

EXAFS investigations of Cobalt electrodeposition

Dirk Lützenkirchen-Hecht*^a, Damir Hamulić^b, Ralph Wagner^a, and Ingrid Milošev^c

^(a) Fk. 4 – Physik, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany.

^(b) University of Ljubljana, Faculty of Chemistry and Chemical Technology, SI-1000 Ljubljana, Slovenia. ^(c) *Jožef Stefan Institute, Department of Physical and Organic Chemistry, SI-1000 Ljubljana, Slovenia.*

*dirklh@uni-wuppertal.de

Introduction

In comparison to ultrahigh vacuum techniques, electrodeposition is an interesting and versatile alternative for the synthesis of thin films on conducting or semiconducting substrates. Since the composition of the electrolyte can easily be varied, the structure and the composition of the electrodeposits can be directly influenced, with the possibility to prepare tailored materials. Here we investigate the effect of the electrolyte composition and the deposition temperature on the composition and the atomic structure of Cobalt electrodeposits on Gold-coated Kapton substrates with EXAFS experiments.

Methods

The Co electrodeposition was done using electrolytes prepared from appropriate amounts of CoCl_2 , $\text{Co}(\text{NO}_3)_2$ and CoSO_4 (all from Alfa Aesar) and deionized water (Millipore). We employed a SimPot 300 potentiostat (M. Schramm, University of Düsseldorf) and a small electrochemical cell (ca. 25 cm^3) with an Au-coated Kapton tape as working electrode, a Pt wire as counter electrode and an Ag/AgCl reference electrode. After identifying potentials suited for electrodeposition from cyclic voltammograms, the deposition was performed under potentiostatic conditions for the desired time. The samples were subsequently removed from the electrolyte, thoroughly cleaned with deionized water and investigated by transmission mode EXAFS at the Co K-edge (7709 eV) at beamline 10 at the DELTA storage ring (Dortmund, Germany) using a Si(111) channel-cut monochromator and gas-filled ionization chambers as detectors. In addition, the samples were investigated using SEM and EDX.

Results and discussion

Co-electrodeposits from $\text{Co}(\text{NO}_3)_2$ electrolytes show completely different XANES features and morphology in contrast to films prepared in CoCl_2 and CoSO_4 solutions. The comparison to reference data shows that $\text{Co}(\text{OH})_2$ crystallites are formed in $\text{Co}(\text{NO}_3)_2$, while deposition in Co-sulphate or Co-chloride solution leads to metallic Co films with hcp-structure, irrespective of the temperature, pH and concentration of the electrolytes. For the deposition in CoCl_2 , the Co-film thickness as derived from the EXAFS experiments increased linearly with Co concentration in the electrolyte and with deposition time, while an exponential increase with temperature was found. A detailed analysis of the EXAFS reveals small structural changes as a function of the film thickness, and deposition temperature. The structure of the films tends to relax stress and the Co-Co bond distances are approaching values close to the values for bulk Co-metal.

Conclusions

EXAFS studies have shown that Cobalt electrodeposition leads to Co-metal deposits from CoCl_2 and CoSO_4 , while deposition from $\text{Co}(\text{NO}_3)_2$ results in Co-hydroxide films. The short range order structure of the deposits was identified for films in the thickness range from ca. 10 nm to about $3 \mu\text{m}$, giving rise to structural modifications as the film grows.