Available online at www.sciencedirect.com
ScienceDirect

Electrochemistry Communications 9 (2007) 1382–1387

electrochemistry communications

www.elsevier.com/locate/elecom

Electrochemical formation of ultrathin Ag/Cd films onto Au(1 1 1) substrates

M.C. del Barrio, D.R. Salinas, S.G. García *

Instituto de Ing. Electroquímica y Corrosión (INIEC), Departamento de Ingeniería Química, Universidad Nacional del Sur, Avda. Alem 1253, (8000) Bahía Blanca, Argentina

Received 19 September 2006; received in revised form 20 December 2006; accepted 3 January 2007
Available online 4 February 2007

Abstract

The formation of an ultrathin bilayer of Ag/Cd in the system Au(1 1 1)/Ag^+, Cd^{2+}, SO_4^{2-} has been studied by conventional electrochemical techniques and in situ scanning tunneling microscopy (STM). Cyclic voltammetric measurements carried out in a solution containing both Ag^+ and Cd^{2+} ions have shown that the deposition of Cd onto the Au(1 1 1) modified with 3.75 ML of Ag originates adsorption/desorption UPD peaks which are similar to those obtained in the system Ag(1 1 1)/Cd^{2+}. These results demonstrate that the Au(1 1 1) surface was completely screened by the Ag layers which were epitaxially oriented respect to the substrate. Therefore, an ultrathin Ag(1 1 1) film was formed onto the Au(1 1 1) surface, on which a Cd ML was subsequently deposited by UPD, with the final product of an ultrathin Ag–Cd bilayer on the gold substrate. The morphological surface changes during the Ag deposition and subsequent Cd UPD on the modified substrate were followed by in situ STM imaging.

Keywords: Thin films; Surface alloys; Ag/Cd/Au system; Structured layers; UPD–OPD transition

1. Introduction

The formation of ultrathin metal films on foreign substrates (metals, superconductors and semiconductors) has received considerable attention due its theoretical interest in surface chemistry and physics, and practical importance in fields such as micro- and nano-electronics, sensors, electrocatalysis. Electrochemical processes become of great interest in modern thin layer technology, especially for the development of heterostructures formed by more than one deposited metal constituting metallic sandwich layers and/or surface alloys, since supersaturation and undersaturation can be well adjusted and also rapidly changed via the electrode potential. The electrochemical formation of ultrathin metal films, sandwich-structures layers and surface alloys can be electrochemically obtained in the underpotential deposition (UPD) range or in the overpotential deposition (OPD) range. The UPD process, which occurs due to a strong adatom–substrate bonding, is referred to the electrodeposition of a metal (Me) monolayer on a foreign metal substrate (S) at potentials more positive than the Nernst equilibrium potential of the three dimensional (3D) metal bulk phase, and it is the first stage of electrochemical heteroepitaxial growth for many systems. This phenomenon can control the growth behavior and the resulting structures, especially as a function of surface coverage [1,2]. On the other hand, the OPD process is referred to the electrodeposition at potentials more negative than the Nernst equilibrium potential of the 3D metal bulk phase, and different deposition mechanisms can be distinguished depending on the binding energies of Me–adatoms on the foreign and on the same substrate, and the crystallographic Me–S misfit [1]. These parameters determine the phase formation characteristics in the supersaturation range or OPD range. Layer growth mode can be achieved by OPD in systems with strong binding energies and negligible deposit-substrate misfit.

---

* Corresponding author. Tel./fax: +54 291 4595182.
E-mail address: sgarcia@criba.edu.ar (S.G. García).

1388-2481/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2007.01.057

Several studies have been reported about thin composite films but only few used the single metals UPD [3–11]. The aim of the present paper is to demonstrate, by in situ STM and electrochemical measurements, the ability to prepare an ultrathin Ag/Cd bilayer on Au(1 1 1) from the multi-component system Au(1 1 1)/Ag^+, Cd^{2+}, SO_4^{2-} using a defined polarization routine. This system was selected because the binary systems Au(1 1 1)/Ag^+, Au(1 1 1)/Cd^{2+} and Ag(1 1 1)/Cd^{2+} have a pronounced UPD [12–16] with very low Me–S misfit ($d_{0,\mathrm{Au}} = 0.2884$ nm, $d_{0,\mathrm{Ag}} = 0.2889$ nm, $d_{0,\mathrm{Cd}} = 0.2978$ nm), opening an excellent possibility to study the preparation of sandwich-structure metal films [1,10].

