	Experiment title: Growth, Structure and Magnetism of Electrodeposited Co/Au(111) Films	Experiment number: 28-01-823
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Report:

1. Background and Experimental

Ultrathin magnetic layers are important devices from a fundamental as well as from a technological viewpoint. Among specific properties, perpendicular magnetization anisotropy (PMA) is one phenomenon of strong interest for high density data storage. Many different systems exhibit interface driven PMA, for instance PMA at Co/Au(111) layers mainly arises from a modification of the magnetic moment of cobalt atoms due to their hybridization with gold atoms. To be observable PMA requires, in this peculiar case, cobalt layers that are thinner than 5-6 cobalt atomic planes and the method of sample preparation is key in determining the inner structure of the deposited metal layers and the morphology of the interfaces, e.g. roughness, intermixing etc. In this respect electrochemistry stands as a powerful method for preparing epitaxial films and nanostructures over large surfaces [2]. Initial studies have shown that Co/Au(111) layers can be grown from a modified Watts bath [3] and the method was extended to produce thin Au/Co bilayer structures. In our experiment we followed this procedure to monitor the structure of the electrodeposited Co films using surface x-ray diffraction.

The Au(111) surface was prepared by flame annealing in a butane flame before being transferred to the x-ray electrochemical cell for cyclic voltammetry (CV) and surface x-ray diffraction (SXRD) measurements. The modified Watts bath electrolyte contained 0.5 mM CoSO₄. Standard hexagonal units are used for the Au reciprocal lattice whereby H and K lie in the surface plane and subtend 60° and the L axis is along the surface normal direction.

2. Results and Discussion:

2.1 Electrochemistry:

Figure 1 shows a CV in the x-ray electrochemical cell. It resembles that obtained in a regular electrochemical cell. Although the reduction of protons (-1.34 V), deposition of Co bilayer (-1.51 V) and Co

multilayer regime ($U < -1.55$ V) can all be seen it is difficult to estimate how much of the deposition / dissolution is taking place on / from the surface of the crystal due to the geometry of the cell in which electrolyte also contacts the side and back of the gold electrode. The cobalt thickness is not uniform over the entire single crystal and we suspect that, due to the geometry of the electrodes in the cell, deposition is faster at edges than on the top flat surface.

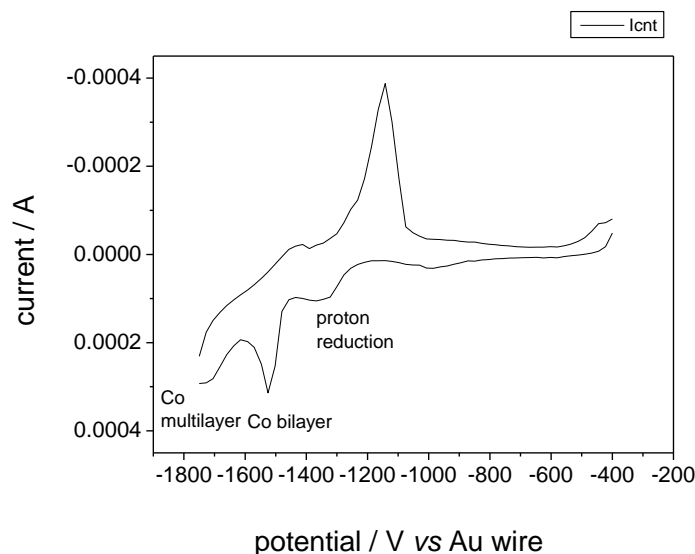


Fig. 1: CV of Au(111) in 0.5 mM CoSO₄.

2.2 SXRD data for *bare* cobalt layers:

Figure 2 shows a (H, 0, 0.2)-scan of one Co/Au(111) deposit (scan 363) and after its stripping (scans 365 & 366). The peak at $H = 1.13$ is due to scattering from the Co layer and indicates residual tensile strains in accordance with previous STM data (tensile strains are ~2.5% for 3 ML and 4.4 % for 2 ML). Totally relaxed *hcp* cobalt with the c-axis perpendicular to the surface would give scattering at $H = 1.15$ (recall that the lattice mismatch is ca 14% between Co(0001) and Au(111)).

