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Underpotential deposition of Cd on Ag(111): an in situ STM study

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Abstract

The kinetics and mechanism of Cd underpotential deposition (UPD) and involved surface alloy formation processes in the system Ag(111)/Cd²⁺, SO₄²⁻, are studied by means of combined electrochemical measurements and in situ scanning tunneling microscopy (STM). The results show that the UPD process starts with a formation of an expanded (diluted) adlayer with a superlattice structure Ag(111)- $(\sqrt{3} \times \sqrt{19})R23.4^\circ$. In the underpotential range 50 mV < ΔE < 80 mV this adlayer transforms to a condensed close packed Cd monolayer via a first order phase transition. At long polarization times the condensed monolayer undergoes structural changes involving place exchange processes between Cd atoms and surface Ag atoms. A formation of a second Cd monolayer and a significant Ag–Cd surface alloying take place at lower underpotentials ($\Delta E < 50$ mV). The kinetics of surface alloying are analyzed on the basis of a recently proposed diffusion model including a relatively fast initial formation of a very thin surface alloy film and a subsequent slow alloy growth controlled by solid state diffusion. The anodic dealloying results in an appearance of monatomically deep pits, which disappear quickly at relatively high underpotentials ($\Delta E > 550$ mV) indicating a high mobility of surface Ag atoms.

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1. Introduction

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Underpotential deposition (UPD) of metals taking place at electrode potentials (*E*) more positive than the equilibrium Nernst-potential (E_{3DMe}) of the corresponding three-dimensional metal bulk

phase (3DMe) is of great importance for the chemistry and physics of solid/liquid interfaces, electrocrystallisation, electrocatalysis, and electrodeposition of alloys and heterostructured ultrathin films [1]. In the last decade the UPD processes were studied extensively combining electrochemical measurements with in situ scanning probe techniques such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) [1-7]. It has been shown that the substrate surface inhomogeneities play an important role in the UPD processes, which cause the formation of various low-dimensional metal phases (systems) [8,9]. The formation mechanism and the atomic structure of low-dimensional metal phases were found to be strongly influenced by specifically adsorbed electrolyte anions [1–9].

In many UPD systems the strong metal-substrate interaction induces place exchange processes, which lead to the formation of surface alloys [1]. A pronounced surface alloy formation, however, is usually observed in systems exhibiting sufficient miscibility between the substrate and the UPD metal. Typical examples represent the UPD systems Au/Cd^{2+} and Ag/Cd^{2+} [1,10–14]. These systems attracted in the last years a renewed interest not only as model systems for the study of surface alloy formation processes but also due to their application in the electrochemical atomic layer epitaxy (ECALE) [15,16]. Recent in situ STM and AFM studies of Cd UPD on gold single crystal substrates provided new important information on the atomic structure of initial low-dimensional Cd phases, which act as precursors for the subsequent Cd-Au surface alloy formation [17-23]. Expanded UPD adlayers with novel "linear" structures have been observed by in situ STM at relatively high underpotentials in the system Au(111)/Cd²⁺, SO₄²⁻ [17,18]. The appearance of these structures has been related to a partial charge transfer between Au substrate atoms and Cd adatoms as well as to the specific adsorption of SO_4^{2-} anions. Detailed studies on Cd deposition and stripping in the system Au(100)/Cd²⁺, SO₄²⁻ applying in situ AFM have been performed by Vidu and Hara [19–22]. They showed that the UPD process in this system starts with the formation of an expanded Au(100)-c(2 \times 2)Cd structure. A similar behaviour has also been observed previously in the system Ag(100)/Cd²⁺, SO₄²⁻, where the formation of an initial UPD Cd-overlayer with a Ag(100)-c(2×2)Cd superlattice structure was suggested on the basis of charge measurements [12]. The identical superlattice structures of the initial Cd UPD adlayers in both systems are obviously related to very similar crystal structures of Ag(100) and Au(100) substrates. However, experimental results clearly show that on Au(100) the Cd UPD starts at much higher underpotentials, which indicates that the chemical nature and electronic properties of the substrate play also an important role in this process. Comparative kinetic studies of surface alloy formation processes occurring at lower underpotentials in both systems show also a much higher rate of surface alloying on the Au(100) substrate [24]. Very interesting in situ STM studies of the initial stages of Cd electrodeposition on a herringbone reconstructed Au(111) surface have been reported recently by Maupai et al. [25,26]. They observed during Cd UPD a preferential formation of nanoclusters of monatomic height and very uniform lateral size at the elbow sites of the reconstructed Au(111) surface. According to the so-called low-dimensional system (LDS) concept [8,9], these clusters can be considered as 0D systems stabilized by the elbow sites. An understanding of the role of numerous factors affecting the kinetics and mechanism of UPD processes, however, requires further in situ STM and AFM investigations in well-defined model systems. The UPD of Cd on Ag(111) has been investigated up to now primarily with classical electrochemical methods [12,13,27]. In situ STM studies are restricted only to the participation of this process in the formation of compound films such as CdS by ECALE [28].