2. Experimental

The experiments were performed in the system Au(1 1 1)/Ag^+, Cd^{2+}, SO_4^{2-} using a Au(1 1 1) single crystal electrode with a diameter of 4 mm. 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 according to a standard procedure [17].

The main electrolyte solution used throughout the study was 0.015 mM Ag_2SO_4 + 1 mM $CdSO_4$ + 7.7 mM H_2SO_4 + 0.1 M Na_2SO_4. This solution was prepared from suprapure chemicals (Merck, Darmstadt) and fourfold quartz-distilled water, and deaereated by nitrogen bubbling prior to each experiment. Additional experiments related to the behavior of the binary systems Au(1 1 1)/Ag^+, Ag(1 1 1)/Cd^{2+} and Au(1 1 1)/Cd^{2+} were carried out in solutions containing only the corresponding cation and they are described in the respective paragraph.

Conventional electrochemical studies were performed in standard three-electrode electrochemical cells. The counter-electrode was a platinum sheet (1 cm^2) and the reference electrode was a $Hg/Hg_2SO_4/K_2SO_4$ saturated electrode (SSE), mounted inside a Luggin capillary. The actual electrode potential, E, is referred to the SSE, whereas the underpotential, $\Delta E_{3\mathrm{DMe}}$, or the overpotential, $\eta_{3\mathrm{DMe}}$, are related to the corresponding Nernst equilibrium potential of the 3D Me phase ($E_{3\mathrm{DMe}}$) by $\Delta E_{3\mathrm{DMe}} = E - E_{3\mathrm{DMe}} > 0$, or $\eta_{3\mathrm{DMe}} = E - E_{3\mathrm{DMe}} < 0$, respectively. The measurements were carried out with a potentiostat–galvanostat EG&G Princeton Applied Research Model 273A.

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 (Digital -Veeco, USA). A Pt wire was used as counter-electrode and a Au wire as quasi-reference electrode. The potentials of the gold substrate and the STM tip were controlled independently by a Nanoscope III-bipotentiostat optimised for the STM set-up used. The tip potential was held constant at a value of minimum faradaic current and the tip current varied in the range $2 \leqslant I_{\mathrm{tun}}/\mathrm{nA} \leqslant 20$. The experimental set-up for the in situ STM technique has been checked by cyclic voltammetric measurements and the results were identical to those obtained in the conventional electrochemical cell.

3. Results and discussion

Fig. 1 shows typical cyclic voltammograms obtained for the binary systems Au(1 1 1)/Ag^+, SO_4^{2-}, Ag(1 1 1)/Cd^{2+}, SO_4^{2-}, and Au(1 1 1)/ Cd^{2+},SO_4^{2-} which are in good agreement with those obtained in previous works [13–16]. In the UPD range $15 \leqslant \Delta E_{3\mathrm{DAg}}/\mathrm{mV} \leqslant 720$ the cyclic voltammogram for Ag UPD on Au(1 1 1) shows two characteristic sorption peaks at $\Delta E_{3\mathrm{DAg}} = 600 \pm 120$ mV and at underpotentials close to the $E_{3\mathrm{DAg}}$ (Fig. 1a). It was demonstrated [13] that the first Ag UPD peak is related to the formation of an expanded Ag overlayer with a Au(1 1 1)–(4 × 4)Ag structure. This overlayer is transformed to a Au(1 1 1)–(1 × 1)Ag phase at lower $\Delta E_{3\mathrm{DAg}}$. Finally, due to the negligible metal/substrate misfit the Ag deposition is expected to follow a layer-by-layer growth in the OPD range. García et al. [12] have demonstrated that this deposition mechanism is operative in the system Au(1 0 0)/Ag^+ during the UPD–OPD transition, and more recently, Kolb et al. [18] reported a similar behavior in the system Au(1 1 1)/Ag. In this case a layer-by-layer growth up to at least 10 Ag ML was detected. Additionally, a multilayer growth behavior was also observed which produced a remarkable leveling effect.

