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Investigation of nucleation processes under the influence of magnetic fields

A. Krause · M. Uhlemann · A. Gebert · L. Schultz

Abstract The present work demonstrates the possibilities and the limits of the in situ electrochemical scanning tunneling microscopy for investigation of nucleation processes in magnetic fields on the examples of Cu and Co electrodeposition onto Au(111) electrodes from sulfate electrolytes with pH 3. Cyclic voltammograms of Cu in the underpotential range (UPD) exhibit no significant change in the cathodic and anodic peaks recorded in magnetic fields parallel to the surface. In magnetic fields of a permanent magnet, the reconstruction of Au has been annihilated during UPD of Cu. In the overpotential range, the dissolution of Cu is inhibited. This triggers the formation of a Cu–Au surface alloy. The UPD deposition of Co onto Au(111) could be proven without magnetic field, which leads to the formation of two monolayers. The nucleation in an applied field could not be observed due to higher induced fluctuations and microconvective effects.

Keywords Underpotential deposition · In situ ECSTM · Copper deposition · Cobalt deposition · Magnetic field

Introduction

The understanding of the nucleation and the growth mechanisms of the first atomic layers of thin metallic films are of fundamental interest and important for the further evolution of the film microstructure and their magnetic and

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electric properties. The deposition of Cu and Co is of particular interest because of the miniaturization in semiconductor industry. Since at least 10 years, the electrodeposition of Cu onto Au(111) has been extensively investigated by several groups [18, 26] with respect to the nucleation and formation of the first monolayers (ML) summarized in [3]. Furthermore, the initial stage of the electrodeposition of Co onto Au has been studied widely [1, 5, 6, 9, 12, 19] by in situ electrochemical scanning tunneling microscopy (ECSTM). Especially the results of the latter depend strongly on the experimental conditions (electrolyte, pH value) and are not always comparable. Kleinert et al. [12] observed the formation of atomic flat Co twin layers and twin layer islands onto Au(111) and Au (100) electrodes deposited in the overpotential deposition (OPD) range from pure acidic cobalt sulfate electrolytes. Starting from the first monoatomic layer (ML), the hcp structure was formed. In situ STM investigations of Allongue et al. [1] have shown that Co grows epitaxially on Au(111) at an overpotential of 0.25 V. Cagnon et al. [5, 6] discovered an SCN^--induced underpotential deposition (UPD) of Co onto Au(111) electrodes in electrolytes containing 10^{-3} M H_2SO_4. Mendoza-Huiza et al. [19] investigated the deposition from a complex-forming electrolyte ($[Co(NH_3)_5H_2O]^{2+}$) containing $CoCl_2$ and NH_4Cl at pH 9.5. They found two peak pairs more positive than the equilibrium potential (E_{eq}), which they attributed to the UPD of cobalt. Flis-Kabulska [9] reported that, in pure sulfate electrolytes with pH 3, the Co deposition starts at an underpotential of 0.26 V with monoatomic islands.

Due to the high interest in monoatomic thin metallic layers with defined physical properties and microstructure, new methods for preparation are required. One possibility is the superimposition of external magnetic fields during the deposition. The influence of magnetic fields on all partial

stages of the electrodeposition, except the nucleation, was the focus of numerous works in the recent years. It has been shown recently by the authors [14, 16] that the superimposition of external magnetic fields during the deposition process improves the quality (roughness) of layers with a thickness between 10 and 50 nm significantly. The structure of Cu and Zn dendrites has been changed at high overpotentials [8, 20]. First results to the change in the phase composition of Co deposited in applied fields are reported in [11, 17]. To our knowledge, so far, nothing has been published on the effect of external magnetic fields on the nucleation and the growth of the first ML, which determines the growing microstructure.

In the present work, in situ ECSTM investigations of the initial stages of the deposition of Cu and Co on Au(111) in the UPD and OPD range with and without applied magnetic fields are reported. The results are discussed with respect to magnetically induced changes of the deposition mechanism and the modification of the film structure. This work is related to recent investigations of the authors [13–16, 24] and shows for the first time the possibilities and the limits of in situ ECSTM investigations of nucleation processes in magnetic fields.