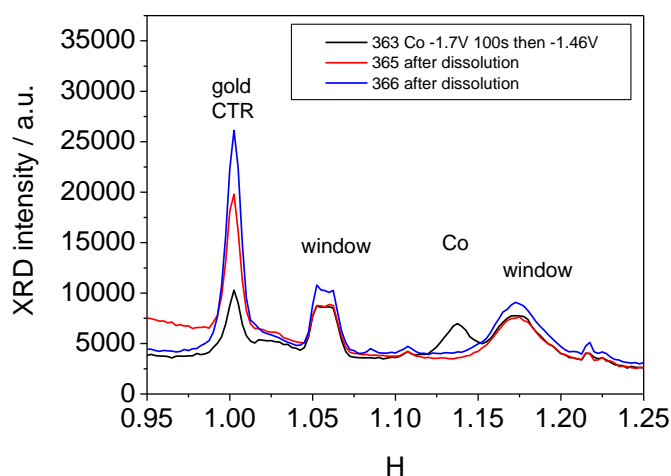


Fig. 2: (H, 0, 0.2)-scans. **S363:** Co deposited at $U = -1.7$ V for 60 s (black curve). **S365 & S366** (Red and blue curves) were recorded after stripping the cobalt film.

Figure 3 shows (H, 0, 0.2)-scans for Co/Au(111) deposits with decreasing deposition time. (S389 → S404) corresponds to deposition times 60s to 10s. The green curve was obtained after stripping the Co layer.

It can be seen that the Co peak shifts towards lower H-values with decreasing Co thickness t_{Co} . This indicates that tensile strains relax upon Co layer thickening.

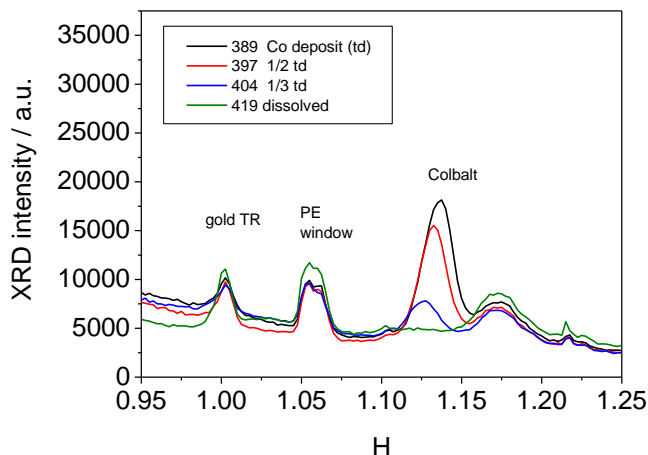


Fig. 3: (H, 0, 0.2)-scans. Co was deposited at $U = -1.9$ V. Deposition time $t_D = 60$ s (**S389**), 30s (**S397**) and 10s (**S404**). **S419**: same scan after stripping the cobalt film. S455 Co deposit ($U = -1.7$ V) for comparison.

2.3 XRD data upon CO adsorption:

In **Figure 4** the (H, 0, 0.2)-scan of the Co deposit (**S566**) before CO adsorption is consistent with previous results of Figs. 2-3, with the Co-related peak at $H = 1.13$. After CO adsorption (**S571**) this peak seems to disappear. There is now a broad peak at $H \sim 1.03$ with a shoulder at the commensurate Au position ($H=1$). After stripping the Co layer (**S578**), the strong gold CTR is restored and the peak at $H=1.03$ disappears confirming that it is due to Co.