The cyclic voltammogram for the system Ag(1 1 1)/Cd^{2+}, SO_4^{2-} (Fig. 1b) displays four adsorption/desorption peak pairs in the underpotential range $0 \leqslant \Delta E_{3\mathrm{DCd}}/\mathrm{mV} \leqslant 400$, corresponding to the Cd UPD on Ag(1 1 1) [14]. In this case the Cd UPD starts with the formation of an expanded adlayer with a superlattice structure Ag(1 1 1)–$(\sqrt{3} \times \sqrt{19})R23.4°$ which transforms to a condensed close packed Cd monolayer at lower $\Delta E_{3\mathrm{DCd}}$. At long polarization times the condensed monolayer undergoes structural changes involving place exchange processes between Cd atoms and surface Ag atoms. At $\Delta E_{3\mathrm{DCd}} < 50$ mV a second Cd monolayer and a significant Ag–Cd surface alloying take place.

The cyclic voltammogram for Cd UPD on Au(1 1 1) exhibits three adsorption/desorption current peak pairs in the underpotential range $0 \leqslant \Delta E_{3\mathrm{DCd}}/\mathrm{mV} \leqslant 800$ (Fig. 1c) and starts with the formation of expanded structures at relatively high underpotentials [19]. At $\Delta E_{3\mathrm{DCd}} = 300$ mV, 2D Cd islands start to nucleate on the fcc regions of the Au(1 1 1) reconstructed surface and continue to grow acquiring a linear morphology, which indicates that the underlying reconstructed substrate is influencing on the deposition [15,16]. At $\Delta E_{3\mathrm{DCd}} \approx 0$ mV, the islands tend to merge forming a complete Cd monolayer. Current–potential desorption spectra recorded after long polarization time, as well as STM studies demonstrated the formation of 3D Au–Cd alloy phases at $\Delta E_{3\mathrm{DCd}} \leqslant 70$ mV [15,19].

Considering the results mentioned above, it would be possible to obtain an ultrathin Ag–Cd bimetallic layer with epitaxial arrangement on Au(1 1 1) from a solution containing both Ag^+ and Cd^{2+} ions, because the following conditions are fulfilled: (a) both systems Au(1 1 1)/Ag^+ and Ag(1 1 1)/Cd^{2+} show underpotential deposition but the