Materials and methods

The in situ ECSTM investigations were carried out in an STM system of Molecular Imaging (Picoscan). A flame-annealed Pt wire was used as counter electrode, and PtIr 70/30 tips isolated with apiezon wax were used as scanning probes. The potentials were measured vs a Pt pseudo-reference electrode and later vs a $Hg/Hg_2SO_4/K_2SO_4(s)$ electrode (+650 mV vs SHE, [MSE]). The potential difference between the Pt pseudo-reference electrode and the MSE reference electrode was controlled before and after the measurement. It can be assumed that it was stable during the measurement. Therefore, all potentials given in the paper are referred vs the MSE. The working electrode was prepared from glass substrates evaporated with 2 nm Cr and 200 nm Au. To obtain atomic flat Au(111) terraces, the substrates were flame annealed immediately before each measurement. The deposition was performed from 1 mMol $CuSO_4$ and 3 mMol $CoSO_4$ electrolytes with pH 3 adjusted with sulfuric acid.

The measurements under the influence of magnetic fields were carried out in a modified in situ STM cell, where a permanent magnet array was placed directly on the backside of the working electrode, as shown in Fig. 1. The strength of the magnetic field directly on the Au surface was about 400 mT. Due to the small cell and the extremely low scan range, it can be assumed that the magnetic field lines are oriented perpendicular to the surface, and the field gradient in this volume is low. Cyclic
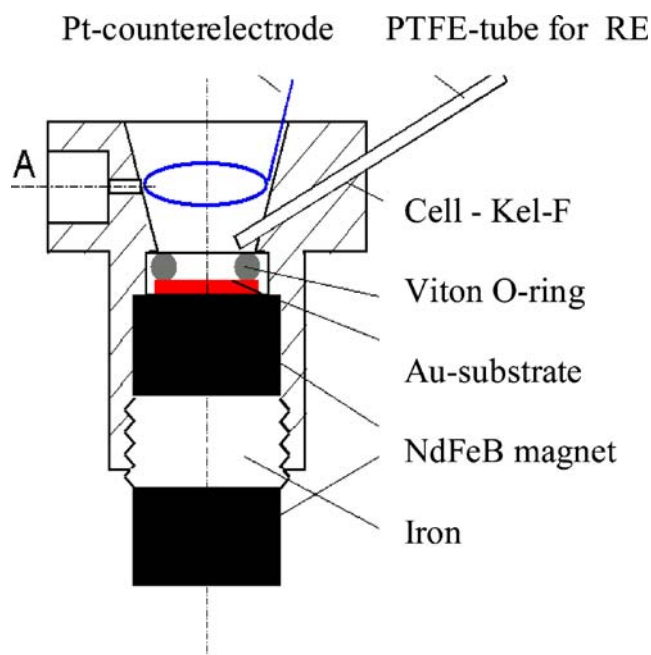

Fig. 1 Scheme of the in situ ECSTM cell equipped with permanent magnets

voltammetry (CV) measurements were carried out in this in situ ECSTM cell. For comparison, CVs were recorded in an electrochemical cell exposed to a uniform magnetic field of 1 T of an electromagnet oriented parallel to the electrode surface described in detail in [13, 15]. The two different orientations of the magnetic field allow to consider different magnetically induced convective phenomena. The different scan rates used in the experiments are due to the technical possibilities of the experimental setup.

Results and discussion

Copper deposition

Figure 2a shows CVs representing the electrochemical behavior of Cu on Au(111) in the UPD range with and without superimposition of a uniform magnetic field of 1 T parallel to the electrode surface. In the applied parallel oriented magnetic field, the $I(E)$ curve is noisy compared to the curve recorded without magnetic field, which can be due to fluctuations and micromagnetoconvection in the electrochemical double layer [13, 15]. Generally, a significant change in the position of the characteristic adsorption–desorption ($A_{1–3}$–$D_{1–3}$) peaks has not been expected and also has not been observed in the magnetic field. The Nernst equilibrium potential for Cu (E_{eq}) is indicated in the Fig. 2a and b with an arrow. All peak pairs (A–D) occur at potentials positive of E_{eq} and reflect clearly the adsorption–desorption behavior of the UPD phase as described in detail