In this paper, we present first in situ STM studies of Cd UPD on Ag(111). A special attention is paid to the atomic structure and the local mechanism of formation of different low-dimensional UPD phases including Cd–Ag surface alloys. Kinetic information is obtained combining in situ STM observations with voltammetric and charge measurements.

2. Experimental

The experiments were performed in the system $Ag(111)/5 \text{ mM} \quad CdSO_4 + 5 \text{ mM} \quad H_2SO_4 + 0.5 \text{ M}$ Na_2SO_4 at a temperature T = 298 K. The electrolyte solution was prepared from suprapure chemicals (Merck, Darmstadt) and fourfold quartzdistilled water. Prior to each experiment the solution was deaerated by nitrogen bubbling. In situ STM studies were carried out with a standard NanoScope III (Digital Instruments, Santa Barbara, CA, USA) equipment using Pt-Ir tips coated with Apiezon wax. Platinum wires served as counter and quasi-reference electrodes. In each STM experiment the tip potential, E_{tip} was held constant at a value of minimum faradaic current. The corresponding tunneling voltage, $E_{\text{bias}} = E_{\text{sample}} - E_{\text{tip}}$ and the tunneling current, I_{tun} are indicated in the figure captions. Additional conventional electrochemical measurements were performed in a standard three-electrode electrochemical cell with saturated mercury sulfate (SSE) reference electrode and a platinum sheet (1 cm^2) counter electrode. All electrode potentials are referred to the Nernst equilibrium potential of the pure 3D Cd bulk phase $E_{3DCd} = -1150 \text{ mV vs. SSE}$ (for $c_{Cd^{2+}} = 5 \text{ mM}$).

Ag(111) single crystals with a diameter of 0.65 cm were used as substrates. Before each experiment the substrate surface was mechanically polished with diamond paste of decreasing grain size down to 0.25 μ m and subsequently chemically etched according to a standard procedure [29], including etching for 10 s in a solution containing 4.8% CrO₃, 4% HCl and 20% HClO₄, for 20 s in 4 M H₂SO₄ and finally for 300 s in 25% aqueous solution of NH₃. After etching, the electrodes were thoroughly rinsed with fourfold distilled water. This procedure was repeated until a highly reflecting surface exhibiting relatively large atomically flat terraces separated by monatomic steps was obtained.

3. Results and discussion

Fig. 1 shows a typical cyclic voltammogram for deposition and dissolution of Cd on Ag(111) in



the underpotential range $\Delta E = E - E_{3DCd} \ge$ 0 mV. The voltammogram corresponds well to that observed in a previous electrochemical study of this system [12] and is characterized by four adsorption(A)/desorption(D) peak pairs. In situ STM imaging of the substrate surface in the potential range positive of the voltammetric peaks $(\Delta E > 400 \text{ mV})$ shows a two-dimensional hexagonal lattice with an interatomic spacing of 0.29 ± 0.02 nm, which corresponds to the atomic structure of the Ag(111) surface (Fig. 2). The nearly symmetrical voltammetric peak pairs $A_1/$ D_1 and A_2/D_2 observed in the UPD range $100 \text{ mV} \leq \Delta E \leq 400 \text{ mV}$ indicate the occurrence of reversible adsorption/desorption processes, which have been attributed previously to the formation of an expanded adlayer with a superlattice structure Ag(111)- $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -Cd [12]. However, in situ STM imaging with lateral atomic resolution at underpotentials $100 \text{ mV} \leq \Delta E \leq$ 150 mV reveals overlayer structures, which are very similar to those reported for the UPD of Cd on Au(111) [17,18]. Fig. 3a shows the appearance of such structure by stepping the underpotential from $\Delta E = 450 \text{ mV}$ to $\Delta E = 125 \text{ mV}$. The 2D hexagonal lattice of the Ag(111) surface can be identified in the lower part of the STM image in Fig. 3a (corresponding to $\Delta E = 450 \text{ mV}$). The upper part of the STM image (corresponding to





