Contents lists available at ScienceDirect





Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Pd deposition onto Au(111) from nitrate solution

C. Köntje, L.A. Kibler¹, D.M. Kolb^{*,1}

Institute of Electrochemistry, University of Ulm, Ulm D-89069, Germany

ARTICLE INFO

ABSTRACT

Article history: Received 5 August 2008 Received in revised form 28 January 2009 Accepted 1 February 2009 Available online 10 February 2009

Keywords: Au(111) Electrodeposition Nucleation Palladium STM

1. Introduction

Metal deposition from aqueous solutions is still a process of great industrial relevance. The production of metal coatings for either protection or decorative purposes requires a detailed knowledge of the influence of all the deposition parameters, including substrate structure and electrolyte composition. The initial stages of metal deposition are of particular interest as they play a decisive role in the growth behaviour and the emerging morphology of overlayers [1–3]. Furthermore, since bimetallic surfaces are often used in electrocatalysis, deposition of small amounts of metal A onto a metal B is frequently employed for creating model catalysts, for which structure-reactivity relations can be studied in detail. In this respect, Pd on Au(111) may serve as an example [4].

Initiation of the deposition process requires nucleation centres, and it is generally agreed that surface imperfections are the preferred sites for the new phase to grow. Based on simple thermodynamic considerations monoatomic high steps in general, and kink sites in particular, are considered to be the most effective nucleation centres for well-prepared single crystal surfaces like Au(111). For less-ordered surfaces like textured Au(111) films on glass, grain boundaries and regions of step-bunching add to the available nucleation sites.

In a number of publications on the initial stages of metal deposition we have shown by in situ STM, that indeed monoatomic high steps are the preferred and only nucleation sites for low overpoten-

E-mail address: dieter.kolb@uni-ulm.de (D.M. Kolb).

The initial stages of palladium deposition onto Au(111) from 0.1 M HNO₃ + 0.2 mM Pd(NO₃)₂ have been studied by cyclic voltammetry and in situ scanning tunnelling microscopy. It is demonstrated that nucleation starts exclusively at surface defects such as monoatomic high steps, which is at variance with recently published work. From this and our previous work it thus appears that surface defects are the

preferred nucleation sites indeed for nitrate, sulphate and chloride containing solutions. © 2009 Elsevier Ltd. All rights reserved.

tials [5–7]. This was demonstrated in great detail for Pd on Au(111), deposited from either chloride or sulphate containing electrolytes [8,9]. Only in the case of high overpotentials deposition starts also on flat terraces [10]. In a recent paper by Pandelov and Stimming [11], describing Pd deposition onto Au on glass from 0.5 mM $Pd(NO_3)_2$ in perchloric acid solution, it was stated that nucleation starts on the flat terrace in such a solution. The conspicuous absence of defects as nucleation sites was explained by a weakly adsorbing anion, namely nitrate.

Since such an observation would severely question the validity of our current understanding of electrocrystallization [12,13], it seems justified to revisit Pd deposition onto Au(111) from nitrate solution. Our results from cyclic voltammetry and in situ STM for the initial stages of Pd deposition onto a freshly prepared massive Au(111) crystal in 0.2 mM Pd(NO₃)₂ + 0.1 M HNO₃ are described in the following. Special consideration has been given to the fact that Au(111) surfaces reconstruct and that lifting of the reconstruction at positive potentials is an inherent source of surface imperfections. Attention is also drawn to nitrate reduction on Au(111) at negative potentials, which is shown to occur preferentially at step edges.

2. Experimental

The STM images were recorded with a Topometrix TMX Discoverer 2010. For the preparation of the STM tips, a Pt/Ir wire (80/20) was etched in 4.5 M NaCN and coated with an electrophoretic paint to reduce Faraday currents at the tip/electrolyte interface. All images were recorded in the constant-current mode, typically at $I_T = 2$ nA. Pt wires were used as counter and quasireference electrodes for the STM. The potential difference between

^{*} Corresponding author. Tel.: +49 731 50 25400; fax: +49 731 50 25409.

¹ ISE member.

