

## Experiment Report Form



	<b>Experiment title:</b> Structure of a Co/Au(111) under electrochemical oxidation by surface x-ray diffraction and scattering	<b>Experiment number:</b> MA-2254
<b>Beamline:</b> ID03	<b>Date of experiment:</b> from: 04 Dec 2015                      to: 09 Dec 2015	<b>Date of report:</b> 27 February 2015
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Francesco Carla	<i>Received at ESRF:</i>
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### Report:

Electric field-induced switching of the magnetization in ferromagnetic nanoscale structures is of key importance for the development of modern data storage devices. Although this newly discovered phenomenon has attracted a lot of interest, the origin of the measured magnetoelectric coupling (MEC) is still under debate. Recently we found that very large magnetization changes can be induced in ultrathin Co films electrochemically deposited on Au(111) by changing the applied electrochemical potential and/or by oxidizing the Co surface [1].

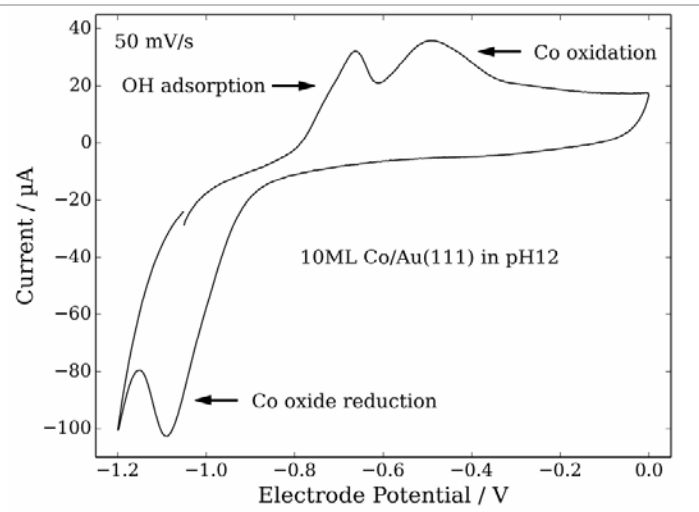
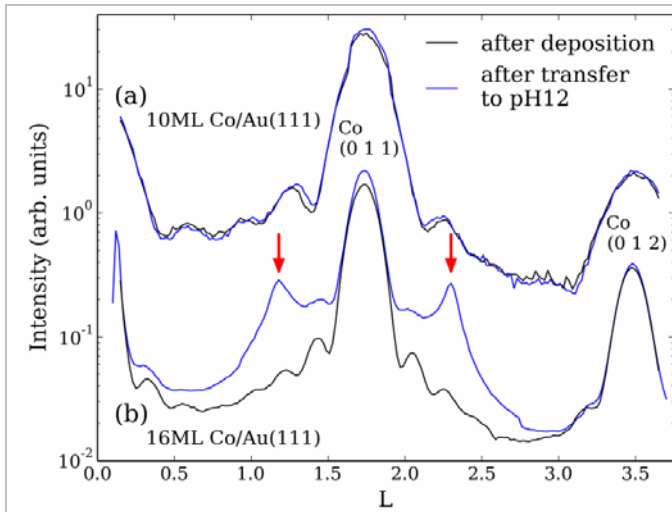
In order to elucidate the origin of this magnetic anisotropy modification on an atomic scale, the crystalline structure and interface properties of the electrochemically deposited Co-layers as well as of the ultrathin Co oxide layer have been investigated *operando* by surface X-ray scattering. Experiments were performed at beamline ID03 ( $E_{\text{ph}} = 22.5$  keV) using a “hanging meniscus” transmission cell, which allows to combine *operando* surface x-ray diffraction studies of rapid structural changes simultaneously with high quality electrochemical measurements [2]. Moreover, the cell enables continuous remote controlled electrolyte flow as well as controlled electrolyte exchange. Electrolyte exchange during the experiment was a critical issue for several reasons: (i) Since the Co deposit is very sensitive to small variations of pH, the stability of the Co

surface chemistry necessitates a continuous renewal of the solution. (ii) The co-evolution of hydrogen gas during Co deposition also makes continuous flow of the solution necessary. (iii) Co ions are not soluble in the alkaline electrolyte. Before starting the oxidation process in alkaline solution, remote controlled exchange to Co free electrolyte with acidic pH, followed by exchange to pH 12 solution were necessary.

