Temperature-Promoted Electrodeposition on Thiolate-Modified Electrodes

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The influence of temperature on the electrodeposition of copper on alkanethiolate-covered Au(111) was studied by means of cyclic voltammetry and in situ scanning tunneling microscopy (STM) in the temperature range from 300 to 345 K. We show that thermally induced defects allow for copper electrodeposition to occur much faster than at 300 K. Only at elevated temperatures can smooth copper layers be grown on the thiolated electrodes, independent of the thiolate chain length. The layerwise growth is mediated by a surfactant-like action of the thiolate.

Introduction

One of the most versatile methods to chemically modify an electrode is the thiolation. Alkanethiols (RSH) form strongly adsorbed and well ordered thiolate monolayers on Au(111) electrodes (RS/Au(111)) (see, e.g., refs 1−3). In the following we give a short description of the properties of the resulting interface.

The alkyl chains R are in the all-trans conformation, and their axes are tilted away from the surface normal.[4,5] The detailed physical behavior is not completely, but rather well, understood. Heating, for example, induces several stages of disorder, progressing from the methyl end group toward the substrate. First, the methyl rotation is activated at $T \geq 100$ K, as revealed by He diffraction studies.[2] Above 200 K, probing of the methylenes' scissor vibration by IR suggests a progressive decrease of the tilt, unlocking of the alkyl azimuth (rotation around the Au−S bond), and development of gauche defects in the otherwise all-trans conformed chains.[6] This behavior compares well with that of other self-assembled monolayers[7] and that of melting bulk alkanes.[8] Heating to temperatures above 300 K can affect the Au−S bond: Thiolate-stacking faults move or vanish, and mass transport of the Au substrate occurs and finally leads to the healing of the typical Au vacancy islands.[9−12] During such mass-transport processes, the thiolate appears to rear-range, for example, by a rotation of the alkyl chain around the C−C bond, the latter causing a gauche defect.[6]

In our laboratory the surfactant action of thiolate layers on metal electrodeposition is investigated. We thereby hope to achieve a better understanding of metal electrogrowth modes and mechanisms. The Cu deposition on thiolate layers is known to proceed very slowly[13−16] and is thus easily followed by in situ STM. Employing a formal electrochemical potential (that is measured with a reference electrode and is not the one of the thiolate/electrolyte interface), we distinguish between underpotential deposition (UPD) and overpotential deposition (OPD) of Cu, referring to the Cu/Cu^{2+} equilibrium potential. If Cu is deposited at 300 K on long alkyl chain (>13 C atoms) thiolate-covered Au(111), it forms *stable* nanometer-sized islands.[13−16] The fact that further electrodeposition stops even at OPD conditions is very rarely observed in other systems (and yet unexplained); it allows us to keep the island diameter in the nanometer range. Only for shorter chains *and* OPD conditions can more than one Cu layer be grown[14,15,17] with a very small rate (<1 layer per hour). The metal film grows in a pseudo-layer-by-layer fashion (i.e. one layer is almost completed before the next one starts to grow), and the thiolate surfactant remains adsorbed on top of the growing layer. Note that metal deposition on thiolate layers in a vacuum does not generally result in the same scenario (see the review by Jung et al.[18]).

In this article we report on the influence of the temperature on the growth process. The tools are in situ electrochemical STM and cyclic voltammetry. Our investigations started with the test of a new high-temperature electrolyte (based on an ethylene glycol/water mixture) that counteracts the evaporation in the open STM cell. We show that it changes neither the characteristics of the well-documented Cu/Au(111) stan-

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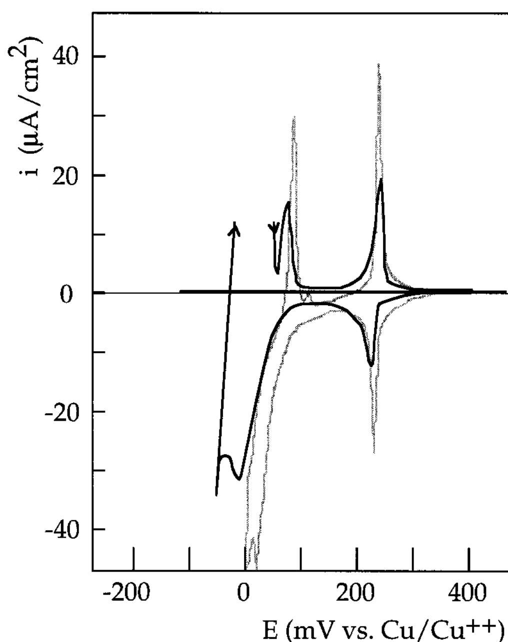