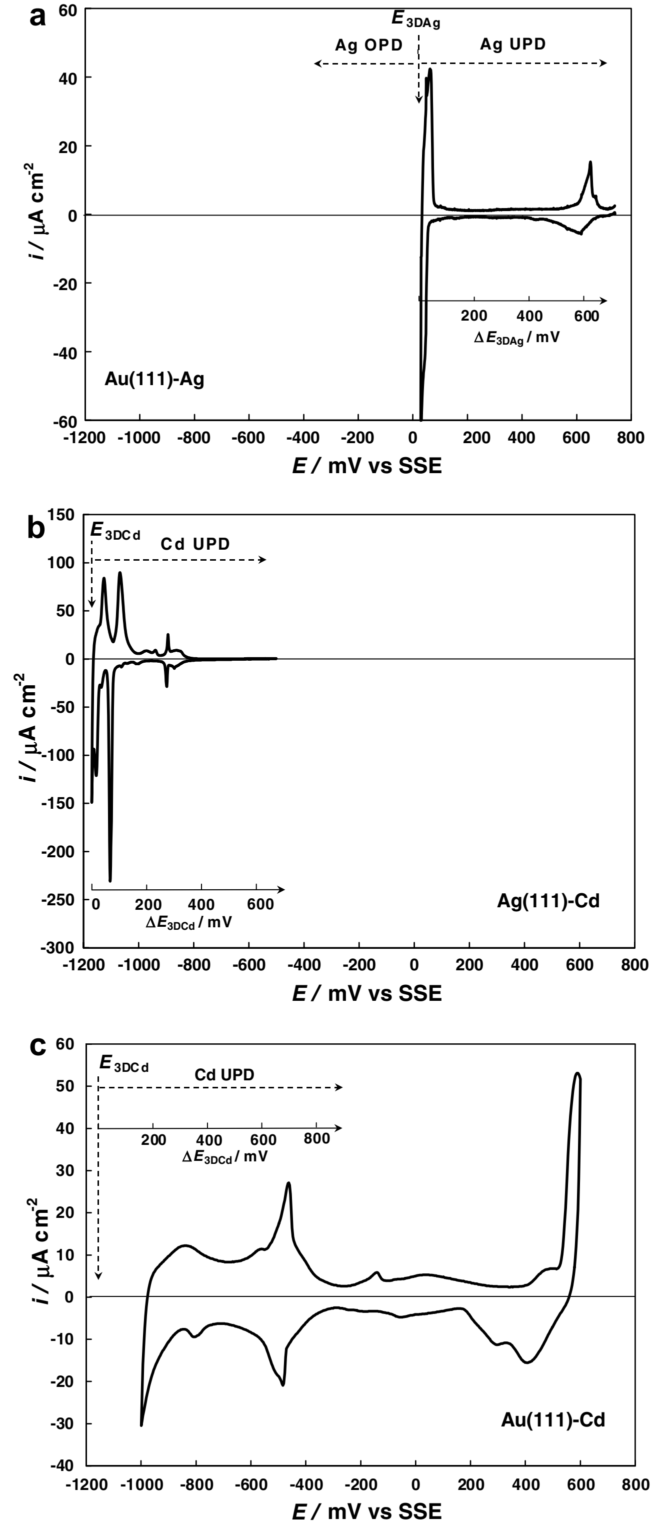

Fig. 1. Cyclic voltammograms for the binary systems: (a) Au(1 1 1)/5 mM Ag_2SO_4 + 0.5 M H_2SO_4, $|dE/dt| = 7\ mV\ s^{-1}$; (b) Ag(1 1 1)/1 mM $CdSO_4$ + 5 mM H_2SO_4 + 0.5 M Na_2SO_4, $|dE/dt| = 10\ mV\ s^{-1}$; (c) Au(1 1 1)/1 mM $CdSO_4$ + 5 mM H_2SO_4 + 0.1 M Na_2SO_4, $|dE/dt| = 50\ mV\ s^{-1}$.

corresponding UPD regions are not overlapped and sufficiently separated; and (b) in the system Au(1 1 1)/Ag^+ a layer-by-layer mechanism operates in the OPD range.

Fig. 2a schematizes the potential ranges for the UPD and OPD phases of the binary Au(1 1 1)/Ag^+ and Ag(1 1 1)/Cd^{2+} systems. Consequently, the following polarization routine is proposed in order to obtain a bimetallic Ag–Cd layer on Au(1 1 1) from a solution containing both Ag^+ and Cd^{2+} ions (Fig. 2b): (a) one or more Ag monolayers can be obtained on the Au(1 1 1) surface by polarizing the substrate in the OPD range of the Ag^+/Ag^o system, at a potential where no Cd UPD occurs; (b) afterwards, the Au(1 1 1) substrate modified with one or more Ag ML is polarized to a potential close to the equilibrium potential of the Cd^{2+}/Cd^o system in order to form a Cd ML. Other

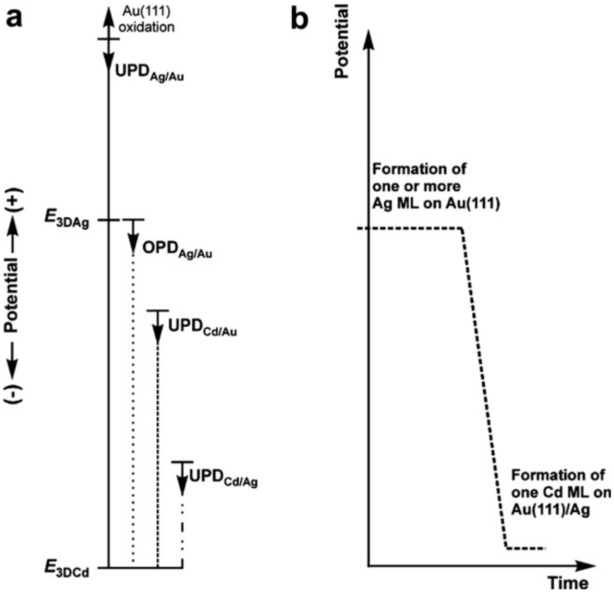

Fig. 2. (a) Schematic representation of the stability ranges for the UPD and OPD phases in the binary systems Au(1 1 1)/Ag^+, Ag(1 1 1)/Cd^{2+} and Au(1 1 1)/Cd^{2+}; (b) polarization routine applied to obtain a bimetallic Ag/Cd layer on Au(1 1 1).