^{0013-4686/\$ –} see front matter $\mbox{\sc 0}$ 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2009.02.005

a saturated calomel electrode (SCE) and the Pt wire is in this case $E_{\text{Pt}} = +0.67 \pm 0.05$ V. An SCE served as reference for the cyclic voltammograms obtained in a standard electrochemical cell. In the following, all potentials are quoted with respect to SCE.

The Au single crystal electrodes were discs (MaTecK Jülich, Germany) which had surfaces oriented to better than 1° and were polished down to 0.03 μ m. Discs with a diameter of 4 mm were used for cyclic voltammetry, while the crystals used for STM were 12 mm in diameter. Before each measurement the electrodes were flame-annealed with a Bunsen burner or in a hydrogen flame at orange heat for typically 5 min and cooled down in air (CV) or in a stream of nitrogen (STM). In order to show the importance of monoatomic high steps for nitrate reduction, a stepped Au(111) crystal was also used for cyclic voltammetry, the surface of which had a miscut of 6°. After each deposition study, the electrode was polarized in 0.1 M H₂SO₄ for around 10 s at 10 V to remove Pd residues [14]. The brown Au oxide overlayer was then dissolved in 1 M HCl, before the electrode was again flame-annealed.

All electrolytes were made from HNO₃ (Merck, suprapur), palladium powder (Aldrich, 99.999%) and high-quality Milli-Q water (18.2 M Ω cm at 25 °C and <2 ppb total organic carbon). Commercially available Pd(NO₃)₂ turned out to be not sufficiently pure; it caused speckles in the STM images of the gold surface, which prevented high-resolution viewing of Pd deposition. We mention in passing that Pd deposition was also studied in 0.1 M HClO₄ + 0.2 mM Pd(NO₃)₂ with essentially identical results.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows the cyclic current–potential curve for Au(111) in 0.1 M HNO₃, recorded at $10 \,\mathrm{mV}\,\mathrm{s}^{-1}$. The Au(111) surface is thermally reconstructed at the immersion potential of 0V, the scan being started in negative direction. The peak pair between 0.15 V and 0.4 V represents the lifting of the reconstruction for positive scan direction, while the potential-induced reconstruction starts in negative direction. At the negative end of the cyclic voltammogram for nitric acid a slight down-bending is noticed, indicative of a reduction current superimposed on the double-layer charging current in a potential region, where hydrogen evolution does not yet occur. Hence, this current can be assigned to the electroreduction of nitrate [15], which occurs preferentially at surface



Fig. 1. Cyclic current–potential curve (first cycle) for Au(111) (miscut < 1°) in 0.1 M HNO₃. Scan rate: 10 mV s^{-1} . The curve for Au(111) in 0.1 M H₂SO₄ is included for comparison. The inset shows the negative part of the CV for stepped Au(111) (miscut 6°) in 0.1 M HNO₃ and 0.1 M H₂SO₄.



Fig. 2. Current-potential curve for the deposition of palladium onto Au(111) from 0.1 M HNO₃ + 0.2 mM Pd(NO₃)₂ showing formation of the first Pd monolayer in a peak at +0.55 V. Scan rate: 1 mV s^{-1} .

defects of the otherwise catalytically rather inactive Au(111) surface. To demonstrate the importance of monoatomic high steps on the substrate for nitrate reduction, a cyclic voltammogram has been recorded with a stepped Au(111) crystal (miscut 6°). It is obvious that the activity for nitrate reduction is significantly enhanced for the Au(111) surface with larger density of monoatomic high steps. The negative end of the CV is shown in the inset of Fig. 1 together with the corresponding curve in 0.1 M H₂SO₄, for comparison.

The current–potential curve for palladium deposition onto Au(111) from 0.1 M HNO₃+0.2 mM Pd(NO₃)₂, starting at +0.72 V in negative direction, is shown in Fig. 2. The sharp peak around 0.55 V indicates underpotential deposition of the first monolayer. The charge for this peak is about 460 μ C cm⁻² (integration limits set to 0.40 and 0.64 V), which is in good agreement with the calculated charge of 445 μ C cm⁻² for the electrodeposition of a pseudomorphic Pd monolayer on Au(111). On the basis of our STM



Fig. 3. STM image (300 nm \times 300 nm) of Au(111) in 0.1 M HNO₃ after lifting of the reconstruction. E_{SCE} = 0.77 V.

measurements, we can tentatively assign the small shoulder at 0.47 V to Pd deposition on top of the monoatomic high gold islands, which completes monolayer formation (see below).