Typical experiments began by depositing Co layers with controlled thickness (2 - 20 ML) on Au(111) single crystal electrodes at  $E = -0.90 V_{\text{Ag}/\text{AgCl}}$  in  $0.1 \text{ NaClO}_4 + 1.3 \text{ mM HCl} + 1 \text{ mM CoCl}_2$ . The increasing time-dependent intensity monitored at the hcp Co(011) peak during deposition allows to follow the epitaxial growth of the Co layer. Series of grazing incidence in plane scans along  $\langle 0, K, 0.15 \rangle$  reveal Co peak shifting with increasing deposition time. This indicates the presence of in-plane strain with respect to bulk hcp Co which decreases down to 1.2% expansion for 16 ML thick films. This effect has been found already in our previous experiments, but could now be followed in direct *operando* studies. Subsequently, the deposition process was stopped at  $E = -0.90 V_{\text{Ag}/\text{AgCl}}$ . Measurements of the extended specular reflectivity as well as of the hcp Co(01L) crystal truncation rod (CTR) show pronounced Laue oscillations (Fig. 1), indicating preparation of smooth hcp Co(0001) layers. We could successfully exchange the electrolyte from acidic to alkaline without altering the Co surface structure as shown in Fig. 1a (blue curve). Emerging fcc domains (Fig. 1b) could be avoided by carefully choosing potentials and flow rates, demonstrating the importance of the well-controlled electrolyte exchange made possible by the employed cell. These Co films could be kept stable for several hours, allowing to obtain a full data set of the Au and Co CTRs and the reflectivity. A quantitative analysis of these data, which should enable determining the structure of the deposit as well as of the Au/Co and Co/electrolyte interfaces, is still in progress.

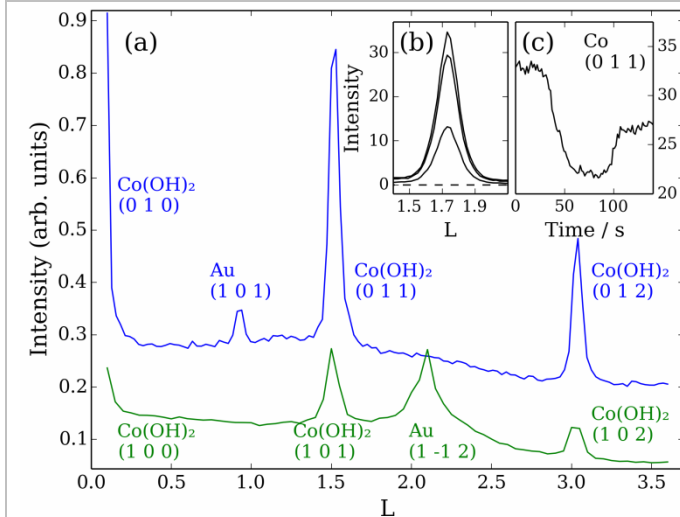
Co dihydroxyde overlayers were formed by cycling to potentials more positive than the respective oxidation peak at  $\approx -0.50 V_{\text{Ag}/\text{AgCl}}$  and fixing the potential at  $-0.70 V_{\text{Ag}/\text{AgCl}}$  during the cathodic sweep (see Fig.2). Grazing incidence in plane scans along  $\langle 0, K, 0.15 \rangle$  yield an in-plane lattice constant of  $3.17 \text{ \AA}$ , consistent with recent DFT calculations for  $\text{Co}(\text{OH})_2$  (0001) performed by our collaborators as well as with electrochemical scanning tunneling microscopy (STM) studies [3].  $\text{Co}(\text{OH})_2$  (01L) and (10L) CTRs shown in Fig. 3 confirm the formation of hcp Co dihydroxyde overlayers at an expense of crystalline Co (the features labelled Au(101) and Au(1-12) in Fig. 3a belong to feet of the Au bulk bragg peaks). *Operando* studies during oxidation/reduction cycles (Fig. 3c) show the decay and subsequent growth of the ultrathin Co film under these conditions. Due to Co loss into the electrolyte these processes are irreversible and result in the film dissolution after a few cycles (Fig. 3b).

In summary, the experiments have demonstrated that ultrathin epitaxial and smooth ultrathin hcp Co films with well defined thicknesses between 2 and 20 ML can be deposited on Au(111) single crystal electrodes and can be kept stable for several hours, making a detailed structural analysis possible. The use of the hanging meniscus cell and the remote controlled exchange system allowed to perfectly preserve these ultrathin ferromagnetic films during transfer from acidic to alkaline electrolyte. This enables atomic-scale investigation of the subsequent oxide forming process as we demonstrated by the structural characterization of the Co dihydroxyde layer. Future experiments on the magnetic anisotropy effect of Co/Au(111) by surface modification will address the more subtle structural changes due to the formation of Co monohydroxyde.



**Fig. 1:** Hcp Co(01L) rods, taken at  $E = -0.68 V_{Ag/AgCl}$  directly after 50s (a) and 100s (b) deposition ( $E_{dep} = -0.90 V_{Ag/AgCl}$ ) of Co layer in acidic solution (pH4, black) and after exchange to alkaline solution (pH12,  $E = -1.05 V_{Ag/AgCl}$ , blue). Growth of domains exhibiting fcc structure [(b), red arrows] can be avoided by carefully choosing the exchange conditions (a).

**Fig. 2:** Electrochemical current as a function of the electrode potential. The anodic peak corresponds to the Co oxide formation and the cathodic peak to Co oxide reduction.



**Fig. 3:** (a)  $Co(OH)_2$  (01L) (blue) and (10L) (green) rods, recorded after oxidation of the epitaxial hcp Co layer in alkaline solution (pH12,  $E = -0.70V$ ). The inset shows (b) the hcp Co(011) peak after one, two and three oxidation/reduction cycles and (c) the time dependent hcp Co(011) peak intensity during the 2nd potential cycle into the oxidation regime.

## References

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