



Spontaneous deposition of Sn on Au(111). An in situ STM study

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ABSTRACT

The tin adlayer formed by spontaneous deposition on Au(111) was characterized by cyclic voltammetry and in situ scanning tunneling microscopy (STM) in sulphuric acid solution. Cyclic voltammetry measurements showed oxidation peaks in the potential range $-0.60 \leq E/V$ vs SSE ≤ 0 , which can be ascribed to the dissolution of the Sn adsorbed layer. STM images of the Au(111)/Sn modified surface showed that tin nucleated both on step edges and on the flat terraces forming two dimensional islands. The anodic polarization of this modified surface produced the gradual dissolution of the Sn adlayer which was evidenced by the formation of some holes and the reduction of the initial terraces to many small islands. STM images with atomic resolution obtained on these islands displayed an hexagonal expanded atomic structure. After the anodic stripping of this Sn adsorbed layer the images exhibited the typical Au(111) terraces with a (1×1) atomic structure. However, at more anodic potentials another dissolution process was observed producing noticeable changes on the surface morphology which could be ascribed to the dissolution of a Au–Sn surface alloy.

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1. Introduction

The deposition of metal monolayers onto a foreign metal surface is one of the most extensively studied subjects in surface electrochemistry because some of these modified surfaces have electrocatalytic or catalytic properties better than those of the pure components [1]. In some cases the metal overlayers can be generated onto the foreign metal substrate by underpotential deposition (UPD) [2,3], namely, by deposition at potentials more positive than the Nernst equilibrium potential of the corresponding 3D metal bulk phase. In other cases the formation of such modified bimetallic surfaces can be achieved by “spontaneous deposition” using the so-called immersion technique [4–7], which deals with the reduction as well as the oxidation of metal adspecies that has been introduced spontaneously onto the electrode surface at open-circuit from solutions containing the metal ions. The surface concentration of the deposited species depends on the immersion time and the bulk concentration of the adsorbing species.

The spontaneous adsorption of tin on polycrystalline and single-crystal gold surfaces was first analyzed by Rodes et al. [8,9] and they concluded that this process could be explained by the adsorption of Sn^{II} species followed by a disproportionation reaction in which the product with the lower valency state is adsorbed. The formation of a Sn–Au surface alloy during this process was also

suggested. More recently, Fonticelli et al. [10] studied the adsorbed tin species on evaporated gold films electrodes obtained by UPD and spontaneous deposition. They observed that Sn⁰ adatoms were generated on the surface either, by reducing Sn^{II} present in the solution through UPD or by first irreversibly adsorbing Sn^{II} and then reducing it in the supporting electrolyte.

In the present work, we present the first STM studies concerning the spontaneous deposition of Sn on Au(111). The possibility of surface alloying during this process is also discussed.

2. Experimental

A Au(111) single-crystal electrode ($\Phi = 4$ mm) was used as working electrode. The substrate surface was first mechanically polished with diamond paste of decreasing grain size down to 0.25 μm and subsequently electrochemically polished in a cyanide bath [11].

Conventional electrochemical studies were performed in standard three-electrode electrochemical cells. The counter electrode was a platinum sheet (1 cm²) and the reference electrode was a Hg/Hg₂SO₄/K₂SO₄ saturated electrode (SSE). All potentials in this study are referred to the SSE.

A standard Nanoscope III equipment (Digital Instruments, Santa Barbara, CA, USA) was used for the in situ STM studies, employing Apiezon insulated Pt–Ir tips. Pt wires served as counter and quasi-reference electrodes. The tip potential was held constant at a value of minimum faradaic current and the tip current varied in the range $2 \leq I_{\text{tun}}/\text{nA} \leq 20$.

