



Experiment title: In-situ surface X-ray diffraction of electrodeposited Co film covered by electrodeposited Pd and Pd hydride overlayers

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MA-2858

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Report:

1) Introduction:

The reversible control of the magnetic properties of ultrathin ferromagnetic layers is a continuously expanding field. Different means for such magnetic properties modification using an electric field has been investigated. In this work, we investigated ferromagnetic Co layers (deposited electrochemically on Au/Si(111)), electrochemically capped by a Pd overlayer and in contact with an electrolyte. Our in situ magnetic characterizations showed that the Co magnetic properties may be reversibly modified by electrochemical incorporation and removal of atomic hydrogen into/from the Pd overlayer. The origin of this induced magnetic properties change is unclear. The in situ SXRD characterizations aimed at investigating whether the elastic strain variations within the Pd overlayer upon H incorporation are responsible for the Co magnetic properties modifications.

2) Results:

The experiments were performed at 22.5 keV using our “hanging meniscus” transmission cell [1] which has been upgraded (additional syringes and more compact tubing system) allowing rapid exchange of electrolyte. The time required for changing the electrolyte which took about 30 minutes with our old setup (as used for MA-2254) [2] was reduced to one minute. This significantly improved the quality and the reproducibility of the Co films and avoided any uncontrolled Co growth during the electrolyte exchange process.

All experiments started with the deposition of a thin epitaxial Co film (~6 ML) on flame annealed Au(111) single crystals. Co deposition was initiated by applying a potential of $-0.90 V_{Ag/AgCl}$ in 0.1 M NaClO₄ + 1.3 mM HCl + 1 mM CoCl₂. Deposition was stopped after ~50 s by stepping the potential to $-0.71 V_{Ag/AgCl}$ where the deposition is significantly slowed down and by an immediate exchange of the solution to 0.1 M NaClO₄ + 1.3 mM HCl. The Co film was then characterised by measuring sets of Co CTRs. From the width of the Bragg peaks and the number of the subsidiary maxima between the Bragg peaks the film thickness was determined.

After characterisation of the Co film, Pd was deposited in 0.1 M KCl + 1 mM HCl + 0.1 mM K₂PdCl₄ at $-0.71 V_{Ag/AgCl}$. Since Pd deposition onset is $\sim 0.3 V_{Ag/AgCl}$, Pd deposition on Co starts as soon as the electrolyte reaches the cell. However, at $-0.71 V_{Ag/AgCl}$ the deposition of Pd is very slow because of the concomitant H₂ evolution reaction, so that deposition times of > 10 minutes are required to completely cover the Co film and protect it from dissolution at more positive potentials. Then, in order to grow thicker Pd films, we stepped the

potential to $-0.41 V_{\text{Ag}/\text{AgCl}}$. At the potentials used for Pd deposition, Pd is loaded by H, however, the film still grows epitaxially with Co as evidenced by the Pd(01) rod (Fig. 1).

The aim of the experiment was to determine the influence of the hydrogen loading of Pd on the underlying Co film. By measuring the Co(011) Bragg peak during CVs (see Fig. 3) and a series of potential steps (see Fig. 4) the influence of hydrogen loading could be monitored in operando. All pixels positions in the detector images were mapped to their reciprocal space coordinates. This allowed us to measure the changes in intensity, position and width of the Bragg peak from which the in-plane strain and crystallite size was calculated. The strain obtained during a CV and a series of potential steps can be seen in Fig. 3 and Fig. 4, respectively. Very small and reversible changes in the strain of the same size were observed in both experiments. Preliminary analysis suggests that this induced strain cannot be responsible for the observed magnetic changes of the Co film.

We also investigated the behaviour of the films in the presence of adsorbed CO on the Pd surface. In this case, hydrogen incorporation and removal into/from the Pd layer is largely modified. Integrated intensities of the Bragg peaks at the position of Pd(011) and hydrogen loaded Pd(011) were recorded during CVs of the film without (top) and with (bottom) adsorbed CO (see Fig. 2). The potential at which hydrogen loading occurs are shifted more negative by about 300 mV. Furthermore the potential at which the hydrogen is released again is shifted to more positive values by more than 400 mV.

3) Conclusions:

In summary, we succeeded in growing in-situ in the electrochemical environment a stack composed of a thin epitaxial Co films of about 6 ML thickness covered by a thin Pd film. The Co and Pd films grow epitaxial with the underlying Au lattice. Small reversible changes in the Co strain were observed when cycling or stepping the potential between the regimes of hydrogen free and hydrogen loaded Pd. The hydrogen loading and removal was found to be strongly hindered by a monolayer of CO adsorbed on the Pd surface. A publication is in preparation.

References

- [1] K. Krug et al, Phys. Rev. Lett. **96**, 246101 (2006)
- [2] F. Reikowski et al, Electrochim. Acta **197**, 273 (2016)

