

Nanoscale electrodeposition: A new route to magnetic nanostructures?

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Localized electrochemical deposition of small Co clusters on Au (111) has been achieved by using the tip of a scanning tunneling microscope (STM) as an electrochemical nanoelectrode. In contrast to most of the reported techniques to create nanostructures, this approach avoids irreversible modifications of both substrate and deposit during the preparation process. A special polarization routine of the STM tip allows a purely electrochemical growth of Co clusters with diameters as small as 15 nm. © 2000 American Institute of Physics. [S0021-8979(00)47308-1]

I. INTRODUCTION

The physics of nanometer sized particles and structures with lateral dimensions of less than 100 nm achieved increasing interest in the recent years, driven on the one hand by the requirements of the chip and magnetic storage technology to decrease the structure size, but on the other hand by novel properties of the nanostructures, which deviate from the bulk material properties.^{1–3} In order to study the intrinsic material properties of nanostructures, it would be desirable to grow these structures without preparation induced irreversible modifications of either substrate or deposit, which are likely to be introduced by conventional lithographic preparation techniques. Thus, a variety of techniques using a scanning tunneling microscope (STM) tip as a tool to generate nanostructures have been reported. Among these techniques, the generation of nanostructures at the solid–liquid interface is advantageous for at least two reasons: The STM tip can be used as an independent electrochemical electrode, and Fermi levels of tip and substrate can be independently controlled. Second, over and undersaturation during cluster deposition can be well controlled, and rapidly changed by a simple variation of the potentials, which is difficult to achieve in ultrahigh vacuum STM based deposition.

However, even among the electrochemical methods, unwanted mechanical interaction between STM tip and substrate cannot be excluded in most of the reported techniques.^{4,5} The mechanism of Kolb *et al.* achieves the cluster deposition onto the substrate by a soft “jump to contact” mechanism,^{6,7} which may prevent damage of the substrate, whereas the mechanism of Penner *et al.* is based on the generation of defects on the substrate surface, which act as nucleation centers for subsequent growth of nanosized clusters.⁸

The imponderabilities of these approaches may be overcome by a purely electrochemical deposition, using the STM tip as a reversible “nanoelectrode.”⁹ Deposition onto the substrate may be initiated by a local increase of the ion concentration in the electrolyte around the STM tip, which makes the effective, local Nernst potential for deposition at the substrate surface underneath the STM tip more positive. We will show in this article exemplarily for Co that this

purely electrochemical mechanism is able to generate clusters of diameters as small as 15 nm, as measured by *in situ* STM, even if the STM tip is withdrawn more than 10 nm from the substrate surface during deposition.

II. EXPERIMENTAL DETAILS

The experiments have been performed in an electrochemical version of the Nanoscope III scanning tunneling microscope, which has been modified to allow the application of external voltages independently to either the substrate or to the STM tip.

The deposition experiments were performed in a deaerated aqueous electrolyte of 0.25 M Na₂SO₄ and 1 mM CoSO₄ ($pH \approx 4-5$, $T = 298$ K). Au (111) surfaces were chosen as substrates, which show atomically flat terraces of several hundreds of nanometers. STM tips were prepared by electrochemical etching from 0.25-mm-diam Au wire, and manually coated with Apiezon wax. The area of the unisolated apex is of the order of 10 μm^2 , as measured by scanning electron microscopy. These tips have been found to be well suited as electrochemically inert nanoelectrodes, which can simultaneously be used to image the deposited clusters by *in situ* STM.

Figure 1 shows the current–voltage characteristics of the

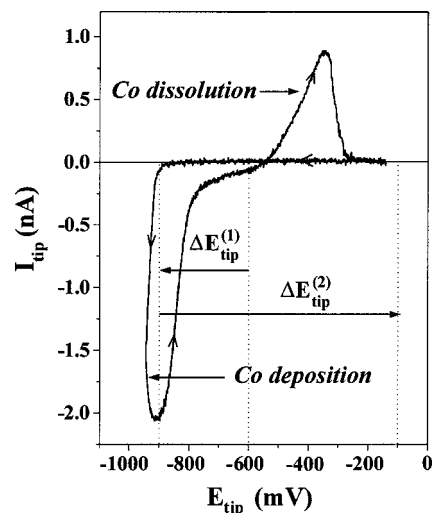


FIG. 1. Current–voltage characteristics of the Co deposition and dissolution at the Au STM tip. Potentials are quoted with respect to the standard calomel electrode.