Fig. 2 Cyclic voltammetry on Au(111) of 1 mMol CuSO$_4$ (pH 3) without and in applied magnetic fields oriented parallel $B=1$ T, $dE/dt=5$ mV/s (**a**) and perpendicular to the surface $B=0.4$ T (ECSTM), $dE/dt=50$ mV/s (**b**)
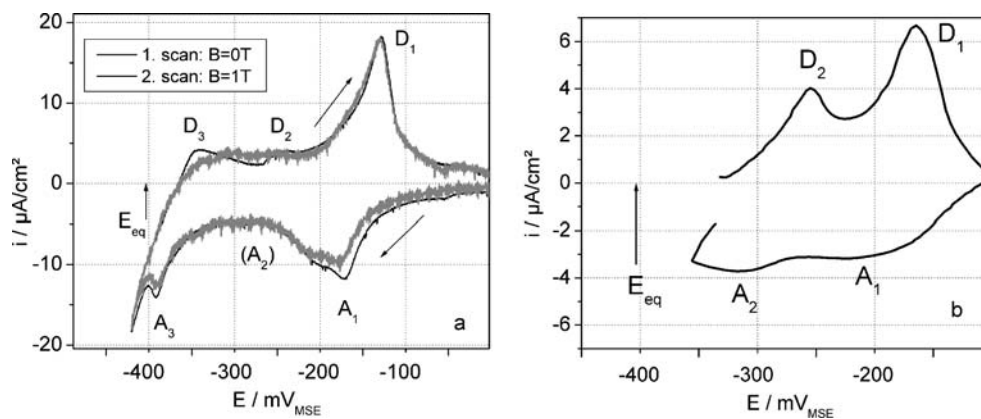
by many authors [3, 26]. The A$_2$–D$_2$ peaks without magnetic field are less developed and rather negligible and could not be observed in the applied field. Therefore, the effect of external uniform magnetic fields on the current density-potential behavior is marginal. The in situ ECSTM images without magnetic field confirm the well-known UPD behavior. One 2D-Cu adsorbate monolayer (ML) is formed at potentials more positive of E_{eq}, which is not shown here but frequently described by several authors [3, 26] and observed in own experiments [15].

The CV recorded directly in the ECSTM cell with a magnetic flux density of 0.4 T of the permanent magnet oriented perpendicular to the surface is shown in Fig. 2b. The CV proves also clearly the appearance of two A–D peak pairs in the UPD range as it is known and similar as it is shown in Fig. 2a recorded without magnetic field and with uniform magnetic field. The peaks A$_2$–D$_2$ are in the background of the slow scan of Fig. 2a and only visible in the scan without magnetic field. A slight shift of the peak maxima has been observed. It has been mentioned that a direct comparison of the CVs shown in Fig. 2a and b is

restricted because the scan rate is faster in the ECSTM cell and the current density must be lower. The slight shift of the A–D peaks could be due to the same reason and requires strongly more detailed investigations.

The nucleation of the Cu deposits more positive of the equilibrium potential under the influence of the external magnetic field of a permanent magnet is shown in Fig. 3a–c by in situ ECSTM. Without applied potential, the quality of the scanned images is not affected by the magnetic field. Figure 3a shows the typical 60° facets after the thermal reconstruction of the Au surface. After applying a potential of $E=-350$ mV$_{MSE}$ for about 5 s, the surface has been changed completely (Fig. 3b). This image as well as the following one (Fig. 3c) have been scanned after switching off the potential. These images show that the reconstruction of the Au surface has been annihilated. The following potential steps lead to the formation of small islands with a height of one ML Cu, as the images were always scanned after switching off the potential, i.e., the metastable adsorbed Cu layer was probably partly desorbed, and the image reflects not directly the in situ behavior. From the literature,
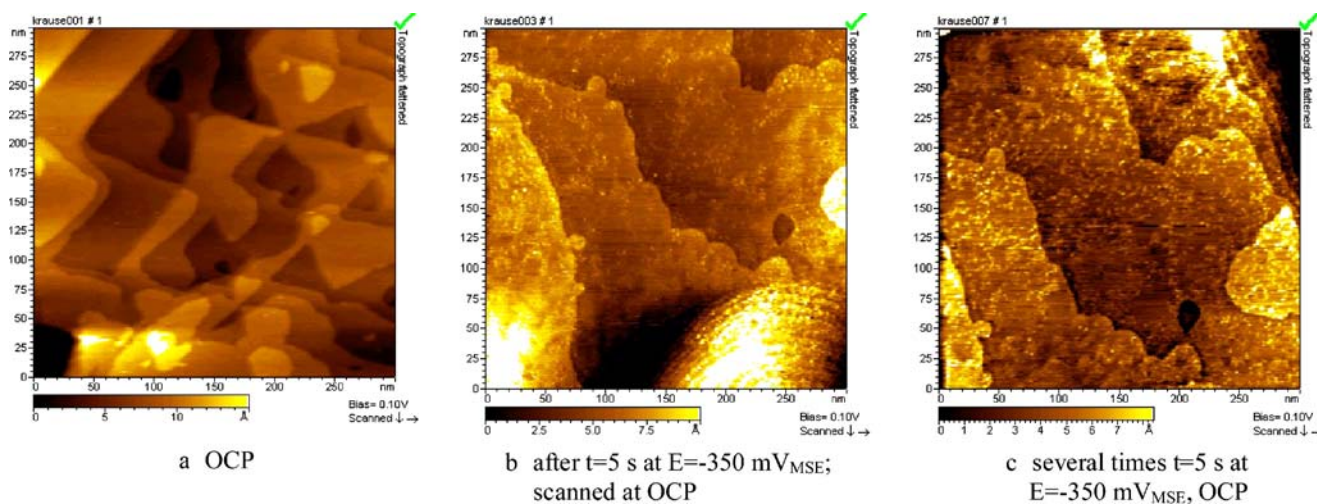