The Nernst potential of Pd^{2+}/Pd for our solution has been determined to 0.53 V. However, bulk deposition is seen to start only around 0.35 V, suggesting a very slow deposition kinetics in nitrate solution.

3.2. In situ STM measurements

A freshly prepared, flame-annealed Au(111) electrode is reconstructed, the surface structure being identical to the ($\sqrt{3} \times$ 22) structure observed for samples prepared in UHV [16]. The reconstructed surface is stable under electrochemical conditions, provided negative surface charges are applied (E < pzc) and specific adsorption of anions is avoided. However, under the conditions of Pd deposition, which starts at rather positive potentials (E> pzc), reconstruction inevitably is lifted. As a consequence, formerly perfectly flat terraces of the reconstructed surface are littered with monoatomic high gold islands, which cover about 5% of the total surface and which constitute nucleation centers for the metal deposition reaction. Hence it is desirable to characterize the structure of a Au(111) electrode after lifting of the surface reconstruction in nitrate solution and before Pd deposition.

Fig. 3 shows an Au(111) surface after lifting of the reconstruction at a potential of 0.77 V. The flame-annealed reconstructed surface was immersed into 0.1 M HNO₃ at -0.05 V, where reconstruction is stable, and the potential was then stepped to 0.77 V. The terraces are covered with monoatomic high gold islands with diameters of around 4–8 nm.



Fig. 4. Sequence of 6 STM images (350 nm × 350 nm) showing the initial stages of Pd deposition onto Au(111) from 0.1 M HNO₃ + 0.2 mM Pd(NO₃)₂. Deposition potentials and times as indicated in the figures. Tunneling current: 2 nA. Tip potential: 0.8 V vs SCE.



Fig. 5. STM images showing nucleation and growth of Pd on Au(111) in chloride (a,b), sulphate (c,d) and nitrate (e,f) containing acidic solutions. Images a, c and e: Au(111) before Pd deposition. Images b, d and f: initial stages of Pd monolayer formation at underpotentials.

The same type of surface is seen again in Fig. 4a, which shows bare, unreconstructed Au(111) in 0.1 M HNO₃ + 0.2 mM Pd(NO₃)₂ at 0.62 V as a starting point for Pd deposition. Lowering the electrode potential to 0.57 V initiates Pd deposition, which is seen to occur exclusively at the monoatomic high steps. The rims of the gold islands seem to be most effective nucleation centers, quickly leading to a Pd overlayer which uniformly covers the lower terraces (Fig. 4c). As noted on previous occasions [8], a clearly higher overpotential is required for Pd deposition on the tops of the gold islands, which obviously lack the classic nucleation sites like kinks. At 0.49 V an STM image emerges (Fig. 4d) which is practically identical to that of the bare surface (see Fig. 4a), indicating completion of the first Pd monolayer, i.e., terraces and islands are now covered with Pd. Nucleation and growth of the second Pd layer is demonstrated in Fig. 4e and 4f. Although at such high overpotentials the Pd-covered gold islands still provide nucleation sites, Pd deposition is also noted to occur on the first Pd monolayer in regions where the Au(111) substrate apparently had no surface defects (see region on the upper terrace near the step in the centre of Image 4a). This may be a consequence of the rather negative deposition potential. The third layer starts to grow before the second layer is completed. This is seen by the bright spots in Fig. 4f, indicating the beginning of 3-dimensional growth.