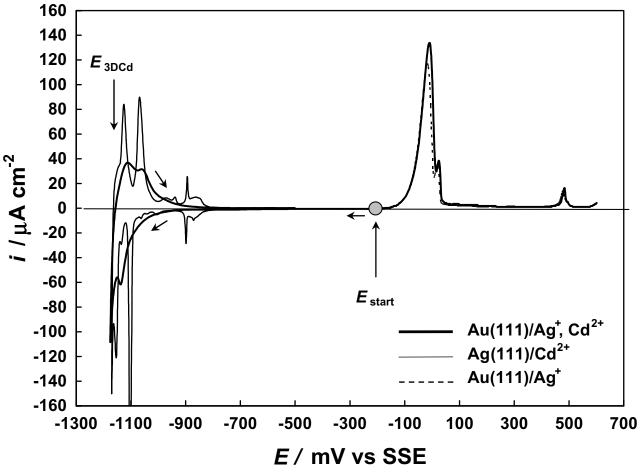

Fig. 3. Voltammetric adsorption/desorption behavior of the system Au(1 1 1)/Ag^+, Cd^{2+}, SO_4^{2-} after a potentiostatic experiment at $E = -200$ mV during 40 min, $|dE/dt| = 10\ mV\ s^{-1}$.

authors [7,10,11] have indicated that in this type of experiments the concentration of the less noble species (Cd^{2+} ions) should be sufficiently higher than the more noble ones (Ag^{+} ions) so as to produce the 3D bulk deposition of the more noble metal very slowly under diffusion control. As a consequence, the co-deposition of both metallic ions is diminished.

Fig. 3 shows the voltammetric behavior of a Au(1 1 1) substrate in the multi-component solution 0.015 mM Ag_2SO_4 + 1 mM $CdSO_4$ + 7.7 mM H_2SO_4 + 0.1 M Na_2SO_4. Initially, the Au(1 1 1) surface was polarized in the Ag OPD range at $E_{\text{start}} = -200$ mV during a polarization time $t_p = 40$ min. This potential is positive enough to prevent the Cd adsorption [19]. Therefore, throughout this polarization time the Au(1 1 1) surface was modified only by Ag deposition. Subsequently, the modified substrate was scanned towards more negative potentials up to $E = -1170$ mV, where the Cd UPD was verified. During this cathodic scan the characteristic peaks corresponding to the Cd UPD on Au(1 1 1) (cf. Fig. 1c) were not observed. In contrast, the adsorption spectra (Fig. 3) exhibited peaks more related to the Cd UPD on Ag(1 1 1). This effect is an evidence that the Au(1 1 1) surface was completely screened by an epitaxially deposited thin silver layer formed during the polarization at E_{start}, on top of which the Cd UPD took place. However, the first peaks associated to the formation of a Cd expanded adlayer were absent and that related to the formation of a condensed phase was slightly displaced