Fig. 3 ECSTM investigation of Cu on Au(111) in the UPD range with $B=0.4$ T (1 mMol CuSO4, pH 3)

it is known that the thermal reconstruction can be annihilated at certain potentials [3] mainly due to the high mobility of the Au atoms and the desorption of adsorbed species. This has been discussed also by Nakamura et al. [22]. They found that the Au reconstruction has been annihilated during the Cu-UPD. The physical background why the annihilation might be proceeded easily in applied magnetic fields and the mechanism are not clear, yet. The results give only a first hint for this effect and need further investigation.

The nucleation of Cu in the OPD range was carried out in an applied field of $B=0.4$ T at high overpotentials ($E=-950$ mV_{MSE}). This leads immediately to the formation of numerous small nuclei with a diameter of 5 nm. Figure 4b shows the STM image after polarization for 3 s in comparison to the reconstructed Au surface (Fig. 4a). Interestingly, these Cu nuclei cannot be dissolved within 10 s at high anodic potentials of $E=+50$ mV_{MSE} (Fig. 4c). This effect can be discussed with respect to the influence of the concentration gradient force (F_p), which hinders the diffusion of the paramagnetic Cu ions away from the electrode surface (4, 13, 15). The paramagnetic force

$$F_p = \chi_{mol} \frac{B^2}{2\mu_0} \nabla c \qquad (1)$$

is deviated from the magnetic energy of the system and depends on the magnetic properties of the species, that means the volume or molar susceptibility (χ_{mol}) and the gradient of the concentration (∇c); μ_0 is the permeability in vacuum. During the dissolution, the concentration of Cu ions is extremely high at the surface, and the concentration gradient is directed towards the electrode surface. This local high concentration of Cu ions can trigger a preferred formation of a Cu–Au surface alloy [15]. Additionally, the high mobility of Au atoms, as has been shown before, supports this assumption. The formation of a Au–Cu alloy can also be expected from the theoretical point of view. Christensen et al. [7] discussed the probability for the formation of surface alloys with the higher free surface energy of Cu ($\gamma_{(111)}=1.95$ J/m^2) in comparison to Au ($\gamma_{(111)}=1.28$ J/m^2) [15]. The lower free surface energy of Au and the tendency to minimize the energy of the system Au atoms can diffuse easily to the surface.
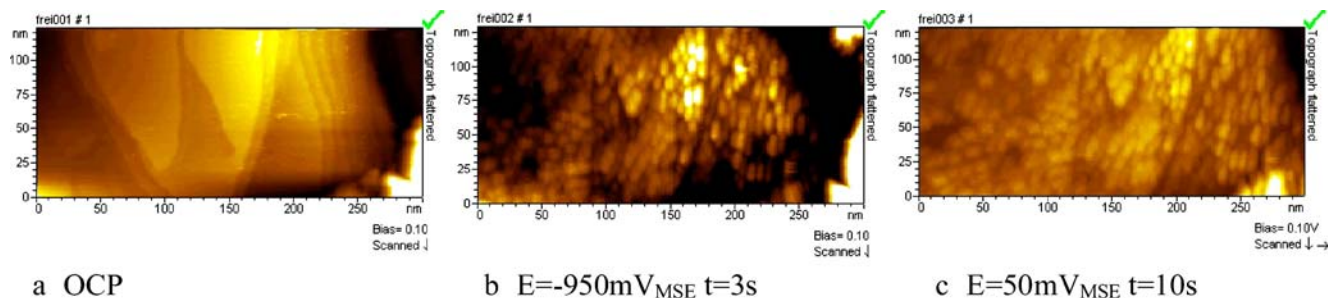