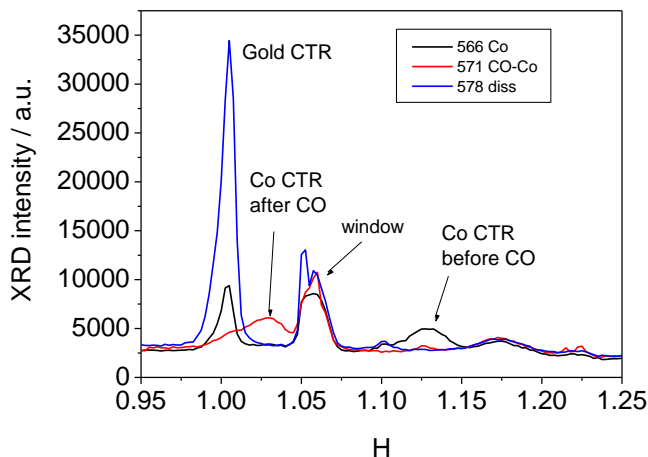


Fig. 4: (H, 0, 0.2)-scan of Co deposited at $U = -1.7$ V before (**S566**) and after (**S571**) CO adsorption. **S578** was obtained after stripping the cobalt film.

The exact nature of the scattering at $H=1.03$ was explored in a series of rocking scans and the K and L dependence was also probed. The scattering arises from the cobalt layer with the CO adlayer atop since it disappears after film stripping (compare **S571** and **S578**). If we assume that the peak at $H = 1.03$ is related to an *extended* Co lattice, the cobalt strain would drastically increase from 2-3% (**S566**) to by almost 11% (**S571**). This interpretation supposes a huge in plane expansion of the Co lattice. There is some electrochemical evidence (**Fig. 5**) that CO was indeed adsorbed on the cobalt layer. However, CO adsorption would shift the cobalt stripping peak by 300 mV towards more anodic values. Here the electrochemical answer is not as clear as anticipated. There are 2 stripping peaks:

- a first peak which is only shifted by 100 mV (the maximum of the narrow peak)
- a second one located at -0.5 V, which is more positive than expected.

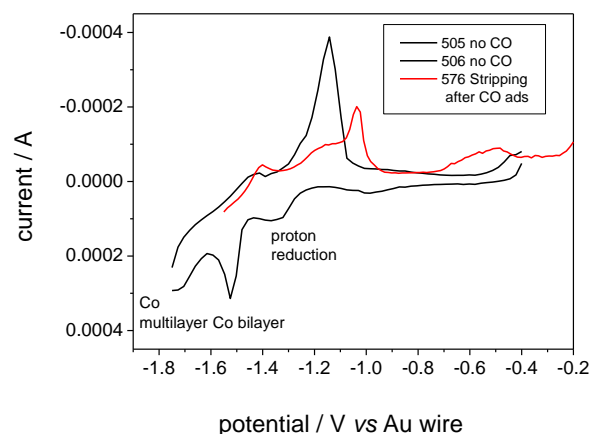


Fig. 5: CV of Au(111) in 0.5 mM CoSO₄. The black line is the original CV. The red line is the stripping curve after CO adsorption, at the end of the experiment shown in Fig. 3.

The first peak might be attributed to a rough Co film on the edges of the crystal, which could explain that CO passivation is not as efficient as on atomically flat Co(0001). The second peak could be assigned to Co dissolved from the (111) surface.

3. Conclusions

The above data are encouraging because an influence of carbon monoxide on the structure of the Co layer is observed. Confirmation of this effect, however, requires further experimentation, in particular because it was difficult to establish the true Co thickness that was electrodeposited onto the gold crystal. This will require modification to the x-ray electrochemical cell for at the cell geometry was not adapted to electrodeposition. Co deposition was probably essentially taking place on the sides (and bottom) of the crystal and not on top of it. Therefore standard stripping data was meaningless. One possibility is to use visible reflectivity measurements to probe / monitor the cobalt thickness. This technique is used for MOKE and it proves to be very sensitive, down to sub ML coverage.