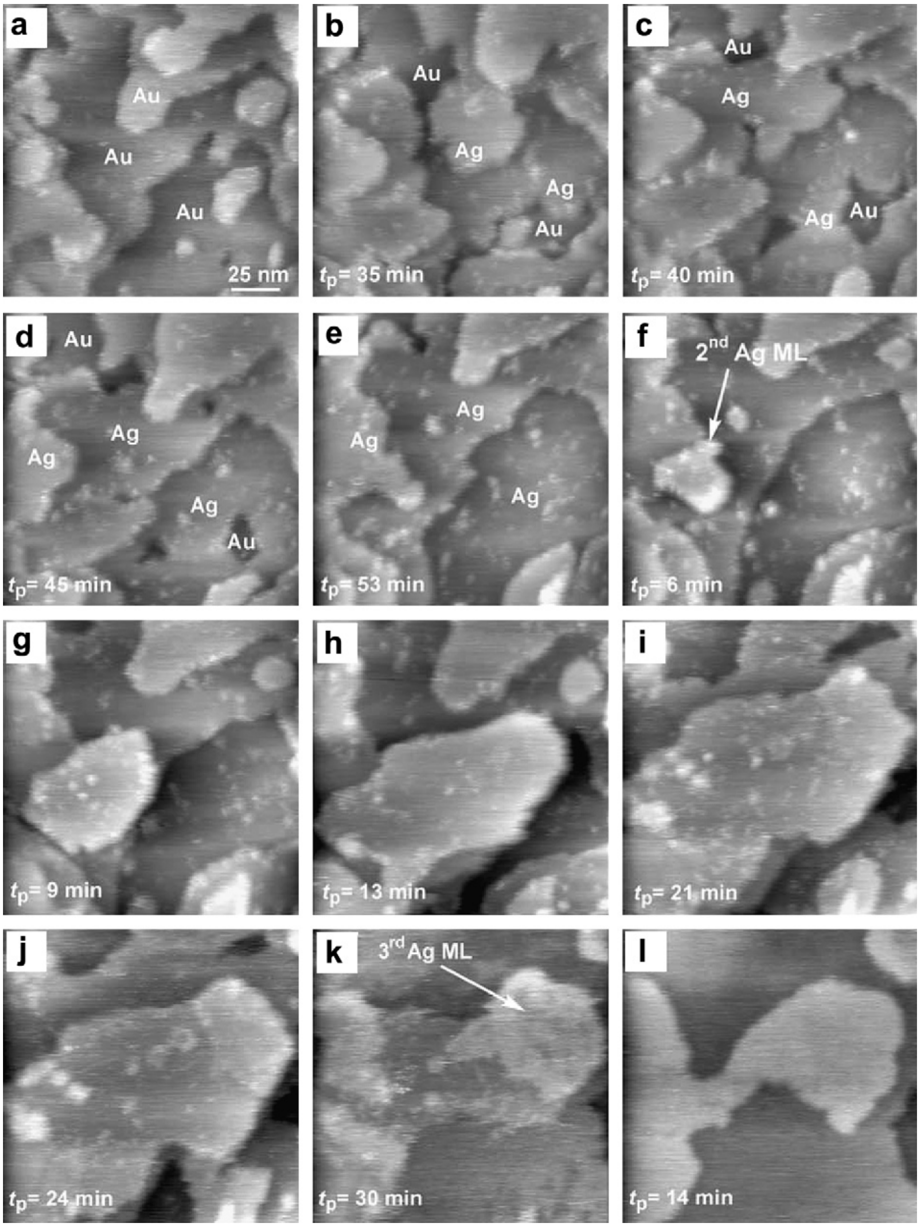

Fig. 4. In situ STM images obtained in the system Au(1 1 1)/Ag^{+}, Cd^{2+}, SO_4^{2-}: (a) initial Au(1 1 1) surface morphology at $E = 550$ mV; (b–e) formation of a Ag ML at $E = -200$ mV; (f–k) Ag growth at $E = -400$ mV; (l) final Au(1 1 1)/Ag surface morphology at $E = -550$ mV.

to more negative potentials. These results would indicate some inhibition for the Cd UPD on the Au(1 1 1) substrate modified with Ag. During the anodic scan (Fig. 3) the first two Cd desorption peaks from a Ag(1 1 1) surface were observed, and at a more positive potential range other anodic peaks were recorded. These more anodic peaks correspond to the stripping of the 3D Ag layer and the desorption of the UPD Ag adlayer initially deposited on the Au(1 1 1) at E_{start}. From the corresponding charge of these peaks ($|\Delta q_{\text{exp}}| \approx 826\ \mu\text{C cm}^{-2}$) it can be concluded that ~3.7 Ag ML were deposited on Au(1 1 1). Fig. 3 also shows the anodic stripping curve obtained in a solution containing only Ag^+ ions (system Au(1 1 1)/0.015 mM Ag_2SO_4 + 7.7 mM H_2SO_4 + 0.1 M Na_2SO_4) after a polarization at $E_{\text{start}} = -200$ mV during 40 min. In this blank experiment the corresponding Ag stripping charge was $|\Delta q_{\text{exp}}| \approx 815\ \mu\text{C cm}^{-2}$. In both experiments the shape of the Ag stripping curves is practically the same. Moreover, the difference between the Ag stripping charges is very low and could be ascribed to the additional Ag deposition produced during the scan up to −1170 mV in the case of the Cd^{2+} containing solution. Therefore, it can be concluded that the amount of Ag co-deposited with Cd when both metallic ions are present is very low.

