

The Morphology And Distribution Of Cobalt Clusters On Au (111)

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Abstract

In situ Scanning tunneling microscopy (STM) and other ex-situ techniques were used in combination to characterize the morphology of Co/Au(111) electrodeposited from CoSO_4 solutions with K_2SO_4 as the supporting electrolyte.

The morphology and distribution of cobalt on Au(111) surfaces can be controlled from epitaxial layer growth to randomly distributed clusters, depending on the applied potential. Bulk deposited layers consist of dispersed clusters or compact layers depending on the deposition potential. The size of the cobalt clusters also depends strongly on the deposition potential.

Only few reports have been found in literature, dealing with the morphology and electrochemical behavior of thin electrochemically grown cobalt films on structurally well-defined substrates [4-7]. The morphological characteristics of the deposit have been proved to be not only dependent on the substrate but also to be very much dependent on the chemistry of the electrolyte [8]. Recent studies indicated that the presence of amount traces of certain anions has a strong influence on the structure and magnetic behavior of electrodeposited Co/Au (111) layers. Cognon et al.[5] found that amount traces of thiocyanate (SCN^-) anions induced a 3-D growth by comparison with the 2-D process observed in films produced in the presence of Cl^- . UPD was only observed for Co/Au (111) in SCN^- solutions. Kleinert et al.[6] did not find evidences for underpotential deposition (UPD) of cobalt on Au(111) and Au(100) in Na_2SO_4 supporting electrolyte.

In this work it was investigated the electrochemical behavior as well as the nucleation process during cobalt electrodeposition on Au(111) substrates in SO_4^{2-} solutions.

Introduction

Recent progress in spin electronics, magnetic data storage and sensors for giant magnetoresistance applications depends very much on the morphological structure of very thin magnetic materials and devices [1-2]. The growth of these structures can be done in ultra high vacuum (UHV) environment as well as in solutions by electrochemical deposition. The growth mode in UHV can be chosen carefully controlling the deposition rate, the annealing procedure and the capping layer [1]. By the other side, electrodeposition presents the advantage of an easy temperature control of nucleation and growth modes by fine adjustment of the potential and choice of solution chemistry [3]. As electrodeposition is a co-adsorption process, the substrate surface and/or the deposit itself can be covered by the species present in the solution. Anions can act as mediators to promote deposition of metal adatoms even at potentials $U > E_0(\text{M}^+/M)$. This unusual process is called anion-induced underpotential deposition (UPD).

Materials and Methods

Cobalt layers were electrodeposited on 100-nm thick (111) textured gold films evaporated on glass substrates. The gold substrates were flame-annealed and cooled down in air. Figure 1 shows an image of the typical gold surface obtained after the annealing procedure. Large terraces can be clearly distinguished as well as regions with a great density of surface imperfections.

In-situ scanning tunneling microscopy (STM) was performed using a commercial A Topometrix TMX 2010 Discoverer system equipped with a Imicron tube scanner and a bipotentiostatic control unit. Tungsten tips were electrochemically etched from a polycrystalline wire in aqueous NaOH solutions and coated with Basf Electrocoating ZQ84-3225. The electrochemical cell was

mounted with a Au(111) film as cathode substrates. A Pt wire was used as a quasi-reference electrode. The Pt wire potential was measured before and after the experiments and for the used electrolyte, 0.1M K_2SO_4 + 1mM $CoSO_4 \cdot 7H_2O$, pH=5.4, $E_{Pt} = 650 \text{ mV} + V_{NHE}$. Cyclic voltammetry was performed to obtain the electrochemical potentials for deposition and dissolution of the metal. STM the images were obtained in each important peak of voltammogram.

Immediately after Co electrodeposition the morphology of the produced film was observed ex-situ by atomic force microscopy (AFM) and the chemical properties of the film analyzed by Auger electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS).

Results and Discussion

Electrochemistry

A basic electrochemical analysis was performed on the different morphologies observed for the cobalt deposition on Au(111) surface in the presence of sulfate ions. The electrolyte composition was chosen in order to reduce hydrogen evolution during the cyclic voltammetry. The use of a low pH electrolyte led to hydrogen evolution before metal deposition.

The freshly prepared Au(111) surface was brought into contact with the solution at its open circuit potential (-60mV). At this potential no considerable changes can be observed on the gold surface even for long analysis time.

Figure 2a presents the voltammogram in the anodic region obtained for the Au (111) surface prior to any cobalt deposition. No anodic peak can be observed before 400mV and a characteristic peak appears at 700mV. Scanning the potential in the reverse direction a peak can be observed at about 285mV. Cycling the potential in this region can induce changes in the arrangement of the gold atoms within the terraces. In addition, an intense movement of the gold atoms can be observed on the step edges.