Fig. 5 CV of Au(111) in H_2SO_4 and 3 mMol CoSO$_4$, pH 3, $dE/dt=$ 50 mV/s

Cobalt deposition

Figure 5 shows the CVs of Au in H_2SO_4 with pH 3 with and without addition of 3 mmol CoSO$_4$ and without applied magnetic fields. Without Co addition, a wide peak pair (S–S′) was observed at about 0 mV_{MSE}, which is due to the anion desorption or anion-induced reconstruction. After addition of Co ions, the cathodic current density decreases at potentials more negative than $E=-450$ mV_{MSE} (A$_1$), and the anodic current density of the peak S′/D increases slightly. The negative current density cannot be caused by the reduction in hydrogen ions, which is obvious from the CV of pure sulfuric acid and the Nernst potential for hydrogen reduction at pH 3 ($E_{eq}=-825$ mV_{MSE}). The occurrence of the additional peak (A$_1$) indicates clearly the UPD of Co on Au(111) substrates because the Nernst potential for Co in 3 mmol CoSO$_4$ is much more negative than $E_{eq}=-998$ mV_{MSE}.

The large potential difference between the cathodic peak (A$_1$) and the anodic peak (S′+D$_1$) is not typical for UPD. It should be expected that the desorption (D$_1$) starts at more negative potentials than S′. But this peak appears only as a slightly increased S′ peak. That means the Co layer has not been dissolved completely. This could be caused by the

Fig. 4 ECSTM investigation of Cu on Au(111) in the OPD range with $B=0.4$ T (1 mMol CuSO$_4$, pH 3), $z_{max}=1.5$ nm

