

Electrodeposition of nanoscale magnetic structures

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Magnetic Co clusters have been electrodeposited from an aqueous electrolyte onto Au surfaces in an electrochemical scanning tunneling microscope (STM). In a two-step electrochemical process, Co is first deposited onto a Au STM tip, then completely dissolved, and locally deposited onto the substrate underneath the STM tip due to local Co^{2+} oversaturation, which results in a laterally varying increase of the Co/Co^{2+} Nernst potential at the substrate surface. Mechanical tip-sample contacts or creation of substrate defects can be excluded. The structure size is of the order of the STM tip apex diameter, and is in detail determined by the substrate potential. © 1998 American Institute of Physics. [S0003-6951(98)00348-9]

The physical properties of nanometer-scale structures and particles are attracting increasing interest in view of studies of chemical reactivity, catalysis, and particularly, magnetism and superparamagnetism in reduced lateral dimensions. Electrodeposition as used for the preparation of nanowires,¹ metal cluster arrays,² or in the scanning electrochemical microscope (SECM)^{3,4} would be advantageous, since electrodeposition prevents preparation-induced irreversible modifications of either substrate or scanning tunneling microscope (STM) tip.

In this work we explore the feasibility of a purely electrochemical deposition of Co without any mechanical tip-sample contact or creation of substrate modifications. This is achieved by a two-step process: The first step is the diffusion-limited deposition of Co from the electrolyte onto the STM tip. The second step is the complete dissolution of Co from the STM tip, and its deposition onto the substrate underneath the tip as determined by the Co^{2+} concentration profile near the STM tip during dissolution. This mechanism differs from that reported by Kolb *et al.*,² particularly in the material transfer from STM tip to the substrate surface, which is achieved by electrodeposition in our case, whereas it is achieved by mechanical contact between the STM tip and substrate in the case of Kolb's mechanism. We will show that the main parameters determining the size of the deposited structures are the diameter of the STM tip apex and the potential of the substrate [working electrode (WE)].

The experiments were performed with the electrochemical version of a Nanoscope III system (Digital Instruments) and the Nanoscope bipotentiostat. Both have been modified to vary the tip potential E_{tip} by external potentials from a wave-form generator independently of the substrate potential E_{WE} , which was adjusted using the Nanoscope software. The actual tip current I_{tip} was monitored by a digitizing oscilloscope. A conventional four-electrode electrochemical STM cell with a volume of about 100 μl was made from Kel-F. Both, E_{tip} and E_{WE} were measured versus a saturated calomel reference electrode (SCE), connected to the cell by a glass capillary. The counter electrode was made from Pt wire. STM tips were prepared from Au wires of 0.25 mm diam, etched in a lamella of HCl (32%) at a voltage of +1.6 V, and then manually coated with Apiezon wax. W as well

as Pt/Ir tips were not applicable in our experiments due to intolerable Faradaic currents in H_2 -containing environment. The Faradaic current of the isolated Au tip is nearly zero down to tip potentials as low as -800 mV (Fig. 1). Capacitive currents, as usually observed in current-voltage characteristics of Co deposition,⁵ were practically zero because of the low capacitance of our STM tips, which is of the order of 1 pF due to the small uncoated tip area of approximately 6 μm^2 . WE was a 200 nm thick polycrystalline Au film on glass with a considerably smaller mean surface roughness on the μm scale, than that found in our flame-annealed Au(111) substrates between the atomically flat terraces. The aqueous electrolyte consisted of suprapure grade Na_2SO_4 (0.25 M), CoSO_4 (1 mM), and ultrapure water (Milli-Q plus, Millipore). All STM images are shown as top view in the constant current mode.

Prior to each experiment the potential of the onset of Co bulk deposition onto the WE was determined by STM measurements to be approximately -790 mV in 1 mM Co^{2+} solution. E_{WE} was held constant 20 mV more positive, i.e., at -770 mV, during the deposition procedure, to prevent undesired Co bulk deposition onto the WE.