The formation of the bimetallic Ag–Cd layer on Au(1 1 1) was followed by in situ STM. Fig. 4 displays the changes of surface topography during the formation of a 3D Ag layer onto the Au(1 1 1) substrate, from a solution containing both Ag^+ and Cd^{2+} ions. Fig. 4a shows the initial free Au(1 1 1) substrate surface at $E = 550$ mV. No changes of this surface topography were observed in the potential range $100 \leqslant E/\text{mV} \leqslant 550$ where the formation of an expanded Ag adlayer takes place [13]. As shown in Fig. 4b a growth front appeared in the in situ STM image after stepping the potential to a value of $E = -200$ mV ($\eta_{3\text{DAg}} = -75$ mV). At this potential a condensed Ag ML was practically completed after $t_p = 53$ min, retaining the Au(1 1 1) substrate topography (Fig. 4c–e). The formation of a second Ag ML is recognized in the STM images after stepping the potential to more negative values in the OPD Ag region (cf. the arrow in Fig. 4f) and up to three Ag layers were formed for the polarization routine used (Figs. 4g–l). The potentials applied in this sequence of images were positive enough ($E > -800$ mV) to prevent the Cd deposition and the very low growth rate observed in the experiment can be attributed to the very low Ag^+ concentration present in the solution [10]. Nevertheless, some STM tip influence on this behavior could not be disregarded [20,21]. When the potential was stepped from $E = -550$ mV to a value of $E = -1070$ mV a relatively fast growth of steps together with nucleation of new 2D islands (Fig. 5) were observed. This behavior, derived from the Cd UPD onto the previously formed Ag layers, is in good agreement with results obtained in the system Ag(1 1 1)/Cd [14]. The deposition was enhanced at potentials closer to the equilibrium potential of the 3D Cd phase and the formation of a complete Cd ML is evident by comparing Fig. 4l with Fig. 5f. From these images it is possible to observe that the underlying Ag layer topography is practically reproduced by the Cd ML.

Taking into account the previous results, the formation of an ultrathin Ag/Cd bilayer on Au(1 1 1) from the multicomponent system Au(1 1 1)/Ag^+, Cd^{2+}, SO_4^{2-} was demonstrated. Nonetheless, considering the significant Ag–Cd

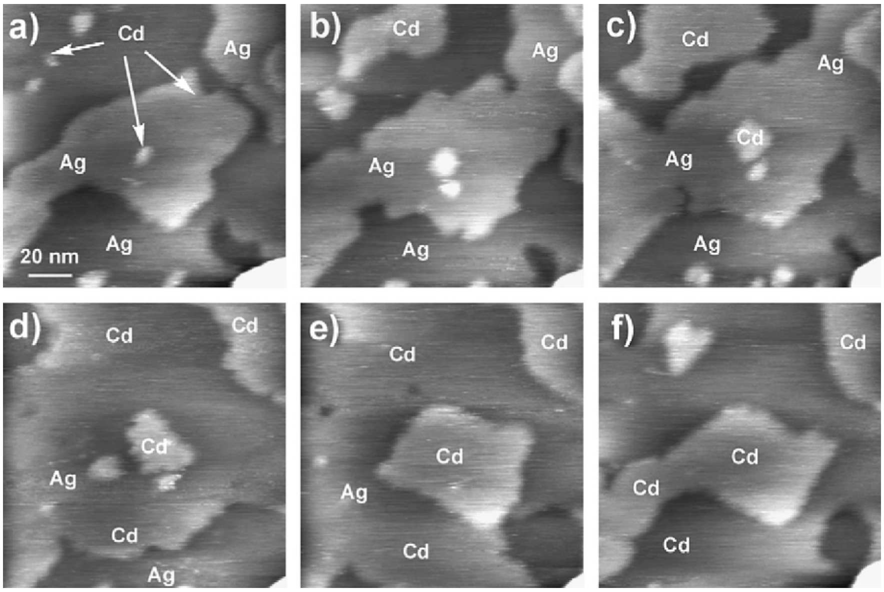

Fig. 5. In situ STM images obtained in the system Au(1 1 1)/Ag^+, Cd^{2+}, SO_4^{2-} (after the sequence showed in Fig. 4) showing the formation of one Cd ML onto the Au(1 1 1) surface modified with Ag. (a) $E = -1070$ mV, $t_p = 60$ s; (b) $E = -1120$ mV, $t_p = 60$ s; (c) $E = -1140$ mV, $t_p = 60$ s; (d) $E = -1140$ mV, $t_p = 120$ s; (e) $E = -1140$ mV, $t_p = 180$ s; (f) $E = -1150$ mV, $t_p = 60$ s.

and Au–Cd surface alloying process reported during the UPD in the binary systems Ag(1 1 1)/Cd^{2+} and Au(1 1 1)/Cd^{2+} [14,19], the formation of a 3D Cd–Ag–Au alloy type heterostructure should not be ignored throughout the present experiments [10]. More studies are necessary to clarify these points which are now in progress.