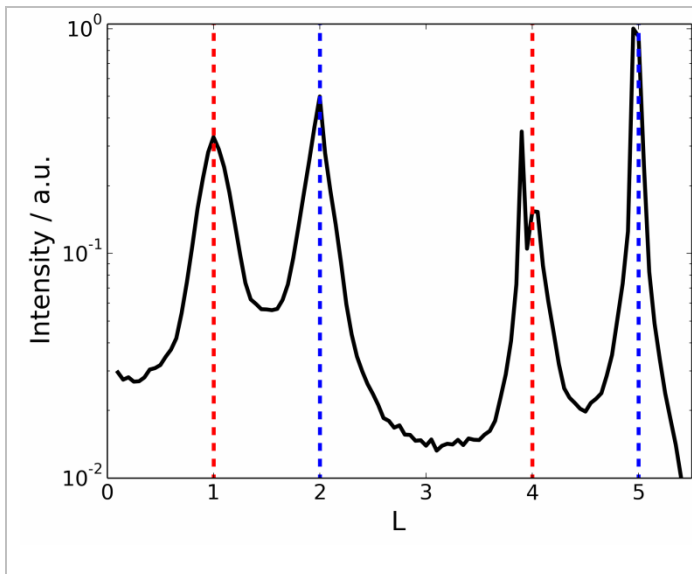


Fig. 1: Pd(01) rod of a thin film of Pd deposited on 6 ML Co/Au(111) demonstrating the epitaxial growth of Pd on the thin Co film. Peaks marked with red and blue lines correspond to two different fcc domains which are rotated by 60 deg with respect to each other. Since the lattice constant of Au and Pd only differ by a very small amount, the feet of the Au Bragg peaks are clearly visible in the data.

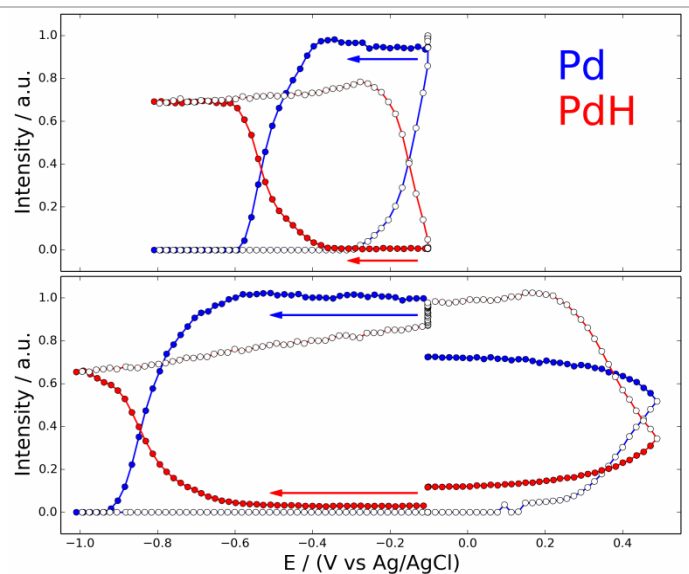


Fig. 2: Intensity of the Pd(011) Bragg peak without (blue) and with (red) absorbed hydrogen during CVs. The figure at the top shows the normal surface termination, the figure at the bottom shows the CO terminated surface. The potential for the hydrogen loading and removal are shifted by about -300 mV and more than +400 mV, respectively.

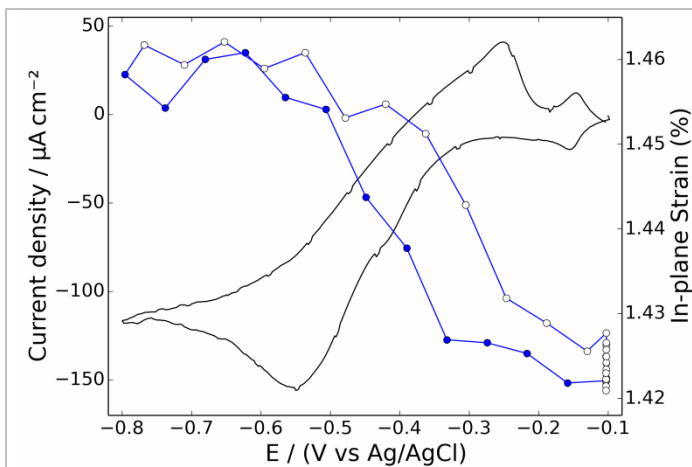


Fig. 3: In-plane strain of Co measured at the Co(011) Bragg peak during cyclic voltammetry of Pd/Co/Au(111) in 0.1 M NaClO₄ + 1.3 mM HCl. The peaks at -0.15 V correspond to the adsorption/desorption of H. Hydrogen evolution and the absorption of H into Pd result in a large increase in current negative of -0.25 V and gives rise to the peak at -0.55 V. The removal of H from Pd results in the peak at -0.25 V. Small reversible changes (0.04%) in the Co strain can be clearly correlated with the H loading of Pd which causes a lattice expansion of Pd by 3.5%.

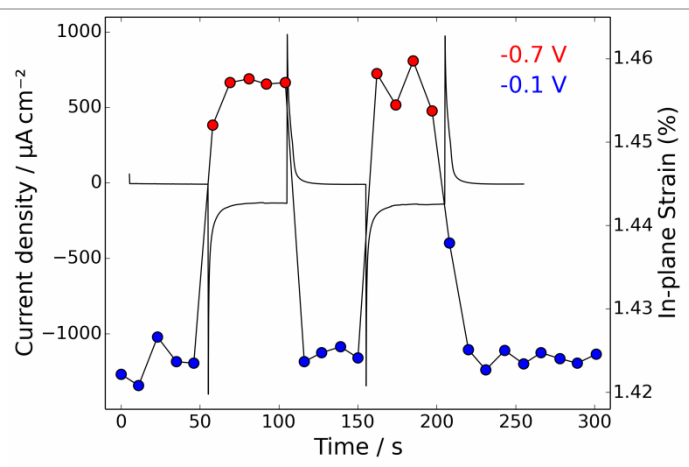


Fig. 4: In-plane strain of Co measured at the Co(011) bragg peak during potential steps between -0.1 V and -0.7 V. The strain obtained at H-free (-0.1 V) and H-loaded (-0.7 V) potentials are in good agreement with the values obtained during the CV.