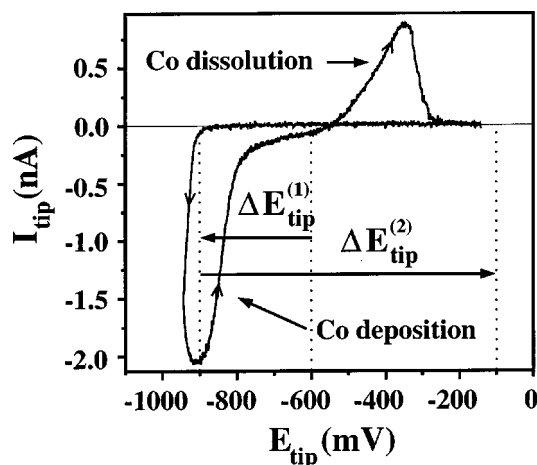


FIG. 1. Current-voltage characteristics of Co deposition onto a Au STM tip from 0.25 M Na_2SO_4 /1 mM CoSO_4 as recorded in the STM cell. The potentials are quoted against a saturated calomel electrode (SCE). The arrows indicate the cycling direction of the voltage at a sweep rate of 10 mV/s.

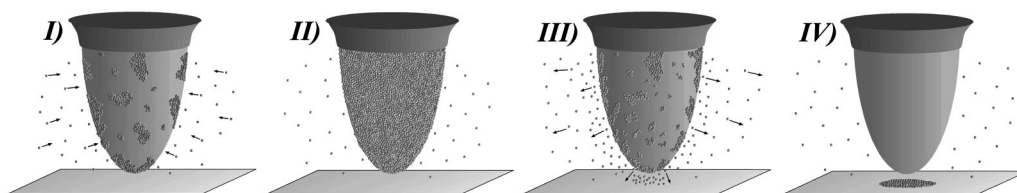


FIG. 2. Schematic illustration of the mechanism at the STM tip. (I) Deposition of Co from the electrolyte onto the uncovered part of the tip. (II) Co-covered STM tip. (III) Complete dissolution of previously deposited Co causing an increase of the Co^{2+} concentration near the tip according to the diffusion profile. (IV) Co dissolved from the very end of the tip is deposited locally onto the substrate.

Before each deposition cycle the tip was withdrawn from the Au surface by 20 nm. Thus, an inadvertent tip–substrate touch during the following electrochemical deposition cycle could be excluded. The tip was laterally positioned within the previously imaged Au surface area by means of the STM scanner piezoelements using the Nanoscope software. Initially, the tip was held at $E_{\text{tip}} = -600$ mV where neither Co deposition nor Co dissolution occurs (Fig. 1).

The first step of the deposition cycle consists of a potential step $\Delta E_{\text{tip}}^{(1)}$ from $E_{\text{tip}} = -600$ mV to $E_{\text{tip}} = -900$ mV (Fig. 1) in order to deposit Co onto the uncoated apex of the tip for, typically, 4 s [Fig. 2(I)]. The final thickness of the deposited Co layer on the STM tip was estimated from the integral of the simultaneous current measurement to be approximately 15 nm, which is sufficiently less than the preset tip–substrate distance of 20 nm. Adjusting this distance below 20 nm resulted in electrical, and hence, mechanical, short circuits between tip and substrate during Co growth, thus proving the estimated thickness of our Co layer covering the STM tip.

The second part of the cycle consists of a potential step $\Delta E_{\text{tip}}^{(2)}$ to $E_{\text{tip}} = -100$ mV (Fig. 1) in order to dissolve Co from the tip [Fig. 2(III)]. This Co dissolution results in a local oversaturation of the electrolyte by Co^{2+} near the tip causing, at the substrate surface, a laterally varying shift of the Co/Co^{2+} Nernst potential to more positive values than the actually preset E_{WE} . Hence, dissolved Co^{2+} ions are locally deposited onto the WE underneath the tip [Fig. 2(IV)]. No deposition occurs outside this area on the surface of the WE, because there the Co/Co^{2+} Nernst potential remains lower than E_{WE} . After the end of the cycle E_{WE} is kept further at -770 mV, and the tip is moved back into the tunneling mode for subsequent *in situ* imaging of the deposited structures.