Fig. 2. In situ STM image with lateral atomic resolution of the Ag(111) surface obtained in the system Ag(111)/Cd²⁺, SO₄²⁻ at $\Delta E = 450$ mV. Grayscale range: 15 nA; $E_{\text{bias}} = -30$ mV; $I_{\text{tun}} = 20$ nA.

 $\Delta E = 125$ mV) shows clearly the appearance of the specific structure characterized by two types of parallel rows, which are composed of brighter spots (A) and darker spots (B), respectively. These rows are rotated by 30° with respect to the Ag[110] atomic rows of the Ag(111) surface and alternate with each other at a distance of $0.55 \pm$ 0.02 nm. The spacing between the spots along both types of rows is 0.5 ± 0.02 nm and corresponds to $\sqrt{3}$ times the Ag–Ag distance in the Ag[110] atomic rows of the Ag(111) substrate. The different intensities of the spots labeled as (A) and (B) indicate that the adatoms in the overlayer are located on surface sites with different symmetry. The observed superlattice structure can be denoted as Ag(111)- $(\sqrt{3} \times \sqrt{19})R23.4^{\circ}$ and is shown schematically in Fig. 3b. The charge density for the formation of a Cd adlayer with such structure, calculated assuming ideal charge/coverage stoichiometry (i.e. $(\partial q/\partial \Gamma_{Cd^{2+}})_E = 2F$) is $q_{calc} = 111 \,\mu\text{C}/\text{cm}^2$. This value is quite close to the experimental cathodic charge density $|\Delta q_{\rm exp}| \approx 120 \,\mu {\rm C/cm^2}$, obtained from the integration of the cyclic voltammogram in the UPD range $100 \text{ mV} \leq \Delta E \leq$ 400 mV. However, this UPD range is located at potentials more positive than the zero charge



Fig. 3. (a) In situ STM image showing the formation of an expanded overlayer structure in the system Ag(111)/Cd²⁺, SO_4^{2-} after a potential step from $\Delta E = 450$ mV to $\Delta E = 125$ mV. Grayscale range: 10 nA; $E_{\text{bias}} = -30$ mV; $I_{\text{tun}} = 10$ nA. (b) Model for the overlayer structure shown in (a).

potentials of both Ag and Cd [30,31]. Thus, we suggest that the overlayer contents also adsorbed sulfate anions with a coverage remaining nearly constant during the UPD of Cd. A similar model has been proposed recently also for the UPD of Ag in the system Au(111)/Ag⁺, SO_4^{2-} [32] and for the UPD of Cd in the systems Cu(111)/Cd²⁺, Cl⁻ [33] and Ag(111)/Cd²⁺, Cl⁻ [27]. We suppose that the specific overlayer structure observed in the

present study (cf. Fig. 3) is stabilized by the coadsorbed sulfate anions, as already suggested for other UPD systems [1,18,32,33]. The identity of the species (Cd or SO_4^{2-}) corresponding to the spots seen in the STM image in Fig. 3a is unknown. However, the consistency between the theoretical and experimental charge densities (q_{calc} and $|\Delta q_{exp}|$) indicates that the spots in the STM image could be attributed to the Cd adatoms.

