EXPERIMENTAL REPORT ESRF 32-03 711

Crystallographic structure of ultra-thin CoO layers on Ag(001) and Fe/Ag(001)

1/ Background:

This experiment was built upon two precedent experiments:

1/ In a first proposal, we studied a layered system of CoO on an ultra-thin PtFe(001) layer on Pt(001). Such CoO layer presented an hexagonal surface with a monoclinic distortion, displaying a clear deflection of the [111] axis from the surface normal. This distortion, observed at room temperature, is similar to that of bulk CoO below the Néel temperature. The same result is obtained for a 3nm CoO layer on a clean Pt(001) substrate.

2/ In a second proposal, we studied ultra-thin Fe/Ag(001) films and observed the limits of the pseudomorphic growth. We demonstrated that there is no relaxation of the Fe films up to coverages of 14 ML. After mild annealing at 470 K, we observed the emergence of a surfactant Ag layer. Such layer would eventually help to match the conditions for growing the CoO on Fe/Ag(001).

2/ Experimental results:

Our main purpose was to investigate the structural properties of ultra-thin CoO film deposited on the Fe/Ag(001) surface. X-ray diffraction at grazing incidence was used to survey the quality of surface and optimize the growth conditions of both Fe/Ag(001) and of CoO/Fe/Ag(001). The CoO oxide was obtained by thermal deposition of Co at a rate of 0.21Å/min (0.16ML/min) in an oxygen atmosphere of about 5.0×10^{-7} mbar.
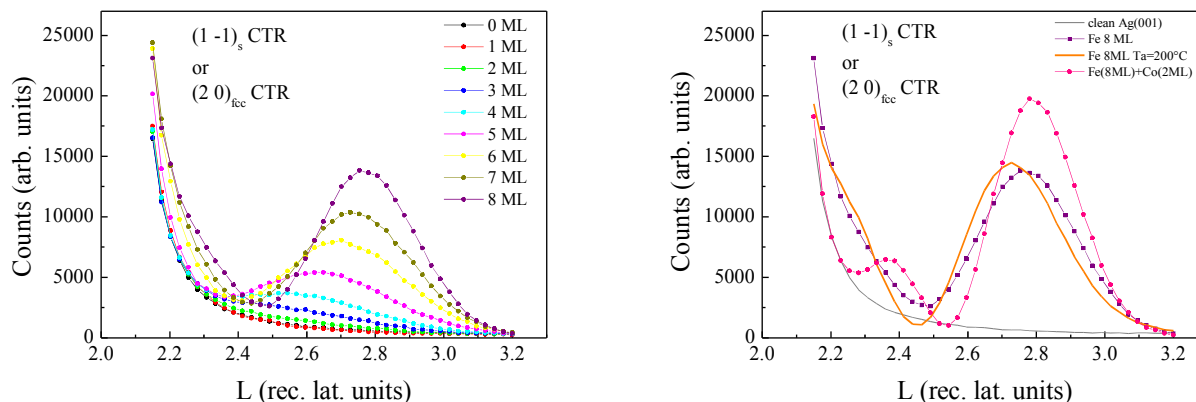

Figure 1: (left) Intensity of the Fe peak during the layer-by-layer growth of Fe/Ag(001); (right) Intensity at the same position after annealing the Fe layer at 200°C and after deposition of 2ML of Co.

We present here the results concerning the CoO deposition done on a Fe(8ML)/Ag(001) surface. The Fe epitaxy is pseudomorph on Ag(001) and develops a small tetragonal distortion (c/a=1.021) compared to the perfect bcc packing (figure 1-left). After annealing at 475 K (200°C) for 30 minutes, the layer display a small relaxation (figure 1-right), keeping the in-plane Ag parameter, but with a slightly larger tetragonal distortion (c/a=1.034). We noted by Auger spectroscopy that some amount of Ag segregated to the surface. Before starting oxidation, 2ML of Co was deposited on the previous layer. The Co atoms grow in perfect pseudomorphism with the Fe layer. For the CoO growth, the substrate was kept at room temperature and studied without further annealing. Sets of truncation rods from the crystal substrate and Fe layer and from the oxide layer were collected to get the description of the whole system.