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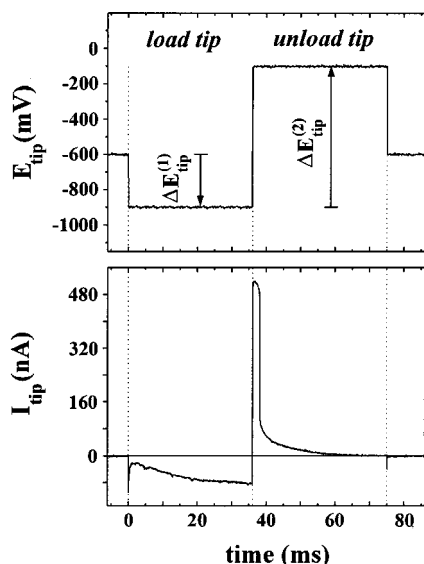


FIG. 2. Time dependence of the applied tip potential, and corresponding current transient, for a complete deposition cycle. The STM tip is in a constant distance of 10–30 nm from the substrate surface; $E_{WE} = -770$ mV is held constant during the complete deposition cycle.

Co deposition and dissolution onto the uncovered apex of the Au STM tip. This is basically the same curve as it is recorded during Co deposition onto the Au(111) substrate. Adjusting the potential below the Nernst potential of Co/Co^{2+} results in a deposition of Co^{2+} from the electrolyte, whereas an electrode potential more positive than the Nernst potential results in a dissolution of previously deposited Co. Around the Co/Co^{2+} Nernst potential there is a balance of cathodic and anodic Co^{2+} currents. During deposition as well as during subsequent STM imaging, the substrate potential is adjusted within this particular potential range, approximately 20 mV more positive than the onset of the Co^{2+} nucleation, in order to prevent Co bulk deposition from the electrolyte onto the substrate, and to stabilize deposited clusters on the substrate surface.

III. RESULTS AND DISCUSSION

The electrochemical growth of Co clusters on the Au (111) surface has been achieved by a two step process: The first step of the deposition procedure consists of Co deposition onto the STM tip which is achieved by a potential jump $\Delta E_{\text{tip}}^{(1)}$ of the tip potential from -600 to approximately -900 mV (Fig. 1). The cathodic tip charge, as measured during Co deposition onto the unisolated apex of the STM tip, corresponds to a coverage of the STM tip apex of approximately 10–20 ML Co. Then, a second potential jump $\Delta E_{\text{tip}}^{(2)}$ to approximately -100 mV (Fig. 1) is applied to the STM tip. This results in the dissolution of Co from the STM tip, observed as a large anodic Co^{2+} current peak in the current transient (Fig. 2), which is limited to approximately 520 nA by the current–voltage converter of our STM. This anodic dissolution peak is nearly rectangular shaped with a full width at half maximum (FWHM) of 0.5–5 ms, depending on the previously deposited cathodic tip charge (Fig. 2).

Figure 3 shows two Co clusters, which have been depos-

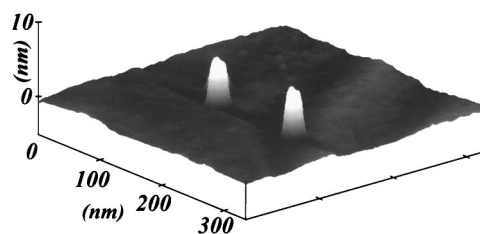


FIG. 3. Two electrodeposited Co clusters on a Au (111) terrace. The height of the clusters, as measured by STM, is 7.5 nm, the FWHM is 15 nm. Tip–substrate distance $\Delta z = 15$ nm during deposition, Co^{2+} emission current 520 nA, cathodic tip charge 400 pC, $E_{WE} = -770$ mV during deposition and subsequent STM measurement. (The scan lines across the two clusters seem to indicate a deeper substrate surface than the scan lines besides the clusters do. This is an artifact of the measurement due to the large height variation during the STM scan.)

ited by applying this deposition procedure twice. The STM tip was withdrawn from the substrate surface by 15 nm during the cluster deposition. The large distance between STM tip and substrate surface avoids any unwanted mechanical contact of the STM tip to the substrate surface or to the growing Co cluster. The absence of electrical, and hence mechanical contacts, is also proved by the current transients as shown in Fig. 2.

The diameter (FWHM) of the clusters, as measured by STM, is approximately 15 ± 1 nm (Fig. 3). The slightly conical shape of the clusters results from the convolution of the approximately spherical shape of our STM tip apex and the real shape of the deposited clusters. For this reason, the real diameter of the clusters would be even smaller than the measured 15 nm.

The mechanism of the cluster formation can be completely explained by electrochemical considerations:¹⁰ During dissolution of Co from the STM tip, Co diffusion into the electrolyte creates a Co^{2+} concentration profile in the electrolyte around the STM tip. Due to the constant Co^{2+} current density during Co dissolution (Fig. 2), this concentration profile is stationary for the time of Co^{2+} emission from the STM tip,¹⁰ which is typically between 0.5 and 5 ms (Fig. 2). The spacial increase of the Co^{2+} concentration around the STM tip results in a laterally varying increase of the Co/Co^{2+} Nernst potential at the substrate surface, according to the concentration dependence of the Nernst equation.