The sequence of in situ STM images shown in Fig. 4 presents the changes of surface topography during the UPD of Cd. Fig. 4a shows the initial Cd free substrate surface at an underpotential $\Delta E = 450$ mV. No changes of this surface topography



Fig. 4. Sequence of in situ STM images obtained in the system Ag(111)/Cd²⁺, SO₄²⁻ at different polarization conditions. (a) Surface topography of the initial Ag(111) surface at $\Delta E = 450$ mV. Grayscale range: 8 nm; $E_{\text{bias}} = -550$ mV; $I_{\text{tun}} = 15$ nA. (b–d) Topography changes in function of t_p after a potential step from $\Delta E = 125$ mV ($E_{\text{bias}} = -875$ mV) to $\Delta E = 70$ mV ($E_{\text{bias}} = -930$ mV); Grayscale range: 8 nm; $I_{\text{tun}} = 15$ nA. (e) Atomic structure of the condensed close packed monolayer at $\Delta E = 70$ mV. Grayscale range: 15 nA; $E_{\text{bias}} = -930$ mV; $I_{\text{tun}} = 15$ nA. (f) Surface topography after changing the underpotential to $\Delta E = 10$ mV. Grayscale range: 8 nm; $E_{\text{bias}} = -990$ mV; $I_{\text{tun}} = 15$ nA. The arrows in (b), (c) and (f) indicate the formation of the 1st and 2nd monolayers (ML).

could be observed in the UPD range $100 \text{ mV} \leq$ $\Delta E \leq 400 \text{ mV}$, where the formation of the expanded Cd adlayer (cf. Fig. 3) takes place. As shown in Fig. 4b, however, a growth front appears in the in situ STM image after stepping the underpotential from $\Delta E = 125 \text{ mV}$ to a value of $\Delta E =$ 70 mV, corresponding to the peak A_3 of the cyclic voltammogram. This observation gives clear evidence for the occurrence of a first order 2D transformation of the expanded gas-like 2D Cd adlayer to a condensed Cd monolayer (ML). The ML formation starts preferentially at monatomic step edges (cf. Fig. 4b), whereas the formation of 2D Cd islands of the condensed ML on top of substrate islands (i.e. on atomically smooth substrate terraces) is observed at longer times (cf. Fig. 4c). This behavior can be attributed to the lower barrier for 2D nucleation and/or to the higher residence time of Cd adatoms at monatomic step edges, in good agreement with theoretical predictions [1,8]. The completion of the condensed monolayer coverage of the substrate surface is shown in Fig. 4c and Fig. 4d. The in situ STM imaging of the condensed monolayer with atomic resolution shows a close-packed 2D atomic structure (Fig. 4e) characterized by an interatomic spacing of 0.3 ± 0.02 nm, which is close to the nearest-neighbor distance in the bulk Cd crystal lattice. The observed formation of a close-packed Cd monolayer under these conditions correlates well with the experimental charge density of $|\Delta q_{\rm exp}| \approx 410 \,\mu {\rm C/cm}^2$ obtained in the UPD range $50 \text{ mV} \leq \Delta E \leq 400 \text{ mV}$. Fig. 4f shows an in situ STM image obtained after application of a lower underpotential, $\Delta E = 10 \text{ mV}$, corresponding to the peak A_4 of the cyclic voltammogram. A formation of a second Cd monolayer is recognized in the STM image (cf. the arrow in Fig. 4f). It should be noted, that extended polarization under these conditions (electrode potentials close to E_{3DCd}) leads to instability of the STM imaging (cf. Fig. 4f). Therefore, it was not possible to perform a more detailed in situ STM study of long time surface topography changes in this underpotential range.

Fig. 5 shows anodic stripping curves obtained after extended polarization at $\Delta E = 70$ mV. The observed change of stripping peaks with increasing polarization time, t_p and in particular the shift of



Fig. 5. Anodic stripping curves obtained in the system $Ag(111)/Cd^{2+}$, SO_4^{2-} after different polarization times, t_p at $\Delta E = 70$ mV (dE/dt = 10 mV/s).