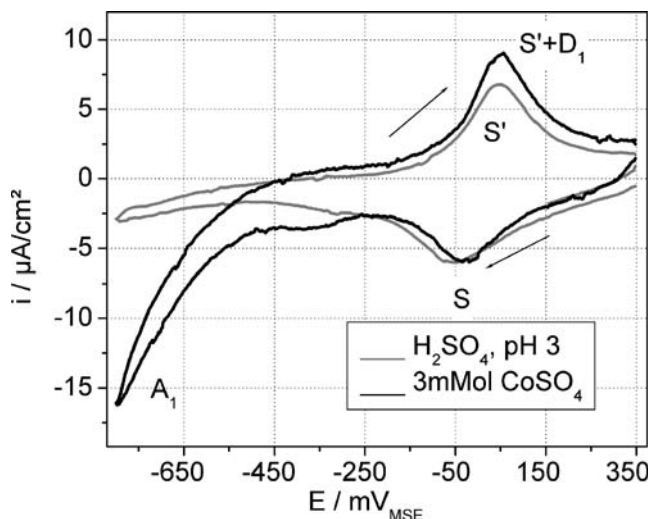formation of 2D or 3D surface alloys according to Budevski and the cited authors within [3]. The dissolution of the surface alloy needs a higher amount of energy or potential and explains the shift of the desorption peak to the position of S'. The probability for the formation of surface alloys has been discussed before, and the condition is also given for the system Co–Au. A higher surface energy of Co ($\gamma_{(111)}$=2.7 J/m^2) in comparison to Au ($\gamma_{(111)}$=1.28 J/m^2) and the tendency to minimize the energy of the system can lead to surface diffusion and alloy formation [15].
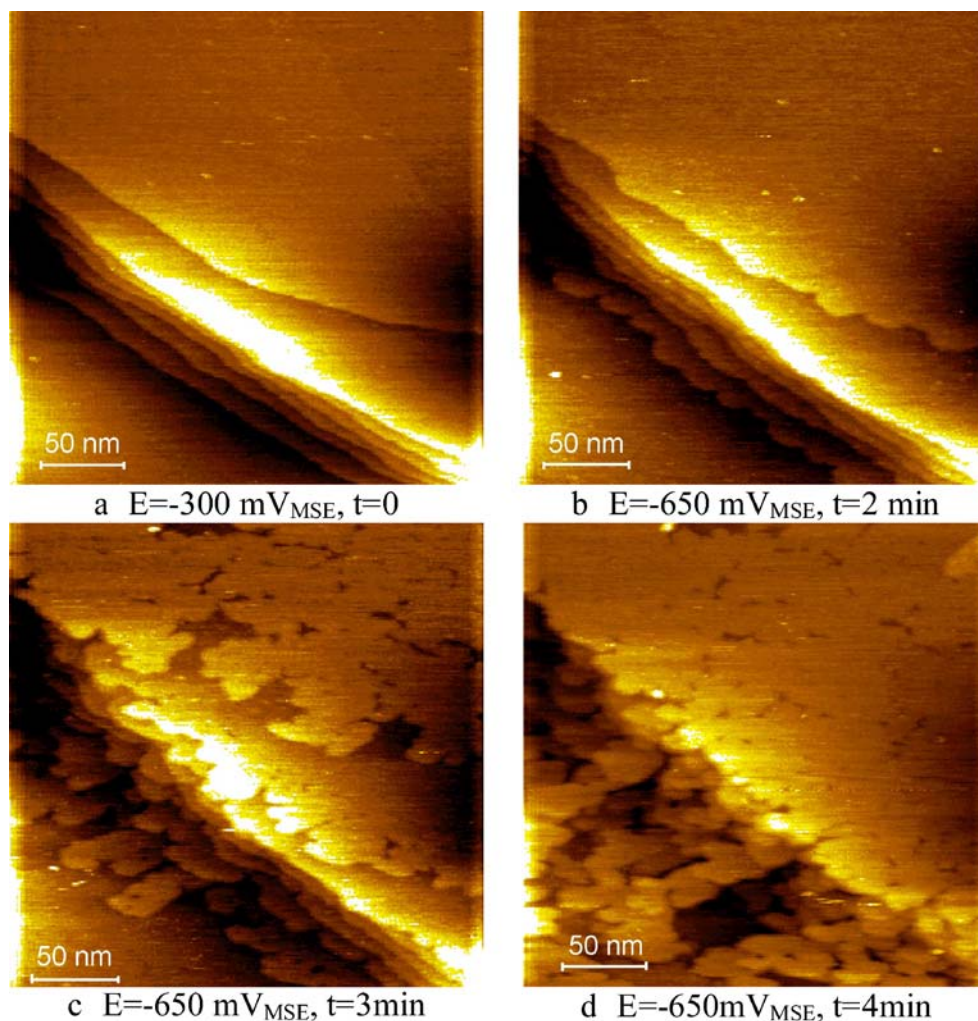
The ECSTM studies confirm the results of the CV measurements. Figure 6a shows images of atomically flat Au(111) terraces in 3 mM CoSO$_4$ at E=−300 mV$_{MSE}$. Between the two large terraces are several steps, each with a height of 0.24 nm ($d_{Au(111)}$=0.235 nm). After 2 min polarization at E=−650 mV$_{MSE}$, the nucleation of Co starts in the UPD range at the step edges of the substrate (Fig. 6b). After about 3 min, one ML covers almost the whole scanned electrode surface (Fig. 6c). The second ML is formed after further polarization of 4 min at E=0 mV$_{MSE}$ (Fig. 6d). The formation of two ML is untypical for UPD, but has been detected also for the deposition of Tl on Ag by Pauling and Jüttner [23].