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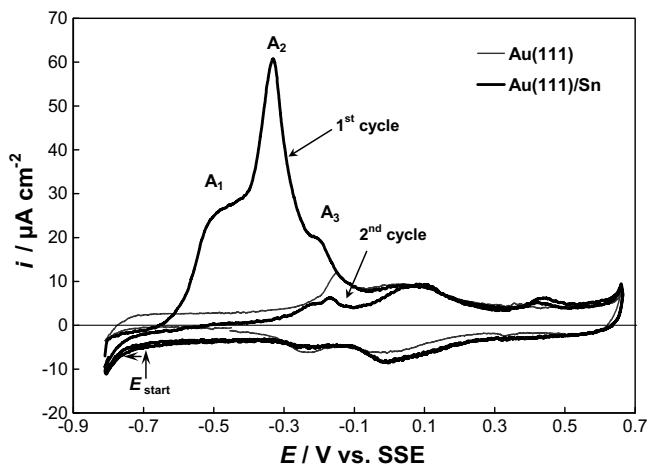


Fig. 1. Voltammetric desorption of tin adspecies by successive voltammetric cycles after the immersion of the Au(111) substrate in 1 mM SnSO₄ + 0.5 M H₂SO₄ solution for $t_i = 60$ s. Test electrolyte: 0.5 M H₂SO₄, $[dE/dt] = 50$ mV s⁻¹.

The Au(111)/Sn modified substrate was prepared by immersing the gold electrode in 1 mM SnSO₄ + 0.5 M H₂SO₄ deaerated solution under open-circuit conditions for different immersion times, t_i ($5 \leq t_i/s \leq 60$), followed by sufficient rinsing with pure water. The stationary mixed potential of the system in the open-circuit experiment was $E \approx -0.27$ V. Subsequently, the electrode was

introduced into another electrochemical cell or into the STM cell containing 0.5 M H₂SO₄ used as test electrolyte, at a controlled potential.

3. Results and discussion

Fig. 1 shows the cyclic voltammogram of the Au(111)/Sn modified substrate ($t_i = 60$ s) obtained in the test solution in the potential range $-0.8 \leq E/V \leq 0.65$. The cyclic voltammogram corresponding to the bare Au(111) surface is also included in the figure for comparison purpose. The potential was fixed at an initial value $E_{start} = -0.70$ V which is more negative than the stationary mixed potential of the system ($E \approx -0.27$ V) and enables to consider that all the adsorbed tin is in its reduced form [8]. During the positive-going sweep the voltammogram displays an anodic broad peak (A_2) with two shoulders (A_1 , A_3) in the potential range $-0.60 \leq E/V \leq 0$, in accordance with previous results obtained by Rodes et al. [9] using a flame treated Au(111) working electrode. These authors indicated that the adsorbed tin on Au(111) is directly oxidized to Sn^{IV} soluble species in the course of these stripping processes. The anodic features related to the dissolution of tin are absent in successive cycles and the final voltammogram approaches to that of the bare Au(111) surface (Fig. 1). This result indicates the almost complete dissolution of the adsorbed tin during the anodic sweep and that the desorbed tin species have not been re-reduced to Sn⁰ during the cathodic scans.

The surface topography of the Au(111)/Sn modified surface was analyzed by in situ STM in the test electrolyte. Fig. 2a displays a