the stripping peak D_3 to more positive potentials, indicate the occurrence of surface transformations. The corresponding stripping charge density, Δq , however, does not change with t_p and is limited to the charge density required for the formation of a closed packed Cd monolayer. These results suggest that under these conditions the close packed Cd monolayer formed at $\Delta E = 70 \text{ mV}$ transforms to a very thin surface alloy layer by a place exchange between Cd atoms and surface Ag atoms. The occurrence of these processes is supported by the behavior observed during a repetitive potential cycling within the potential range 65 mV $\leq \Delta E \leq 155$ mV. As shown in Fig. 6, a cycling for more than one hour leads to almost complete disappearance of voltammetric peaks A_3 and D_3 . A further Cd deposition does not occur in this potential range because the UPD of Cd on the alloyed surface requires more negative potentials (lower underpotentials ΔE). The stripping curve obtained after the long time cyclic polarization (curve (3) in Fig. 6) shows two new stripping peaks D_{01} and D_{02} located at more anodic potentials. The corresponding stripping charge density $(|\Delta q| = 390 \pm 20 \,\mu\text{C/cm}^2)$ is very close to that required for the formation of a close packed Cd monolayer. The electrochemical behavior shown in Fig. 6 is very similar to that observed during the surface alloy formation in the system



Fig. 6. Voltammetric adsorption/desorption behavior of the system Ag(111)/Cd²⁺, SO₄²⁻ after repetitive cycling within the potential range 65 mV $\leq E \leq 155$ mV (dE/dt = 10 mV/s). (1) CV after 1 min potential cycling. (2) CV after 60 min potential cycling. (3) Anodic stripping curve after 60 min potential cycling.

Ag(111)/Pb²⁺ [1,34–38]. The present results, however, show that in contrast to the system Ag(111)/ Pb²⁺, the surface alloying in the system Ag(111)/ Cd²⁺ seems to be not accompanied by a measurable partial desorption of the original Cd monolayer coverage. More detailed voltammetric and in situ STM investigations are in progress in order to clarify the kinetics and mechanism of surface alloy formation processes occurring under these conditions.

The formation of the second Cd monolayer indicated above (cf. Fig. 4f) is accompanied by a significant surface alloy formation, which is reflected in the anodic stripping curves obtained after extended polarization at $\Delta E = 10$ mV (Fig. 7a). The changes of the stripping curves are very similar to those observed in Fig. 5 and show the appearance of an additional stripping peak D'_3 at long polarization times ($t_p > 100$ s). In contrast to the data in Fig. 5, however, with increasing polarization time, t_p the stripping charge density Δq increases significantly, exceeding that required for the deposition of two close-packed Cd monolayers (Fig. 7b). Experimental data presented in Fig. 7b show two different linear $\Delta q - t_p^{1/2}$ dependences for short and long polarization times. The



Fig. 7. (a) Anodic stripping curves obtained in the system $Ag(111)/Cd^{2+}$, SO_4^{2-} after different polarization times, t_p at $\Delta E = 10 \text{ mV}$ (dE/dt = 10 mV/s). (b) Stripping charge density, Δq , as a function of polarization time, t_p at $\Delta E = 10 \text{ mV}$.

parabolic dependence of Δq on t_p at relatively long polarization times ($t_p > 100$ s) has been discussed previously in terms of a model including non-stationary mutual diffusion of Ag and Cd in the Ag/ Ag–Cd/Cd²⁺ system [12]. It has been suggested that the alloy formation process proceeds by a movement of Ag atoms through a highly distorted (vacancy-rich) Ag–Cd alloy layer and simultaneous Cd deposition at the Ag–Cd/Cd²⁺ interface. The linear $\Delta q - t_p^{1/2}$ dependence observed in Fig. 7b at short polarization times can be attributed to the occurrence of place exchange processes leading to a formation of a thin initial Ag–Cd surface alloy film on the substrate surface.