Figure 3(a) shows as an example three Co dots, which have been deposited by applying the pulse sequence described above three times. The base width of the dots as measured by STM varies from approximately 110 nm (A) down to 58 nm (C) while the height covers a range from approximately 18 to 9 nm, respectively. All dots can be completely dissolved from the Au surface if E_{WE} is adjusted around approximately -300 mV [Fig. 3(b)], thus clearly demonstrating that the clusters are Co, and not Au from the tip or substrate surface.

In order to understand the mechanism quantitatively, we consider the local variation of the Co^{2+} concentration in the vicinity of the tip apex, and of the Co/Co^{2+} Nernst potential at the substrate surface. The thickness of the diffuse double layer around the tip and substrate surface is for our experimental conditions of the order of 1 nm,⁶ and thus much

smaller than the tip–substrate distance. We model the tip apex as a sphere of 100 nm diam, in agreement with numerous scanning electron micrographs of our STM tips, and assume a continuously Co^{2+} emitting spherical surface source with constant emission rate. This is admissible, since the Co dissolution from the tip is limited by the current maximum of about 130 nA of the Nanoscope tip current/voltage amplifier for approximately 10 ms.

The stationary radial Co^{2+} concentration profile during Co^{2+} emission was derived solving the diffusion equation for Co^{2+} according to Carslaw and Jaeger,⁷ assuming a Co^{2+} diffusion constant of 7×10^{-6} cm²/s.⁸ This radial concentration profile is correlated with an increase of the Co/Co^{2+} Nernst potential at the substrate surface according to the Nernst equation. The calculated increase ΔNP of the Co/Co^{2+} Nernst potential at the substrate surface with respect to the Nernst potential of 1 mM Co^{2+} solution is shown in Fig. 4. The Co/Co^{2+} Nernst potential at the substrate surface can be increased by up to 26 mV with respect to the Nernst potential of 1 mM Co^{2+} solution in the limit of zero tip–substrate distance. Since E_{WE} was preset approximately 20 mV more positive than the Co bulk deposition potential in a 1 mM Co^{2+} electrolyte, the Co/Co^{2+} Nernst potential is then shifted above E_{WE} within a certain region underneath the tip, as indicated by ‘growth area’ in Fig. 4.

The model calculation shows that the tip diameter and E_{WE} are the most important parameters, which have to be controlled. The condition to locally exceed E_{WE} for Co depo-

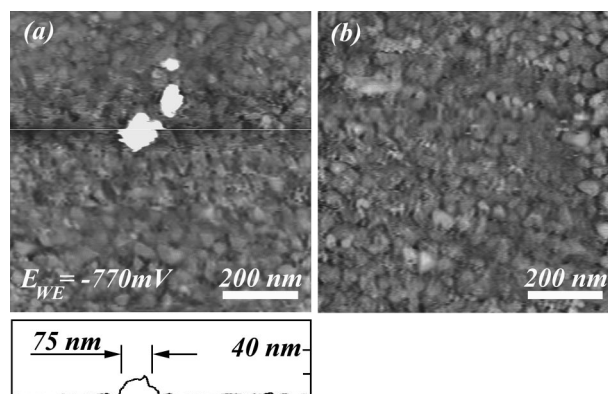


FIG. 3. (a) STM image of three Co dots on a Au surface. The tip was withdrawn 20 nm from the Au surface during deposition; $E_{\text{WE}} = -770$ mV. The line profile shows the cross section of dot A in the STM image. The variations in the dot size are compatible with corresponding variations in the measured tip loading current/time characteristics. A second reason for varying dot sizes may be an inhomogeneous Co deposition onto the tip during the first step of the deposition process. (b) STM image of the same Au surface after stripping off the Co dots by adjusting E_{WE} to -300 mV.