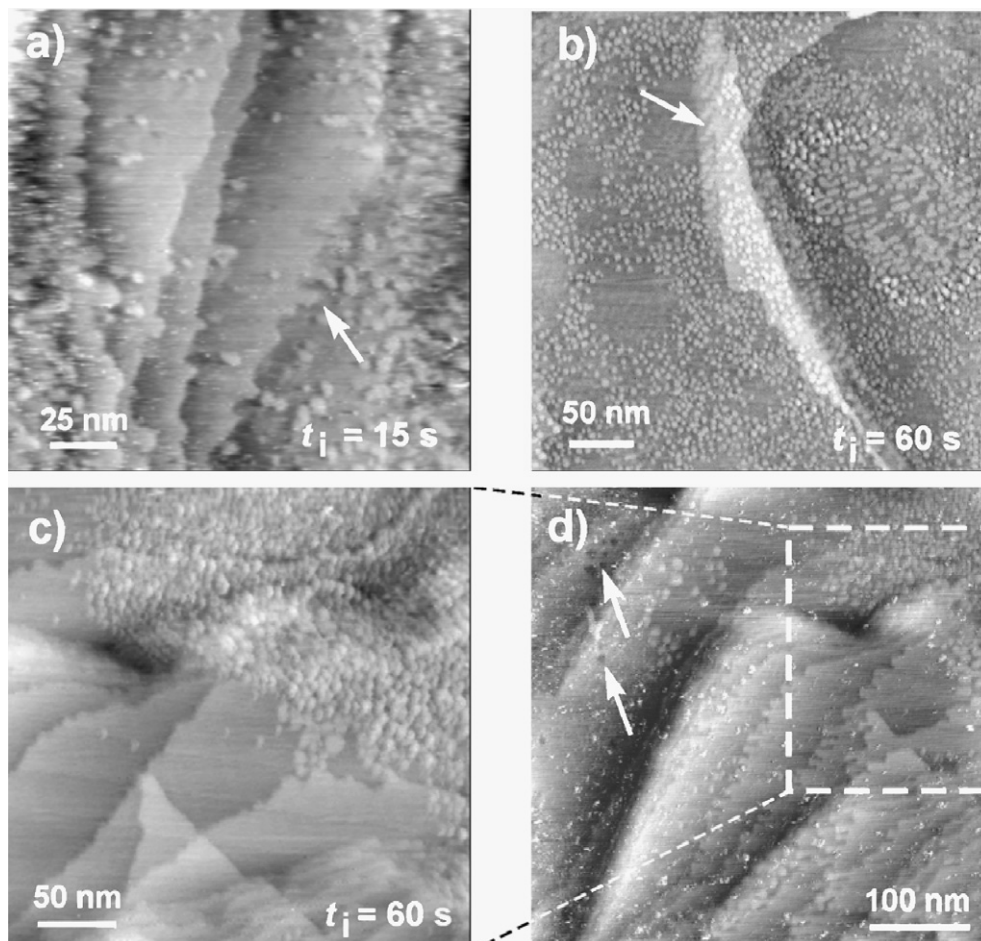


Fig. 2. In situ STM images of the Au(111)/Sn modified surface obtained by immersion in 1 mM SnSO₄ + 0.5 M H₂SO₄ solution during: (a) $t_i = 15$ s; (b–d) $t_i = 60$ s. Polarization conditions in the test electrolyte: (a–c) $E = -0.70$ V, (d) after stripping at $E = 0.55$ V, $t_p = 800$ s.

representative view of the Au(111)/Sn modified surface obtained by immersion of the substrate in the Sn^{2+} containing solution during $t_i = 15$ s. The image showed that tin nucleates on the flat terraces forming two-dimensional islands without any preferential orientation with respect to the surface. This fact suggests that the tin adlayer is formed onto an unreconstructed surface or that the tin spontaneous deposition process produces the lifting of the reconstruction. Otherwise, the characteristic double rows of the Au(111)-($\sqrt{3} \times 22$) surface reconstruction would influence on the tin deposit morphology as was observed during the Sn UPD process on this substrate [12]. In addition, in some places the flat terraces show rounded edges (see the arrow in Fig. 2a) denoting that the adsorbed tin layer also nucleates at the step edges growing in the direction perpendicular to the steps. The number and size of the Sn islands increase with the immersion time as shown in Figs. 2b and c ($t_i = 60$ s). In this case the two dimensional islands tend to merge forming interconnected structures of monatomic height. The images indicate that the adsorbed tin adlayer has different local coverage, showing highly covered zones and others without tin adspecies. These results are in agreement with the tin coverage, θ_{Sn} , determined from the anodic charges ranging from $\theta_{\text{Sn}} \approx 0.03$ for $t_i = 5$ s to $\theta_{\text{Sn}} = 0.25$ for $t_i = 60$ s, and with the maximum $\theta_{\text{Sn}} = 0.3$, reported for the adsorption of Sn on Au(111) [9]. It is

interesting to note that several small islands are present on top of other large 2D islands (see the arrow in Fig. 2b). These second layer formed on top of the previously adsorbed islands, indicates the capability of Sn to spontaneously deposit on the first Sn layer.

