electrochemically grown copper islands with increasing deposition time. In Fig.5, the corresponding cross-sections are shown, illustrating the rapid growth of the islands after nucleation. While after a deposition time of two seconds, the island height is only 3.5nm, it reaches approx. 18nm after a total deposition time of 4 seconds.

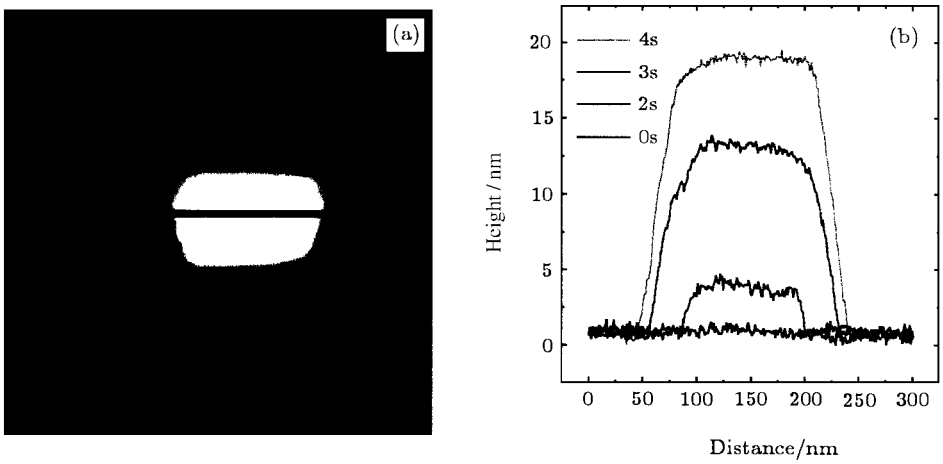


Fig.5. AFM image of the tip induced Cu island of Fig.4(d) together with the corresponding cross-sections of the Cu islands of Figs.4(a)–(d) as a function of the deposition time. Scan size in (a): 500nm×500nm.

IV. DISCUSSION

The above experiments demonstrate that electrodeposition can be induced locally with the tip of an AFM. As no potential was applied to the tip of the AFM and the experiments could be reproduced both with insulating and with electrically conducting tips, the locally selective deposition is most likely related to the mechanical interaction between tip and sample during the scanning process. This is further supported by the observation that the mere presence of the tip in contact with the sample does not lead to locally selective deposition. The scanning process, i.e. the movement of the tip relative to the sample, is necessary to induce local electrodeposition.

Obviously, the scanning AFM tip mechanically activates deposition sites and/or nucleation centers for local copper deposition. A possible explanation of the observed phenomena is the assumption of a passivating layer on the gold surface which prevents deposition of copper on the gold surface at values of the overpotential between –60mV and 0V. Due to the mechanical interaction between tip and sample, this passivating layer could be disrupted locally. This would explain the selective local copper deposition within the areas where the tip is scanning. This explanation is also in agreement with the observation that lateral forces occurring between tip and sample during the scanning process can be used to induce rupture of chemical bonds mechanically.[10,11] Investigations concerning the nature of such a passivating layer are currently in progress. As the experiments have been performed under environmental conditions, especially in the presence of oxygen, the formation of a surface layer on the gold substrate involving copper oxide/hydroxide and/or other compounds such as thiols is possible.

The alternative explanation that the tip induces defects within the gold surface itself, which then act as nucleation sites for the subsequent copper deposition, would well explain a somewhat enhanced copper deposition within the scanning area of the tip. However, with this mechanism alone (i.e. without assuming other additional mechanisms involving e.g. the local activation of a passivating layer), it is difficult to explain the high selectivity of the deposition process. The substrate for deposition in our experiments is not a metal single crystal, but thermally evaporated polycrystalline gold, which was not annealed and which even before interaction with the AFM tip would exhibit a high density of defects (steps, kinks, dislocations etc.). In the experiments, however, metal deposition was observed selectively at the position were the AFM tip was scanning.

V. CONCLUSIONS

The results shown above demonstrate that electrodeposition of copper islands on a polycrystalline gold substrate can be mechanically induced at predefined locations with the scanning tip of an atomic force microscope. Within a certain potential range (from –60mV to –30mV), the deposition process is highly selective, deposition occurring only at positions which are activated with the scanning AFM tip whereas for overpotential values <–100mV, copper island nucleation and copper deposition occur without tip activation. The experiments demonstrate the feasibility of a spatially selective mechanical activation of (electro)chemical reactions locally on the nanometer scale with a scanning probe tip.

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