Figure 1. Voltammograms of Cu deposition on bare Au(111) in 50 mM H_2SO_4 + 1 mM $CuSO_4$ in (gray trace, 10 mV/s) water and (black trace, 2 mV/s) a 2:1 mixture of $HOCH_2CH_2OH/H_2O$ (both not deaerated). The scan rate for the black trace is so slow that significant bulk deposition occurs, causing a very large Cu bulk dissolution peak at 0 mV that was cut off for clarity. Other small differences such as a small shift of the more negative UPD peak are also due to the different scan speeds; otherwise the graphs are very similar, pointing to a negligible influence of ethylene glycol on copper electrodeposition.

dard system[19-21] nor those of the Cu/thiolate/Au(111) system.[13-16,22] Then we focus on electron-transfer blocking properties that were elucidated by high-temperature voltammetry of a redox pair and compared to literature data. Finally, we demonstrate that Cu electrogrowth on thiolate-covered Au(111) can be followed by STM at temperatures up to 345 K. The experiments prove the crucial importance of temperature in the electrodeposition. Increasing the temperature promotes a layerwise growth of Cu also on long chain thiolate monolayers and substantially enhances the growth rate on short chain monolayers.

Experimental Section

STM measurements were performed as described in ref 16. Au was evaporated onto cleaved and preheated mica sheets; these samples were flame-annealed shortly before they were immersed into ethanolic solutions of thiols.[13] As a new feature we coupled a Peltier element (operated in the heating configuration) with a Cu spacer to the bottom of the mica sample, allowing for a stable sample and electrolyte temperature (less than 1 K change per hour). The thiolate/Au-covered top of the mica piece was in contact with the electrolyte-filled STM cell. The electrolyte was prepared with $CuSO_4$ (p.a., Fluka), H_2SO_4 (p.a., Fluka), water (Millipore), and ethylene glycol (1,2-ethandiol, p.a., Fluka). The latter very effectively stopped the otherwise quick evaporation. The reference was a polished Cu wire, etched in HNO_3 and rinsed with water shortly before use. For the redox pair measurements the same setup was used. The electrolyte contained potassium ferricyanide ($K_3Fe(CN)_6$, MicroSelect, Fluka) and HCl (p.a., Fluka) in ethylene glycol/water, and an Ag/AgCl reference was dipped into the cell. All potentials are quoted with respect to the Cu/Cu^{2+} pair in 1 mM Cu^{2+} (i.e., 0 mV read +250 mV on the standard hydrogen scale). The STM image in Figure 5 is shown derivatized; thus, steps ascending from left to right show up as white lines.

Results and Discussion

Test of the Ethylene Glycol/H_2O-Based Electrolyte. To reduce the electrolyte evaporation in the open STM cell that can result in loss of potential control, we changed the electrolyte solvent from water to an ethylene glycol/water mixture. Several experiments were necessary to ensure that the structures and reactions under investigation were not affected. As a test we chose the standard procedure of monitoring the UPD of Cu onto bare Au(111) by voltammetry and STM. The presence of ethylene glycol does not induce any significant change; one can still observe the usual two Cu UPD current peaks as demonstrated in Figure 1. Note that the scan rate for the black trace is so slow that significant bulk deposition occurs, causing a very large Cu bulk dissolution peak at 0 mV that was cut off for clarity. STM images show an unchanged substrate, and at 150 mV the well-known $\sqrt{3}$ structure[19-21] comprising Cu atoms and coadsorbed SO_4^{2-} is observed (see Figure 2).