The surface morphology described above was stable at relatively negative potentials. The image displayed in Fig. 2d was obtained at the same surface region that Fig. 2c and shows the morphology changes of the Au(111)/Sn modified surface produced by an anodic polarization at $E = 0.550$ V. In this case the islands are partially dissolved and the step edges are also affected confirming that tin was deposited at those places. In addition, some holes are also present in the central part of some terraces (see the arrows). This fact could be ascribed to the dissolution of a Sn–Au alloy phase formed at those places due to an intermixing process between both species. The formation of surface alloy phases was also observed during the Sn UPD on gold single crystals [12,13].

Fig. 3 shows a sequence of images corresponding to another experiment illustrating on the dissolution process of the tin layer with more details. The initial state of the Au(111)/Sn modified surface is displayed in Fig. 3a where relatively large islands are observed. The morphology of the step edges also suggests the nucleation of tin adspecies at these places, as was indicated in previous paragraphs. The anodic polarization produces no morphological

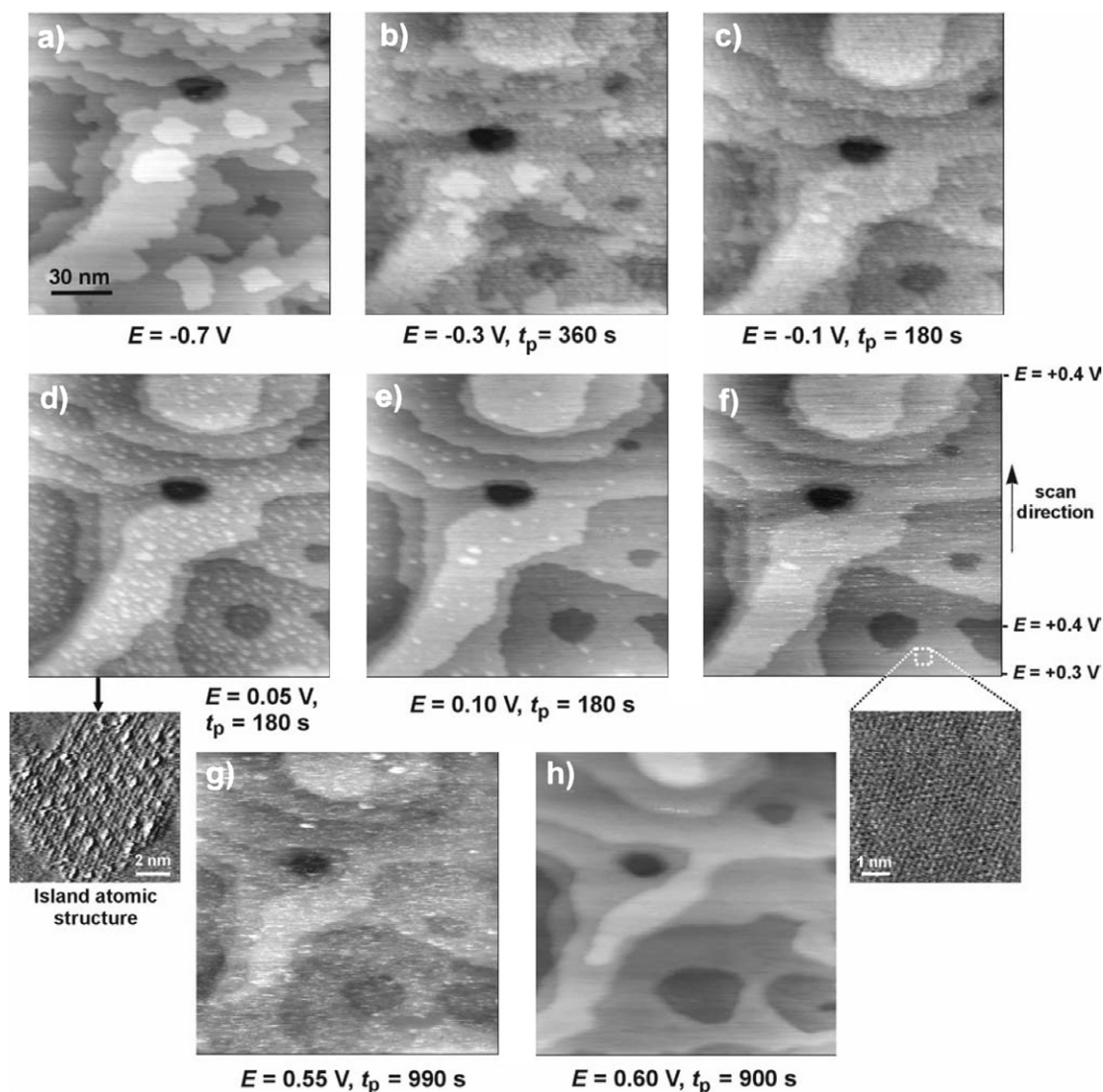


Fig. 3. Sequence of in situ STM images of the Au(111)/Sn modified surface ($t_i = 60$ s) at different polarization conditions in the test electrolyte.

changes in the potential range $-0.60 \leq E/V < -0.45$, where the first anodic shoulder, A_1 , is located. Nevertheless, in the potential range $-0.45 \leq E/V \leq 0$, where the anodic peaks A_2 and A_3 are recorded, the gradual dissolution of the large islands is observed (Figs. 3b and c). During this process an increase of the surface roughness is distinguished and subsequently, the initial terraces are reduced to many small islands. These islands are gradually dissolved in the potential range $0 \leq E/V \leq 0.15$ (Fig. 3d and e). High resolution STM images obtained on top of these islands show evidence of an hexagonal expanded adlayer, but with some noise (see the zoom in Fig. 3d). The apparent distance between spots is ~ 0.37 nm and the noise observed suggests mobility in the adsorbed layer. More STM experiments are now in progress in order to characterize this structure taking into account that the presence of coadsorbed anions should not be disregarded.