4. Conclusions

The formation of an ultrathin bilayer of Ag/Cd in the multi-component system Au(1 1 1)/Ag^+, Cd^{2+}, SO_4^{2-} was studied by conventional electrochemical techniques and in situ scanning tunneling microscopy (STM). The cyclic voltammetric measurements indicated that the deposition of Cd onto the Au(1 1 1) surface modified with an ultrathin 3D Ag film (~3.75 Ag ML) originates adsorption/desorption Cd UPD peaks which are in good agreement with those obtained in the system Ag(1 1 1)/Cd^{2+}. These results have demonstrated that the substrate surface is completely screened by the Ag layers which were epitaxially oriented respect to the Au(1 1 1) surface. Therefore, it was possible to form an ultrathin Ag(1 1 1) film on the Au(1 1 1) surface on which a Cd adlayer could be obtained by UPD. The morphological surface changes during the Ag deposition and the subsequent Cd UPD on the modified substrate, were followed by STM and corroborate the formation of an ultrathin Ag/Cd bilayer on the Au(1 1 1) surface.

Acknowledgements

The authors wish to thank the Universidad Nacional del Sur, Argentina, and the Agencia de Promoción Científica (PICTO-UNS 2004 Cod. 614) for financial support of this work. M.C. del Barrio acknowledges a fellowship granted by CONICET.

References

[1] E. Budevski, G. Staikov, W.J. Lorenz, Electrochemical Phase Formation and Growth, VCH, Weinheim, 1996.

[2] E. Herrero, L. Buller, H.D. Abruña, Chem. Rev. 101 (2001) 1897.

[3] I. Villegas, J.L. Stickney, J. Electrochem. Soc. 139 (1992) 686.

[4] M. Mathe, S.M. Cox, B.H. Flowers Jr., R. Vaidyanathan, L. Pham, N. Srisook, U. Happek, J.L. Stickney, J. Cryst. Growth 271 (2004) 55.

[5] S. Bharathi, V. Yegnaraman, G. Prabhakara Rao, Electrochim. Acta 36 (1991) 1291.

[6] S.A. Abd El-Maksoud, S. Taguchi, T. Fukuda, A. Aramata, Electrochim. Acta 41 (1996) 1947.

[7] S. Takami, G.K. Jennings, P.E. Laibinis, Langmuir 17 (2001) 441.

[8] S.P.E. Smith, H.D. Abruña, J. Phys. Chem. B 103 (1999) 6764.

[9] S. Hwang, J. Lee, J. Kwak, J. Electroanal. Chem. 579 (2005) 143.

[10] H.J. Pauling, K. Jüttner, Electrochim. Acta 37 (1992) 2237.

[11] H.-J. Pauling, G. Staikov, K. Jüttner, J. Electroanal. Chem. 376 (1994) 179.

[12] S.G. García, D. Salinas, C. Mayer, J.R. Vilche, H.-J. Pauling, S. Vinzelberg, G. Staikov, W.J. Lorenz, Surf. Sci. 316 (1994) 143.

[13] S. García, D. Salinas, C. Mayer, E. Schmidt, G. Staikov, W.J. Lorenz, Electrochim. Acta 43 (1998) 3007.

[14] S.G. García, D.R. Salinas, G. Staikov, Surf. Sci. 576 (2005) 9.

[15] M.C del Barrio, C. Mayer, D. Salinas, S. García, J. Braz. Chem. Soc., submitted for publication.

[16] S. Maupai, Y. Zhang, P. Schmuki, Surf. Sci. 527 (2003) L165.

[17] K. Engelsmann, W.J. Lorenz, E. Schmidt, J. Electroanal. Chem. 114 (1980) 1.

[18] M.J. Esplandiu, M.A. Schneeweiss, D.M. Kolb, Phys. Chem. Chem. Phys. 1 (1999) 4847.

[19] M.D. Lay, K. Varazo, N. Srisook, J.L. Stickney, J. Electroanal. Chem. 554 (2003) 221.

[20] U. Stimming, R. Vogel, D.M. Kolb, T. Will, J. Power Sources 43 (1993) 169.

[21] S.G. García, D.R. Salinas, C.E. Mayer, W.J. Lorenz, G. Staikov, Electrochim. Acta 48 (2003) 1.