We also verified that ethylene glycol does not change the properties of *thiolate-covered* Au(111). For example, voltammograms of the redox couple $Fe(CN)_6^{3-/4-}$ (see further discussion in the following section) were unaffected by ethylene glycol. Even the structure of electrodeposited Cu remained: Nanometer-sized Cu islands randomly cover the substrate (see refs 14−16). Not only the structures but also the properties of the interface were reproduced. First, Cu islands stopped growing after reaching a certain diameter (1−4 nm). Second, on short chain thiolates (<13 C atoms), OPD potentials resulted in pseudo-layer-by-layer growth, as usually observed without ethylene glycol. Third, in the presence and absence of ethylene glycol the voltammograms showed little or no sign of peaks and very low capacitive currents (<1 $\mu A/cm^2$).

These results prove that adding even large amounts of ethylene glycol to a water-based electrolyte introduces only very minor (if any) changes of the structure and reactivity of an electrode. The reason is the similarity between ethylene glycol and water; for example, they are both rather redox-inactive, they can both—owing to their OH groups—adopt structures based on hydrogen bonds, and they can both effectively solvate ions. In contrast to water, ethylene glycol may chelate Cu^{2+}, which however does not appear to influence the reduction kinetics.

Electron-Transfer Blocking of Alkanethiolates at 300−335 K: Thermally Induced Defects. The redox reaction between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ was monitored at increasing temperatures. The current peaks were barely visible at 300 K, became more pronounced at 320 K, and were well developed at 335 K where the current was at least 10 times higher than that at 300 K (see Figure 3). This means that the electron transfer that is largely suppressed at 300 K becomes more and more facile; that is, the redox ion can come closer to the Au surface than it can at 300 K and thus transfer an electron much faster.[23,24] In view of the experiments cited in the

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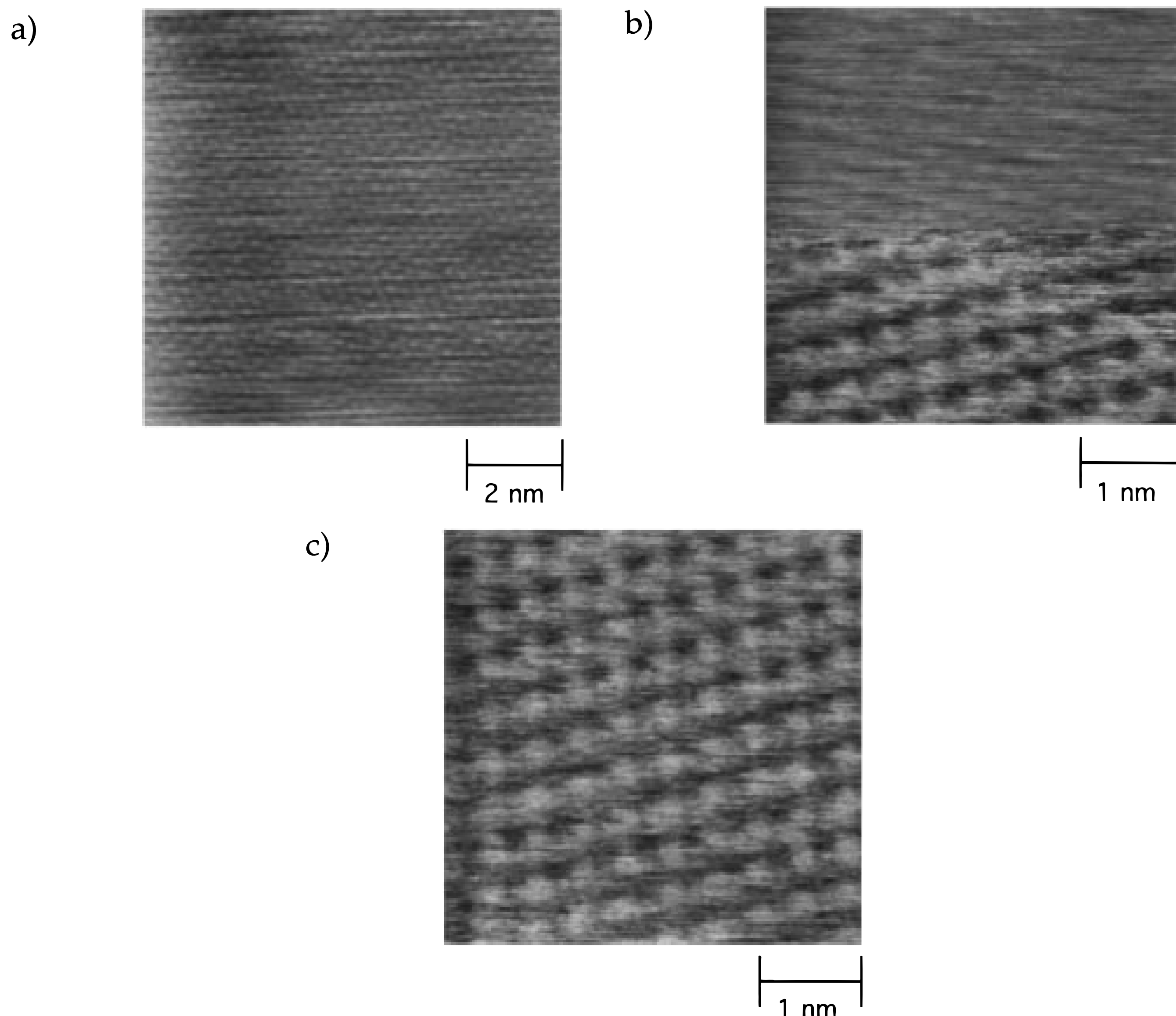