Cycling the potential in the cathodic region where cobalt deposition occurs a typical loop of nucleation is observed by reversing the negative scan when the reduction current begins to appear. One oxidation peak, can be seen at -750mV. The behavior of this oxidation peak depends on the lower limit of the voltammetric scan. When reversing the potential before the beginning of the reduction peak, the oxidation peak at -750mV is no longer observed. This indicates that the oxidation occurring at -750mV is related to the cobalt deposition below -1170mV. By analyzing of the voltammogram presented in figure 2b, it can be readily observed that the amount of metal deposited in the negative scan seems to be not completely dissolved in the reversed one. The

area beneath the dissolution peak is almost 1/3 of the area beneath the deposition peak. This suggests that a considerable amount of deposited metal could remain on the surface after each cycle. Extending the upper limit of the voltammogram to 400mV new oxidation peaks can be observed in the positive scan at the potential range of -100 to -300 mV. Since this peak was not observed during the anodic voltammogram (figure 2a) these phenomena could be associated to further dissolution of the deposited metal, as observed by STM (not shown).

In conclusion, we can state that the bulk deposition potential begins at -1700 mV. The layer dissolution occurs in two peaks: -740 and -695 mV. The remaining deposited cobalt ions on the surface will only be dissolved at 130 and 240 mV.

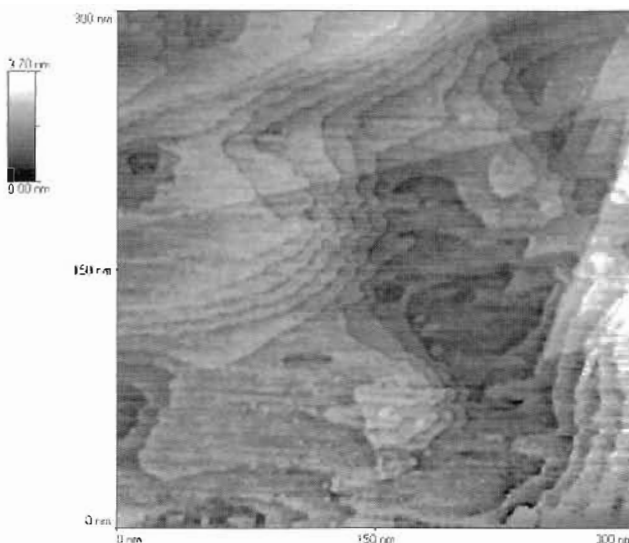
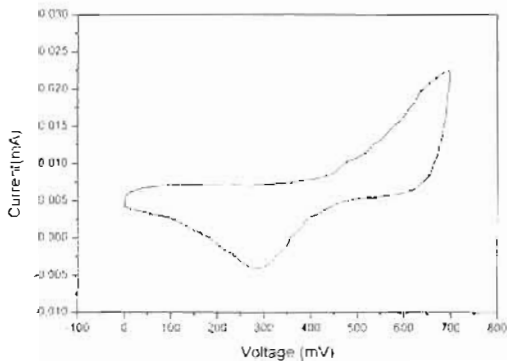


Figure 1 – Au(111) surface after flange annealing observed in 0.1M K_2SO_4 + 1mM $CoSO_4 \cdot 7H_2O$ solution at open circuit potential.

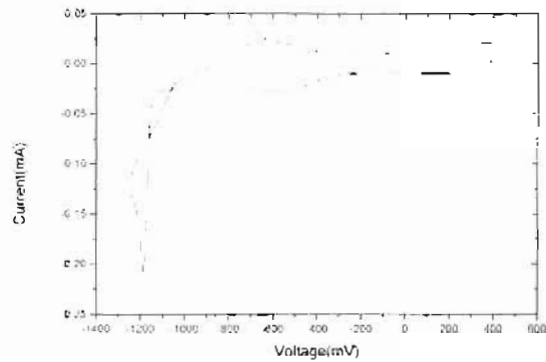
Morphological Study

Figure 3 is a typical ex-situ AFM image showing the compact, granular structure of the electrodeposited layer obtained at -1200mV. The deposition time was 5 minutes. From this image it can be observed that the cobalt film covers all the substrate and the clusters size varies throughout the surface of the film but the mean size of the cobalt grains is 250nm. This film was also analyzed by Auger electron spectroscopy (EAS) and X-Ray photoelectron spectroscopy (XPS) and no trace of potassium or sulfur contamination was found. After sputtering the first, oxidized layer, the position of the XPS peak indicates that the cobalt atoms are in the metallic state.

The morphology of the bulk deposited films is very much similar to the one observed by Munford et al. [8] for Co films produced from 500mM Na_2SO_4 + 104mM $CoSO_4$ electrolytes.



(a)



(b)

Figure 2 – Characteristic voltammograms obtained for (a) the gold clean surface in 0.1 M K_2SO_4 + 1mM $CoSO_4 \cdot 7H_2O$ solution and cobalt deposition (b) from $-1250mV$ to $400mV$.