In order to understand the mechanism and its parameters in more detail, a model calculation has been carried out based on the diffusion equation for Co^{2+} . Since the anodic dissolution current from the STM tip is limited to 520 nA by the current–voltage converter of our STM (Fig. 2), the apex of the STM tip can be simulated by a continuously Co^{2+} emitting hemispherical constant current source. Thus, the stationary Co^{2+} concentration profile, and hence the increase $\Delta NP(x)$ of the Co/Co^{2+} Nernst potential underneath the STM tip, have been calculated with respect to the Nernst potential of the 1 mM Co^{2+} electrolyte solution. The result is plotted as a function of the lateral distance x from the center of the STM tip (Fig. 4).

$\Delta NP(x)$ adds to the uniform Co/Co^{2+} Nernst potential of the 1 mM Co^{2+} electrolyte solution, resulting in a laterally varying effective Co/Co^{2+} Nernst potential. The maximum

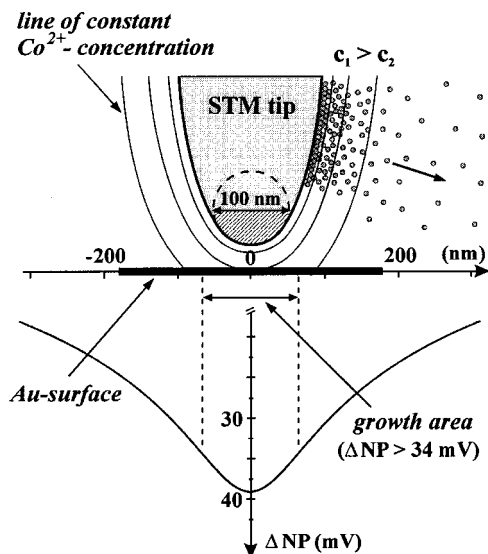


FIG. 4. Calculation of the lateral variation of the increase $\Delta NP(x)$ in the Co/Co^{2+} Nernst potential. Tip-substrate distance $\Delta z = 15$ nm; Co^{2+} emission current 520 nA; tip apex diameter 100 nm.

achievable increase of this effective Nernst potential at the substrate surface underneath the STM tip is equal to $\Delta NP(0)$, which can be as high as 38 mV (Fig. 4) at the same experimental conditions as in Fig. 3. If E_{WE} is adjusted within 38 mV above the Co/Co^{2+} Nernst potential of the 1 mM Co^{2+} solution, the effective Nernst potential exceeds E_{WE} within a particular area, which is named growth area in Fig. 4.

Since $\Delta NP(x)$ is determined by the Co^{2+} concentration profile around the STM tip, the shape of $\Delta NP(x)$, and hence the diameter of the growth area are mainly determined by the diameter of the STM tip apex. A better defined shape, as well as a smaller diameter of the STM tip apex than 100 nm would be desirable for a deposition of even smaller clusters.

Hence, the discrepancies in the cluster size between STM measurement (Fig. 3) and calculation (Fig. 4) are likely to be due to the unknown shape of the very end of the particular STM tip used for the deposition in Fig. 3, whereas the calculation has been based on a STM tip diameter of 100 nm. Also, the effective Nernst potential which is required to initiate nucleation on the substrate may be larger than calculated due to deposition overvoltages, which might be seen in Fig. 1. This would result in a smaller diameter of the growth area than that calculated in Fig. 4.

The STM tip has been held at a fixed lateral position during Co^{2+} emission (Fig. 2) from the STM tip, which results in the observed Co clusters on the substrate surface underneath the STM tip. However, during Co^{2+} emission the STM tip may be also moved laterally across the substrate surface, which is expected to result in the growth of a line showing the same width as the diameter of the clusters in Fig. 3.

IV. CONCLUSIONS

In contrast to the large number of approaches to deposit nanostructures using the tip of an STM, in ultra high vacuum (UHV) as well as in electrolytic solutions, the reported mechanism of electrochemical Co cluster growth is certainly not affected by any mechanical interaction of STM tip and substrate, due to the large distance between STM tip and substrate of more than 10 nm during cluster deposition.

Since the deposition procedure presented here is based on a purely electrochemical process, it can be easily extended to other deposit-substrate systems as, e.g., Cu on Au.¹¹ The growth of clusters does not require any special property of the substrate surface as, e.g., defects or reconstructions. In particular, the presented mechanism is expected to allow both the deposition of clusters showing a strong as well as a weak deposit-substrate interaction. This is important in view of the preparation of metal clusters on semiconducting substrates as, e.g., Si or GaAs, which show usually weak deposit-substrate interactions.

There is no principal limitation by the deposition process which would prevent a further decrease of the cluster diameter and height, except for the critical sizes of stable clusters which are of the order of 10 atoms.¹²

Thus, the technique may be helpful in the investigation of the intrinsic properties of well defined, "as grown" nanometer sized structures.

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