4. Conclusions

In summary we can safely state that Pd deposition onto Au(111) starts always at the monoatomic high rims of islands or the monoatomic high steps of terraces in nitrate, sulphate and chloride containing solutions. This is demonstrated again in Fig. 5. The nature of the anion has no effect on the nucleation behaviour. It does, however, influence the growth and hence the shape of the emerging Pd islands simply by affecting surface atom mobility. As has been shown by various groups, there is a significantly increased surface mobility for gold in chloride containing solution, which leads to the so-called electrochemical annealing [17,18]. As a direct consequence, lifting of the Au(111) reconstruction leads to monoatomic high gold islands that are larger in size, but fewer than those in sulphuric acid solutions (compare Fig. 5a and c). In that case nucleation and growth of Pd can be studied by STM exceptionally clearly. Note the chemical contrast in the STM images for Au and Pd (Fig. 5b). Gold adatom diffusion is much slower in sulphate or nitrate (and perchlorate, not shown) containing solutions. resulting in a high number of small gold islands (Fig. 5c and e). The triangular shape of the Pd islands that grow in sulphuric acid solution is noteworthy [9]. In all three cases the growth is twodimensional up to almost two Pd layers, regardless of the anion in solution. The statement in ref. [11] that scan rates of 1 mV/s should be applied in order to achieve 2-D growth is in clear contrast to our findings. However, it is correct to say that such low scan rates are required to detect different nucleation sites in cyclic voltammetry [9]. It is also incorrect to state that Pd monolayer formation is much faster in nitrate than in sulphate [11]. Our observations published in ref. [9] did not show any inhibiting effect of the adsorbed sulphate laver.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie.

References

- [1] K. Jüttner, W.J. Lorenz, Z. Phys. Chem. N.F. 122 (1980) 163.
- [2] R.J. Nichols, in: J. Lipkowski, P.N. Ross (Eds.), Imaging of Surfaces and Interfaces, Wiley-VCH, Weinheim, 1999, p. 99.

- [3] D.M. Kolb, in: R.C. Alkire, D.M. Kolb (Eds.), Advances in Electrochemical Science and Engineering, vol.7, Wiley-VCH, Weinheim, 2002, p. 107.
- [4] L.A. Kibler, Chem. Phys. Chem. 7 (2006) 985.
- [5] T. Will, M. Dietterle, D.M. Kolb, in: A.A. Gewirth, H. Siegenthaler (Eds.), Nanoscale Probes of the Solid-liquid Interface, Nato-ASI Series E, vol.288, Kluwer, Dordrecht, 1995, p. 137.
- [6] H.-F. Waibel, M. Kleinert, L.A. Kibler, D.M. Kolb, Electrochim. Acta 47 (2002) 1461.
- [7] R. Hoyer, L.A. Kibler, D.M. Kolb, Surf. Sci. 562 (2004) 275.
- [8] L.A. Kibler, M. Kleinert, R. Randler, D.M. Kolb, Surf. Sci. 443 (1999) 19.
- [9] J. Tang, M. Petri, L.A. Kibler, D.M. Kolb, Electrochim. Acta 51 (2005) 125.
- [10] H. Naohara, S. Ye, K. Uosaki, J. Chem. Phys. B 102 (1998) 4366.
- [11] S. Pandelov, U. Stimming, Electrochim. Acta 52 (2007) 5548.

- [12] E. Budevski, in: B.E. Conway, J.O'M. Bockris, E. Yeager, S.U.M. Khan, R.E. White (Eds.), Comprehensive Treatise of Electrochemistry, vol.7, Plenum Press, New York, 1983, p. 399.
- [13] E. Budevski, G. Staikov, W.J. Lorenz, Electrochemical Phase Formation and Growth, Wiley-VCH, Weinheim, 1996.
- [14] M. Baldauf, Ph.D. thesis, University of Ulm, 1996.
- [15] G.E. Dima, A.C.A. de Vooys, M.T.M. Koper, J. Electroanal. Chem. 554–555 (2003) 15.
- [16] A.S. Dakkouri, D.M. Kolb, in: A. Wieckowski (Ed.), Interfacial Electrochemistry, Marcel Dekker, New York–Basel, 1999, p. 151.
- [17] J.L. Stickney, I. Villegas, C.B. Ehlers, J. Am. Chem. Soc. 111 (1989) 6473.
- [18] H. Striegler, P. Skoluda, D.M. Kolb, J. Electroanal. Chem. 471 (1999) 9.