Figure 2. In situ electrochemical STM image sequence showing the formation of the $(\sqrt{3}\times\sqrt{3})R30°$ structure when the electrode potential is decreased below the first UPD peak. Tunneling parameters: current, 15 nA; tip–sample bias, 10 mV. Electrolyte: 50 mM H_2SO_4 + 1 mM $CuSO_4$ in a 2:1 mixture of $HOCH_2CH_2OH/H_2O$. (a) Electrode potential: 400 mV vs Cu/Cu^{2+}. The atomic gold lattice is imaged. (b) The image was downward-rastered; the electrode potential was not fixed but stepped from 300 mV (top part of the image) to 150 mV (bottom part) just when about half of the image was completed. A structural transition becomes visible: The $(\sqrt{3}\times\sqrt{3})R30°$ structure forms within a few seconds after 150 mV is applied (the whole image was scanned in 20 s). (c) Successive image showing the $(\sqrt{3}\times\sqrt{3})R30°$ adlayer. Electrode potential: 150 mV. The bright spots that build the adlattice are presumably due to coasdorbed sulfate anions.

Introduction, we conclude that the smaller thiolate tilt angle, the loss of azimuthal orientation, gauche defects, and perhaps also the mass transport of the substrate material have induced disorder as well as a more open structure of the thiolate. Albeit the gauche defects reduce the effective thiolate thickness, this effect can be balanced by a smaller tilt angle. Hence gauche defects alone cannot provide the necessary reduction of the distance between the surface and the $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions. We rather propose that the increase of the redox current by at least an order of magnitude is due to penetration of the ions into thermally induced defects in the thiolate, as also suggested by Badia et al.[24] Upon cooling, the redox reaction current fell again below the capacitive current. We note that the capacitive current, too, rose by more than an order of magnitude, but this rise—in contrast to that for the redox current—was irreversible (typical values of the capacitive current for the cycle 300 → 340 → 300 K are 1 → 12 → 6 $\mu A/cm^2$). Hence the redox pair does not adsorb (or penetrate) irreversibly, but the thiolate layer may be "damaged", for example, by gauche defects, during a temperature excursion (the onset temperature of the damage was not measured). This "damage", however, does not leave a bare substrate (that forms after partial desorption of thiols[25] above 380 K[26]), since in this case one should observe clear redox peaks as in Figure 3a.

Cu Electrodeposition at Elevated Temperature. The voltammograms of thiolate-covered Au(111) in contact with Cu^{2+} in water-based as well as in ethylene glycol/water-based electrolytes are usually featureless with low capacitive currents; only below the Cu/Cu^{2+} equilibrium potential does the current drop slightly (see Figure 4). Due to the sample-to-sample variability of thiolate lay-