The step height of the two ML was measured on several positions. The first ML has a mean height of 0.2 nm, which fits very good to the Co(111) plane or the c-axis of the first ML of the Co lattice (fcc: $d_{Co(111)}$=0.2035 nm, hcp: $d_{Co(002)}$=0.2035 nm). The height of the second ML deviates with 0.24 nm significantly from that value. Similar phenomena were observed by Kleinert et al. [12] for the system Co on Au(111) in the OPD range and Möller et al. for the system Ni on Au(111) [21]. Both found a smaller height of the first ML than the theoretical value, which they attributed to an electronic contrast. Equation 2 describes the correlation between the distance of the tip and the electrode surface d_T and the tunneling current I_T [10, 27], whereas U_T is the bias, m_e the mass of an electron, Φ the height of the potential barrier, and $\hbar$ Planck constant.

$$I_T \propto U_T \exp\left[-\sqrt{2m_e\Phi/\hbar^2} \cdot d_T\right] \tag{2}$$

Fig. 6 ECSTM investigation of Co on Au(111) in the UPD range, 3 mMol CoSO4, pH 3, scan size 260×260 nm. a–c z_{max}=1 nm, d z_{max}=1.5 nm

a E=-300 mV$_{MSE}$, t=0

b E=-650 mV$_{MSE}$, t=2 min

c E=-650 mV$_{MSE}$, t=3min

d E=-650mV$_{MSE}$, t=4min

Φ includes the difference of the work function for both metals, which might cause such a contrast. To exclude this, different biases were applied. If the measured discrepancy is a material contrast, it would change with d_T, respectively, with U_T. But the thickness of both ML did not significantly change with U_T, which proves that the measured step heights are the real values.

The presented results show a very good conformity between the theoretical value of the lattice distance of Au (111) and the measured step height of the substrate. The formation of a Co ML with different crystallographic orientation is very improbable because this would cause a high stress inside of the monolayer.

Zhou et al. [27] discovered for the deposition of Co on Cu(100) from the gas phase the formation of a Cu ML on top of a previously deposited Co layer, which they explain with the lower free surface energy of Cu similar as for Cu on Au(111) as discussed before.

It was found by STM investigations of annealed Au samples that the surface diffusion of Au is very fast and gives rise to the formation of new two-dimensional structures on top of the Au surface [25]. Therefore, our conclusion is that the second ML formed on top of the Co ML deposited in the UPD range is a Au(111) ML. The desorption of the Co-UPD phase is blocked by the Au(111) layer.

Investigations on the deposition of Co in the UPD as well as OPD range with superimposition of external magnetic fields could not be carried out successfully by in situ ECSTM until now. One reason might be the one-order higher molar magnetic susceptibility of the Co ions ($\chi_{Co}=10^{-8}$ m^3/mol) in comparison to the Cu ions ($\chi_{Cu}=1.46\times 10^{-9}$ m^3/mol). This leads also to higher gradient forces close to the electrode surface. As a result, micromagneto-convection is generated and makes any scanning process impossible [2, 15, 16]. Structural changes of thin Co layers deposited at high overpotentials could be shown and have been discussed in earlier works of the authors [15, 16].

From this point, the in situ investigations of the nucleation process are strongly required and will be a subject of further investigations.

Conclusion

The nucleation of Cu and Co onto Au(111) electrodes from sulfate electrolytes with pH 3 has been investigated under the influence of magnetic fields by cyclic voltammetry and in situ ECSTM measurements. Cyclic voltammograms of Cu recorded in superimposed magnetic fields exhibit no significant change in the adsorption–desorption peaks in the UPD range. In applied magnetic fields, the annihilation of the reconstructed Au layer has been observed at the UPD potential ($E=-350$ mV$_{MSE}$). In the overpotential range

(OPD), the dissolution of Cu is inhibited. It has been concluded that the diffusion of Cu ions away from the surface is hindered due to gradient forces acting in the direction of the concentration gradient. This might trigger a preferred formation of a Cu–Au surface alloy. It can be summarized for Cu that external applied magnetic fields have only a marginal effect on the nucleation process. The UPD of Co onto Au(111) has been proven without magnetic field, which leads to the formation of two ML at $E=-650$ mV$_{MSE}$. It was concluded from the ECSTM measurements that the second ML formed on the first Co ML is a Au(111) layer caused by surface diffusion. The investigation of the nucleation in an applied magnetic field failed in the UPD range as well as in the OPD range. Microconvective effects immediately after switching on the potential makes scanning impossible. Therefore, the effect of applied magnetic fields on the nucleation and structure of Co can be investigated only by external methods. The results have shown the limits of in situ ECSTM in applied magnetic fields.

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