In figure 2 (left) we show the result of the oxidation process, as described above, for a layer with 4ML of Co. After oxidation, the diffraction peak at L=2.8 is drastically reduced. By comparison with the results on figure 1, one can be confident that the whole Co layer is oxidized and about half of the Fe layer is oxidized, too. Based on the intensity and position of the diffraction peak for Fe, one can estimate that the film is left with about 4-5 ML of metallic Fe. Then, once the whole layer is completed

with the deposition of additional 12 ML Co under oxygen atmosphere, the remaining Fe layer is further reduced to about 3-4 ML. This result has been confirmed by further analysis using other techniques (see below).

We observed that the CoO oxide layer was partially relaxed with Co-O mixed planes oriented (001). We looked for hexagonal peaks coming from (111) planes but none was found. The in-plane lattice parameter turn out to be a=4.20Å (H,K=0.972) after the 4ML CoO, and a=4.22Å (H,K=0.967) for the final layer (figure 2-right). This could be related to the FeO oxide, which has a smaller lattice constant. We noted that for the thicker layer, the peak intensity decreased. The origin of such a decrease is not clear at the moment. From the Kiessig oscillations, we estimated a total oxide thickness of 3.8 nm, which gives approximately 18 ML of CoO(001). This is in good agreement with the nominal deposited 16 ML Co. Determining the CoO peak position for the momentum transfer perpendicular to the surface is difficult because it is very close to the one coming from the Ag substrate (for instance the (1 -1 2)). We found it approximately at L=1.962(5) for the CoO (0.96 -0.96) rod, which gives c=4.16Å. Compared to the bulk CoO, there is a small reduction (-4%) in the unit cell volume, $V=(4.22)^2 \times (4.16)=74.1 Å^3$, compared to $(4.26)^3=77.3 Å^3$ for the bulk crystal.
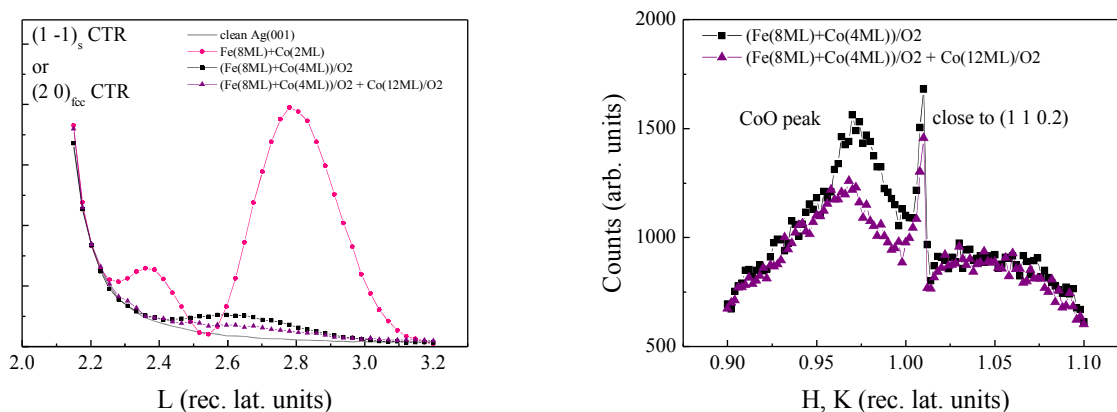

Figure 2: (left) Intensity of the Fe peak after the oxidation process, as described in the text. The diffraction peak at L=2.8 is drastically reduced after oxidation. (right) Intensity of the in-plane CoO peak close to the (1 1 0.2) (or (2 0 0.2) in the fcc lattice).