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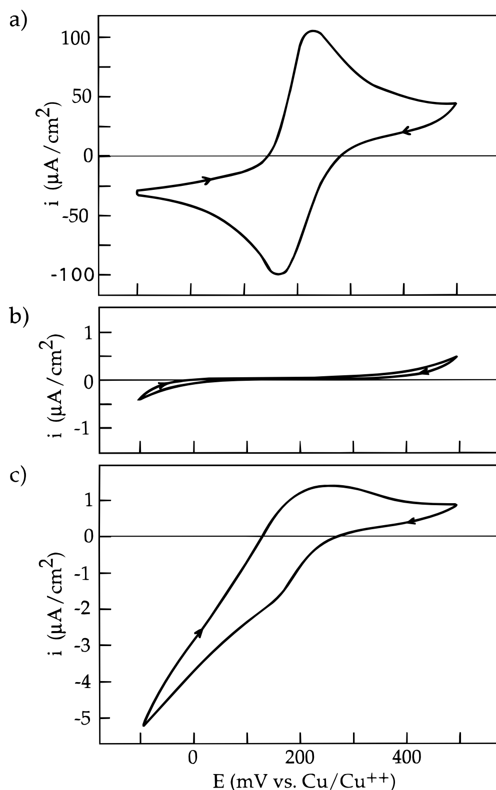

Figure 3. Cyclic voltammograms of the redox reaction between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ on a Au(111) electrode at 300 K (a), on a C_{16} thiolate-covered Au(111) electrode at 300 K (b) and at 335 K (c). Electrolyte: 1 M KCl + 1 mM $K_3Fe(CN)_6$ in a 2:1 mixture of $HOCH_2CH_2OH/H_2O$. Scan rate: 50 mV/s. Potentials were measured versus an Ag/AgCl electrode but are reported versus a hypothetical Cu/Cu^{2+} (1 mM) reference electrode.

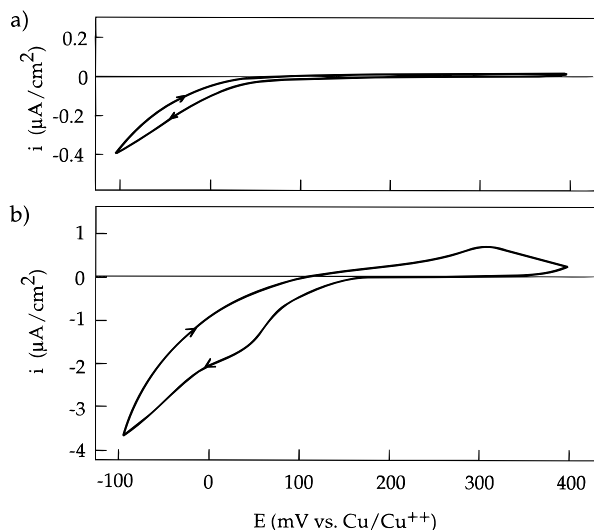

Figure 4. Cyclic voltammograms on a C_{10} thiolate-covered Au(111) electrode at 300 K (a) and 335 K (b) showing the temperature-dependent blocking behavior toward Cu deposition. Electrolyte: 50 mM H_2SO_4 + 1 mM $CuSO_4$ in a 2:1 mixture of $HOCH_2CH_2OH/H_2O$. Scan rate: 10 mV/s.

ers,[22,27] sometimes very shallow Cu UPD peaks can be found. Raising the temperature increases the double layer current at least 10-fold (again irreversibly; the current values are in the 0.5 $\mu A/cm^2$ range before and in the 2 $\mu A/cm^2$ range after heating) and reveals small UPD peaks for all samples. This is in line with the results for the electron-transfer blocking measurements and again points to the gradual development of thiolate defect structures. The deposition and dissolution of UPD Cu (at most 10% of a monolayer in contrast to 50% for the very short propanethiolate[28]) could be connected to the abovementioned reorganization of thiolate during Au mass transport, which might create some patches of bare Au substrate when Cu is deposited. Apart from such rarely forming *local* patches, gauche defects and the change of tilt angle and azimuth will surely permit better penetration by ethylene glycol, water, and ions (Cu^{2+}) *everywhere, that is, globally,* on the sample.