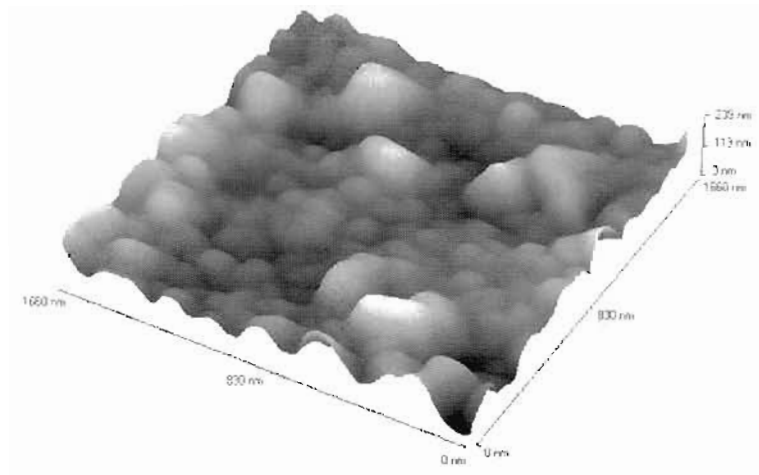


Figure 3 – *Ex situ* AFM image of bulk Co deposit produced at $-1200mV$

Figure 4a presents the *in situ* STM measurements of the first stages of the bulk deposition. It is observed that clusters nucleate almost homogeneously over the surface covering all the substrate immediately after the potential is set to $-1200mV$. When the deposition process starts, besides the nucleation of the clusters, a 4nm thick layer is immediately formed as can be observed in the vertical line scan presented in figure 4b. It can also be observed a step in the left part of the image. The nucleation process on the step edge is only slightly enhanced if compared to the one observed on the terraces since Co clusters form an almost continuous line on the step edge.

Preferential nucleation on the step edge will occur if the electrodeposited layers produced at potentials set to the beginning of the bulk deposition peak as can be observed in figure 5. At more negative potentials, cobalt starts to grow preferentially at surface imperfections such as step edges and almost no deposition is observed on the defect-free terrace as already observed by Kleinert et al [5] for Co deposition in Na_2SO_4 solutions.

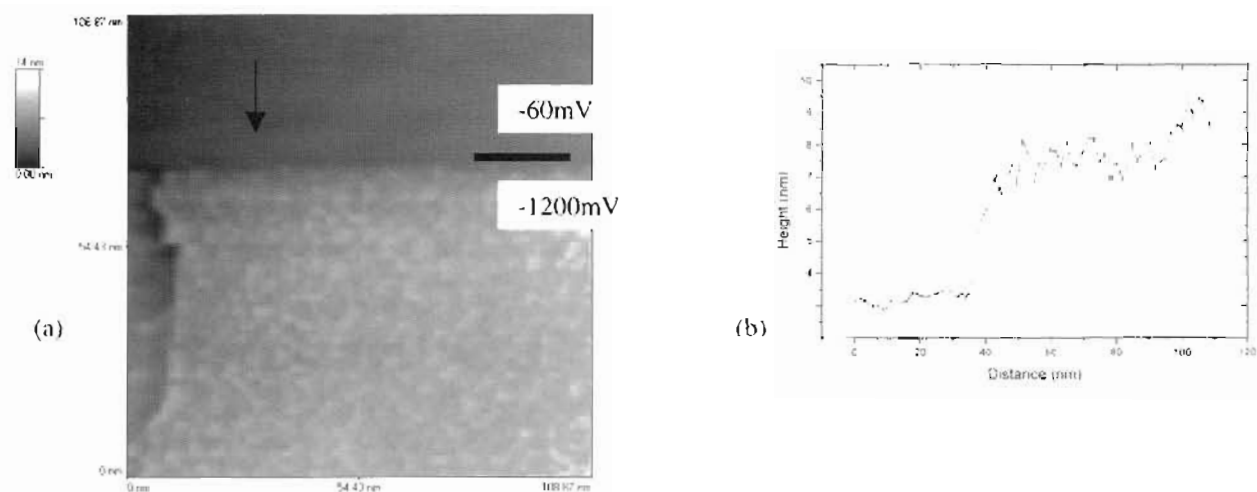


Figure 4 - Growth of cobalt at -1200 mV. (a) AFM image; the arrow indicates slow tip scanning direction. Co deposition was achieved by a potential step from -60 mV to -1200 mV (indicated by an horizontal line). (b) Profile of a vertical line showing the growth of a continuous layer of 4 nm besides the Co cluster.

Conclusion

In this study we have presented a detailed morphology study of the electrodeposition of cobalt on Au(111) surface in $0,1$ M K_2SO_4 + 1 mM $CoSO_4 \cdot 7H_2O$ solution. The films produced by OPD processes lead to the formation of a continuous granular layer covering all the substrate and the size of clusters depends strongly on the film thickness and deposition potential.

Acknowledgments

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