The results presented in Fig. 7b are very similar to those reported recently by Vidu and Hara for the systems $Au(100)/Cd^{2+}$ [22] and $Ag(100)/Cd^{2+}$ [24]. These authors proposed a diffusion model, which can be applied also for the analysis of kinetic data in Fig. 7b. In this model the Ag-Cd alloy layer is considered as consisting of two regions characterized by different diffusion properties as illustrated schematically in Fig. 8 [22]. The region -l < x < 0corresponds to a thin surface alloy layer ("skin") and is characterized by an effective diffusion coefficient D_1 which is larger than the diffusion coefficient D_2 for the rest region x > 0 $(D_1 \gg D_2)$. The Cd concentration c_0 at the electrode/electrolyte interface (x = -l) is considered to be constant for all times. Present in situ STM observations showed that in the system $Ag(111)/Cd^{2+}$ the alloy formation process is preceded by the formation of a close packed Cd monolayer (cf. Fig. 4). Thus, in the present case we considered a surface concentration of $c_0 = 0.0735 \text{ mol/cm}^3$ corresponding to a close packed Cd monolayer. The diffusion coefficients D_1 and D_2 were estimated from the linear $\Delta q - t_{\rm p}^{1/2}$ dependences in Fig. 7b following the procedure described in Ref. [22]. Values of $D_1 = 1.5 \times 10^{-16} \text{ cm}^2/\text{s}$ and $D_2 = 3.5 \times 10^{-19} \text{ cm}^2/\text{s}$ were found in good agreement with those reported for the surface alloy formation in the system $Ag(100)/Cd^{2+}$ [24].

The surface alloy formation occurring in the system is recognized also by substantial surface

topography changes observed after anodic stripping. A typical in situ STM image obtained after extended polarization at E = 10 mV and subsequent anodic stripping at $\Delta E = 450 \text{ mV}$ is shown in Fig. 9. As seen the removal of Cd leads to an appearance of new terraces and a large number of pits and 2D islands of monatomic thickness (cf. Fig. 4a and Fig. 9). This behavior is characteristic for alloy dissolution and has been observed



Fig. 9. In situ STM image obtained in the system Ag(111)/ Cd²⁺, SO₄²⁻ after 10 min polarization at $\Delta E = 10$ mV and subsequent anodic stripping at $\Delta E = 450$ mV. Grayscale range: 5 nm; $E_{\text{bias}} = -200$ mV; $I_{\text{tun}} = 15$ nA.



Fig. 8. Schematic representation of the diffusion model [22] applied for the analysis of experimental results shown in Fig. 7b.



Fig. 10. (a) In situ STM image obtained in the system Ag(111)/Cd²⁺, SO₄²⁻ after 2 min polarization at $\Delta E = 10$ mV and subsequent anodic stripping at $\Delta E = 450$ mV. Grayscale range: 5 nm; $E_{\text{bias}} = -300$ mV; $I_{\text{tun}} = 10$ nA. (b–d) Topography changes after potential step from $\Delta E = 450$ mV to $\Delta E = 650$ mV. Grayscale range: 5 nm; $E_{\text{bias}} = -100$ mV; $I_{\text{tun}} = 10$ nA.

previously in other UPD systems exhibiting surface alloying [1]. Anodic formation of pits and islands on terraces is observed even after relatively short polarization time at $\Delta E = 10$ mV (Fig. 10). The clustering of vacancies created during removal of Cd from the surface alloy at $\Delta E = 450$ mV leads to formation of larger pits, which disappear quickly by changing the underpotential to $\Delta E =$ 650 mV (cf. Fig. 10a–d). This behavior suggests a relatively high mobility of Ag surface atoms at this substrate potential in good agreement with observations reported previously for Ag(100) substrates [39].

4. Conclusions

Present in situ STM studies show that the UPD of Cd on Ag(111) starts with formation of an expanded adlayer with a superlattice structure Ag(111)- $(\sqrt{3} \times \sqrt{19})R23.4^{\circ}$. This adlayer transforms in the underpotential range 50 mV $\leq \Delta E \leq$ 80 mV to a condensed close packed Cd monolayer.

Voltammetric measurements indicate that the close packed monolayer is not stable and undergoes slow transformations involving a place exchange between Cd atoms and Ag surface atoms. At lower underpotentials $\Delta E < 50 \text{ mV}$ the UPD process continues with the formation of a second Cd monolayer, which is accompanied by a significant Ag-Cd surface alloying. Kinetic results are in agreement with those reported recently by Vidu and Hara [24] for the surface alloy formation in the system $Ag(100)/Cd^{2+}$. The anodic dealloying leads to an appearance of a large number of 2D islands and monatomically deep pits. The pits disappear quickly at high underpotentials $\Delta E > 550 \text{ mV}$ suggesting a relatively high mobility of surface Ag atoms under these conditions.

Acknowledgments

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