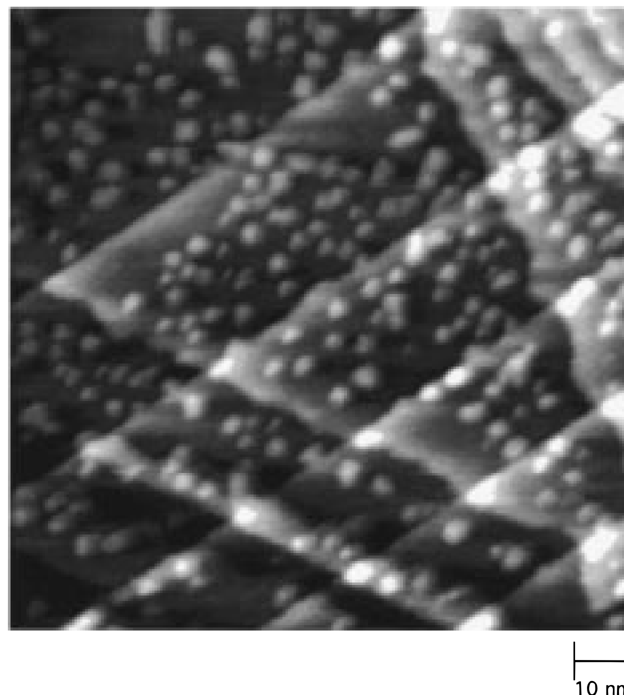

Figure 5. Electrochemical STM image of Cu islands on C_6 thiolate-covered Au(111) at 340 K. Straight steps form angles of approximately 60°; they confine terraces covered by bright spots, the Cu islands. Electrolyte: 50 mM H_2SO_4 + 1 mM $CuSO_4$ in a 2:1 mixture of $HOCH_2CH_2OH/H_2O$. The potential (50 mV vs Cu/Cu^{2+}) is in the UPD range. Tunneling current, 0.8 nA; tip bias, 40 mV versus sample.

A first STM observation was made even in the absence of deposited Cu (above ca. 400 mV): Substrate steps appear to be much more mobile at high temperatures. It was possible to follow the filling of a 12 nm diameter bilayer vacancy island in the course of minutes.[13] This healing phenomenon is closely related to vacancy island coalescence and annealing, as observed on thiolate/Au(111) under nitrogen atmosphere[10] and in a vacuum.[11] The strong Au−S bond weakens the Au−Au bond at a thiolated surface (compared to bare Au), resulting in higher adatom mobility. Such high substrate mobilities were also recorded for similarly strongly bound halogen atoms on Au(111),[29] Au(110),[30] and Pt(110).[31] High-temperature