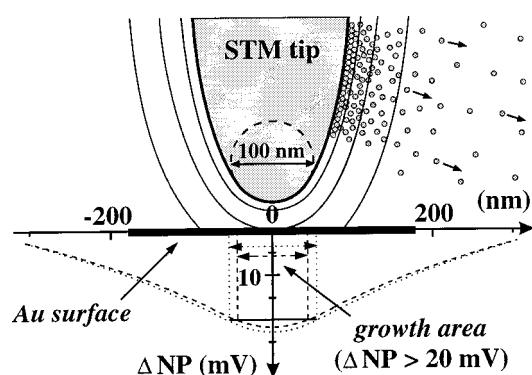


FIG. 4. Calculated radial Co^{2+} concentration profile and shift ΔNP of the Co/Co^{2+} Nernst potential at the substrate surface, assuming a continuously Co^{2+} emitting spherical surface source in order to approximate the parabolic shape of the STM tip as drawn in the graph. Co dissolution from the tip causes an increase of the Co^{2+} concentration around the tip. Lines around the tip indicate surfaces of constant Co^{2+} concentration. The increase of the Co^{2+} concentration at the substrate surface is correlated with an increase ΔNP of the Co/Co^{2+} Nernst potential. The lateral variation of ΔNP is shown for a tip-substrate distance of 20 nm (dotted line) and 30 nm (dashed line). At E_{WE} preset 20 mV above the Nernst potential of a 1 mM Co^{2+} solution, local Co deposition occurs exclusively within the indicated "growth area," where $\Delta NP > 20$ mV. The influence of the substrate on the Co^{2+} diffusion profile has been neglected.

sition underneath the tip due to ΔNP opens up the possibility to tailor the size of the structures by variation of the preset E_{WE} , as has been in fact observed: A more positive E_{WE} results in smaller size of the deposited structures since the Co/Co^{2+} Nernst potential at the substrate surface is exceeded only within a smaller growth area.

In order to estimate the influence of tip-substrate distance variations on the size of the deposits, we plotted in Fig. 4 ΔNP for two tip-substrate distances of 20 nm (dotted line) and 30 nm (dashed line). ΔNP varies by about 1 mV in the maximum of ΔNP , the diameter of the growth area changes from 115 to 90 nm, assuming the same $E_{WE} = -770$ mV (Fig. 4).

This demonstrates that large variations of the tip-substrate distance of 50% (or 10 nm) result in approximately 20% variation in the diameter of the deposits, hence, showing the tip-substrate distance to be an uncritical parameter. In particular, a larger tip-substrate distance is expected to result in a smaller diameter of the deposit.

The shift ΔNP of the Co/Co^{2+} Nernst potential, as shown in Fig. 4, is large enough that E_{WE} can be preset well above the Nernst potential of 1 mM Co^{2+} to prevent undesired Co bulk deposition onto WE. Additionally, a further decrease of the uncoated tip area would result in an increase of the Co^{2+} current density during Co dissolution from the tip, assuming the same current limit of 130 nA as given by the tip current/voltage amplifier. According to our estimate,

this increased Co^{2+} current density would result in a larger increase of the Co^{2+} concentration and thus in a larger ΔNP than was the case in our experiments. The potentials of the STM tip during the deposition sequence, as indicated in Fig. 1, are uncritical for the size of the growth area, since the Co^{2+} oversaturation around the tip is caused by a current-limited Co^{2+} source, which generates during emission a constant Co^{2+} concentration profile.

In contrast to nanoscale deposition using SECM, our deposition process provides identical start conditions at the beginning of each deposition cycle. It uses the infinite Co^{2+} reservoir of the electrolyte and is, therefore, not limited by dissolution of an ultramicroelectrode as in the case of SECM,³ or influenced by the hydrodynamics of nanometer-size capillaries.⁴

Thus, the diameter of the STM tip is the most crucial parameter of the deposition. According to our estimate, the size of the deposited structures is of the order of the tip apex diameter, which was approximately 100 nm (Fig. 4). Within this regime the detailed structure size is determined by E_{WE} . Deposition of much smaller structures than 100 nm seems to require a better defined tip apex than has been the case in our experiments. The tip diameter, however, is expected to decrease with developing suitable tip preparation techniques.

The presented type of electrochemical deposition of Co dots in a STM provides the opportunity to grow nanoscale patterns without irreversible preparation-induced modifications of either substrate or tip surface. The large tip-substrate distance in the range of 20–30 nm guarantees a purely electrochemical deposition. The diameter of the electrodeposited nanostructures is expected to be limited only by the diameter of the STM tip apex.

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