After the anodic stripping of the little islands the images show again terraces with the typical morphology of the bare Au(111) substrate (fig. 3f). The atomic structure on top of the flat terraces is hexagonal (see the zoom in Fig. 3f) with an interatomic distance of 0.29 ± 0.02 nm, which corresponds to the atomic structure of the Au(111) surface. However, when the electrode potential is further scanned in anodic direction another dissolution process is observed in the potential range $0.40 \leq E/V \leq 0.60$, producing noticeable changes on the step edges and the enlargement of holes present on the surface (Figs. 3g and h). Relatively long polarization times are necessary to obtain stable images again. This fact suggests that this slow dissolution process could be related to the stripping of a Au–Sn surface alloy which seems to be formed, in this case, preferentially at step edges.

4. Conclusions

An adsorbed tin layer on the Au(111) surface was obtained by the immersion method in a solution containing Sn^{2+} ions. The presence of this layer was clearly evident from the voltammetric curves in sulphuric acid solutions. During the anodic scan characteristic

peaks were recorded which can be ascribed to the dissolution of the Sn adlayer. The STM images of the Au(111)/Sn modified surface, showed flat terraces with rounded edges and two dimensional islands. The anodic polarization of this modified surface produced the gradual dissolution of the Sn adlayer which was evidenced by the formation of some holes and reducing the initial terraces to many small islands. Images with atomic resolution obtained on top of these islands exhibited a hexagonal expanded adlayer. After the anodic stripping of this Sn adsorbed layer the images displayed the typical Au(111) terraces with a (1×1) atomic structure. However, at more anodic potentials another dissolution process was observed producing changes on the surface morphology. This effect suggests the formation of a Au–Sn alloy phase in the course of tin adsorption.

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