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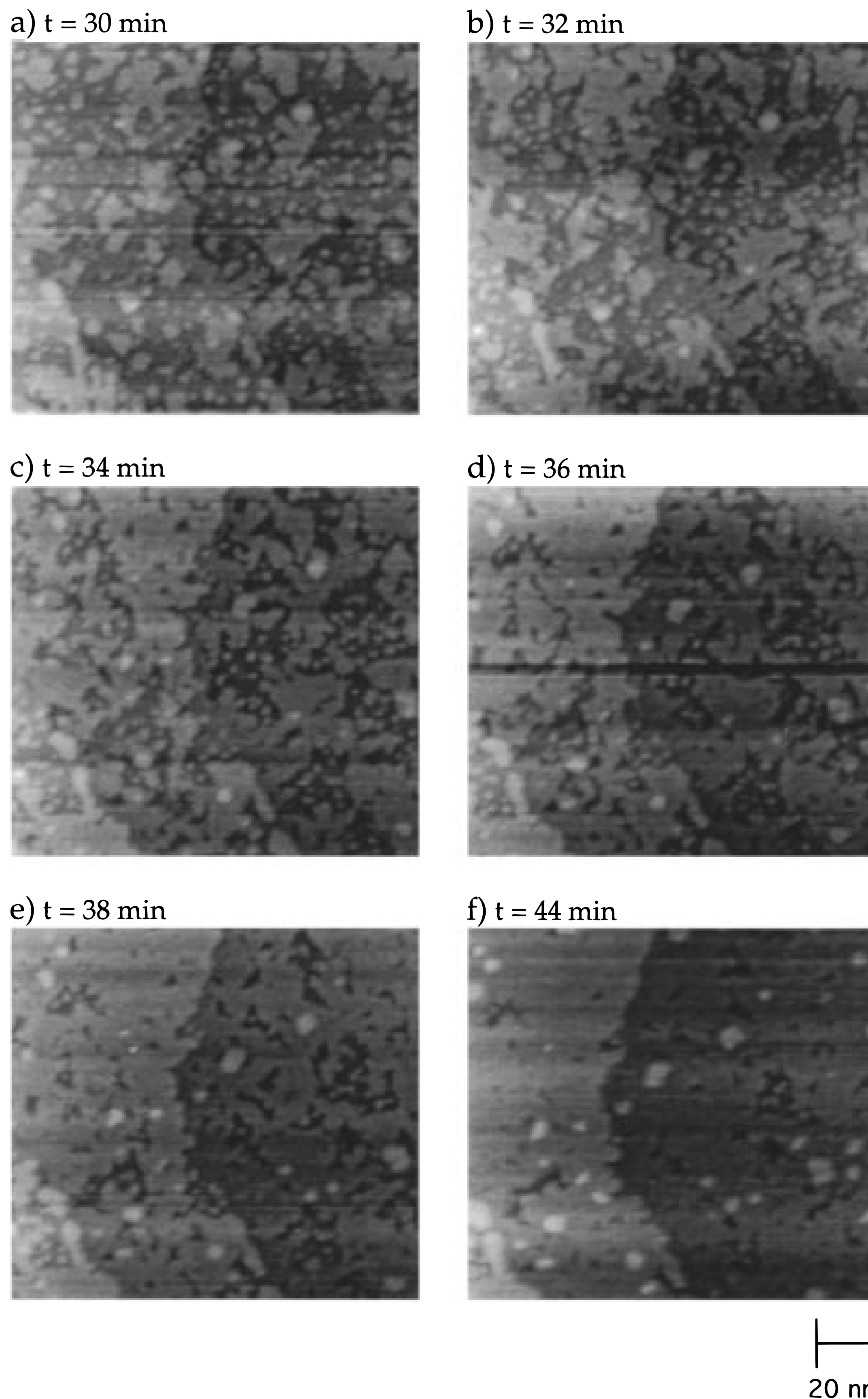

Figure 6. In situ STM image sequence of Cu layer-by-layer growth on C_{18} thiolate-covered Au(111) at 345 K. A constant potential of −50 mV versus Cu/Cu^{2+} (OPD) was applied. Islands grow and coalesce (a)−d) to form an almost complete layer (e and f) with some islands of the following layer. A substrate step divides the image into a bright area (left) and a darker one (right), that is, an upper and a lower terrace. Electrolyte: 50 mM H_2SO_4 + 1 mM $CuSO_4$ in a 2:1 mixture of $HOCH_2CH_2OH/H_2O$. Tunneling parameters: I = 0.7 nA, tip−sample bias = 100 mV.

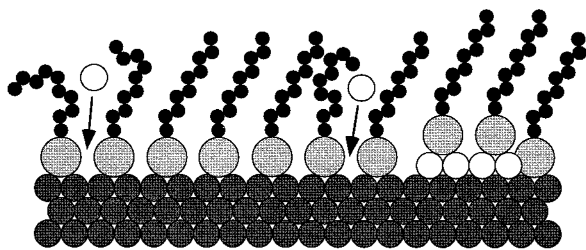

Figure 7. Illustration of a thiol surfactant model. Electrodepositing copper atoms (white) insert between sulfur (light gray) and the gold substrate (dark gray). The alkyl chain carbon atoms are drawn in black. Two or more copper layers can be grown (see Figure 6).

dosing of halogens can even produce virtually defect-free surfaces.[31,32]

Cu deposition in the UPD range at high temperature leads to the same structures as seen at 300 K: Cu islands with 1−4 nm diameters (little dependence on thiolate chain length) develop (see Figure 5). The difference was that above 315 K the islands were observed almost immediately whereas their growth took more than 30 min at 300 K. This much faster reduction kinetics is due to the aforementioned defects in the molecular layer, allowing for some penetration of Cu^{2+} into the thiolate. The smaller distance to the Au substrate promotes a much faster electron transfer, as discussed in connection with the electron-transfer blocking measurements. In passing we note that a pure electron-transfer process without penetration (for almost all values of temperature and chain length) is still much faster than the growth of Cu islands (minute or hour time scale).[13] This means that during or after reduction of Cu^{2+} some processes slow the deposition. The obvious explanation for such a process is Cu penetration into and diffusion of Cu in the thiolate layer, which will both be facilitated by high temperatures. We present a full discussion of the kinetics in ref 13.

In contrast to the discussed Cu UPD, which gives qualitatively the same structures as those at 300 K, the OPD scenario changes substantially. Whereas at 300 K a pseudo-layer-by-layer growth was recorded only for short chain thiolates (<13 C atoms),[14,15] above 340 K even the longest (C_{18}) thiolate permits this growth mode (see Figure 6). On a minute time scale we followed island coalescence and growth of new Cu layers. Note that they are even faster than the related processes on short chain thiolates at 300 K. The necessary overpotentials were only 50 mV (at 300 K: 100 mV), and Cu coverages larger than two layers were easily attainable. These observations nicely fit the UPD results: again thermally induced defects in the molecular layer allow for a rapid Cu reduction, thiolate penetration, and surface diffusion.

Concerning the deposit's structure, we can exclude that Cu islands grow on top of the thiolate layer (in contact with the methyl end groups). If such a structure existed, Cu ions would be reduced at such adatoms or adislands and thus tend to form three-dimensional clusters; such clusters form, for example, on bare Au(111).[33,34] Since in our case two-dimensional growth is found, the preadsorbed thiolate must act as a surfactant (see Figure 7).

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(34) In contrast, some special metal substrates can induce a pseudo-layer-by-layer electrogrowth of Cu; for example, fcc(100) faces of Au,[35] Ag,[36] and Pt[37] permit the formation of bcc-Cu phases[38] growing in this fashion. Such a strain relaxation of Cu layers in the absence of surfactants is not observed on Au(111); indeed, for Cu/Au(111) strain is released via three-dimensional (cluster) growth.[33]

Because a surfactant induces a two-dimensional growth for each new layer, it has to stay adsorbed on the uppermost deposited layer. A surfactant ("additive") is normally added to the electrolyte, for example, crystal violet,[33] benzotriazole,[39] or tetraalkylammonium cations[40] to a Cu^{2+} solution, to change the growth mode (in these cases on Au(111)) from three- to two-dimensional. These surfactants stay adsorbed on each new Cu layer. Accordingly, in the course of Cu deposition on *thiolated* Au(111), the initial Au−S bond is broken and a Cu−S bond is formed; the thiolate layer is now bound to Cu in the same way as the aforementioned surfactants (also found by XPS measurements[13] but questioned by Eliadis et al.[17]). Note that the thiolate/Cu structure shown in Figure 7 also explains why the deposited Cu is passivated at 300 K—the thiolate acts as a protective layer, for example, against attack by mild acids. We assume that the Au(111) surface does not reconstruct during Cu deposition; a Cu/Au interface in sulfate electrolyte can form an alloy only after several hours of polarization.[41] Möller et al.[42] found alloy formation during CuCl deposition only on the more open Au(110) surface.

Why and how surfactants work is still not understood. For example, albeit they should contibute to the relief of the strain of at least the uppermost Cu layer, strain relief might not be necessary, since strained Cu can grow layerwise.[36,37,43] The reduction of the growth rate appears to play a role,[40] but simple models such as atoms only attaching at steps (complete blocking of vertical growth) can be ruled out. In contrast to additives, adsorbed thiolates neither form complexes with the metal ion nor allow a metal−additive coadsorption. Without generalizing our findings, we note that complexing and coadsorption are not prerequisites for surfactant action. At least in our case, the very slow penetration of Cu into the surfactant layer and the resulting slow growth kinetics play key roles.

In conclusion, the surfactant action of a preadsorbed thiolate monolayer can avoid some difficulties of interpretation associated with surfactant additives in electrochemistry, for example, the question of coadsorption or complex formation of the metal ion and the additive. Hence we propose alkanethiolates as a model surfactant whose action on growing Cu layers we presented. Furthermore, elevated temperatures are commonly employed as a control parameter in technical electrodeposition, often in the presence of surfactants; the foundations of this process have been clarified for our model system.

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