To summarize, we found good conditions for the growth of ultra-thin CoO(001) layers (~3 to 4 nm) on Ag(001) and on Fe/Ag(001) surfaces and derived their main structural parameters. One system has been presented in this report and additional analysis is being done for other layers, in particular for CoO layers on clean Ag(001) substrates. It is clearly established that an interface layer has formed between the CoO and the Fe layers. The structural properties of this FeO_x layer has to be studied in more detail.

5/ Additional studies:

The sample described just before CoO/FeOx/Fe/Ag(001), named S7, was taken from the chamber after the in situ diffraction experiments and many other studies have been performed on it. We describe here some first results.

X-ray absorption spectroscopy (XAS) measurements on the S7 sample at both the Co and Fe K edges were performed at the French CRG BM30 FAME beamline at the ESRF, Grenoble. The Co K-edge gives the signature of a CoO and confirms that there is no other detectable Co oxide present in the sample. The Fe K-edge displays the signature of a metal and oxide mixture.

To estimate the relative amount of Fe oxide in the layer, we compare the spectrum with the results of our previous experiment on a Fe wedge sample deposited on Ag(001) and covered by a CoO layer. In figure 3 we show the spectra at different positions along the wedge (x values) compared to the sample S7. The wedge thickness varies from 15 ML down to 4 ML. At 4ML Fe is completely oxidized (f=1.00) while for 15 ML the oxide fraction is only 15% (f=0.15). It can be seen that the S7 spectrum is nicely inserted between f=0.40 and 0.5. So, we deduce that about 3 to 4 ML of Fe are

oxidized, but no more than that. This is in rather agreement with the diffraction results presented earlier, however it yields an amount of metallic Fe larger than predicted by diffraction. From the S7 spectrum alone is not possible to say much about the oxide nature, but based on our previous experiment one can argue that the oxide layer is most likely Fe_3O_4. This point should be tackled in further XAS experiments.
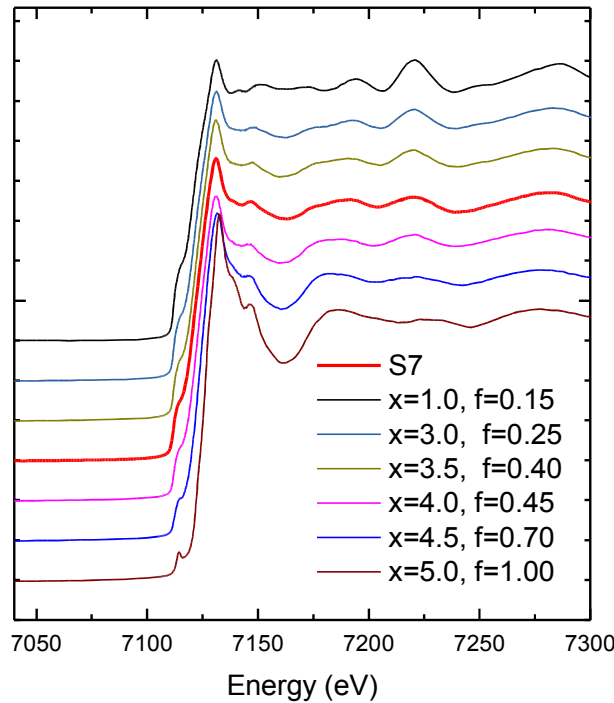

Figure 3: XAS Fe K-edge spectrum of the S7 sample compared to spectra of an Fe-wedge/Ag(001) sample covered by CoO. The Fe layer in the S7 sample has a fraction of oxide between 0.40 to 0.45.

It is a established result that Fe/Ag(001) system shows in-plane magnetic anisotropy at room temperature for thickness above 6 ML. Our sample S7, if we consider that about 3-4 M Fe are oxidized, would have only 4-5 ML of metallic Fe and be in the out-of-plane magnetic anisotropy range, or at least close to the spin reorientation transition. Assuming that the CoO layer is antiferromagnetic, we should expect exchange coupling with the Fe interface.
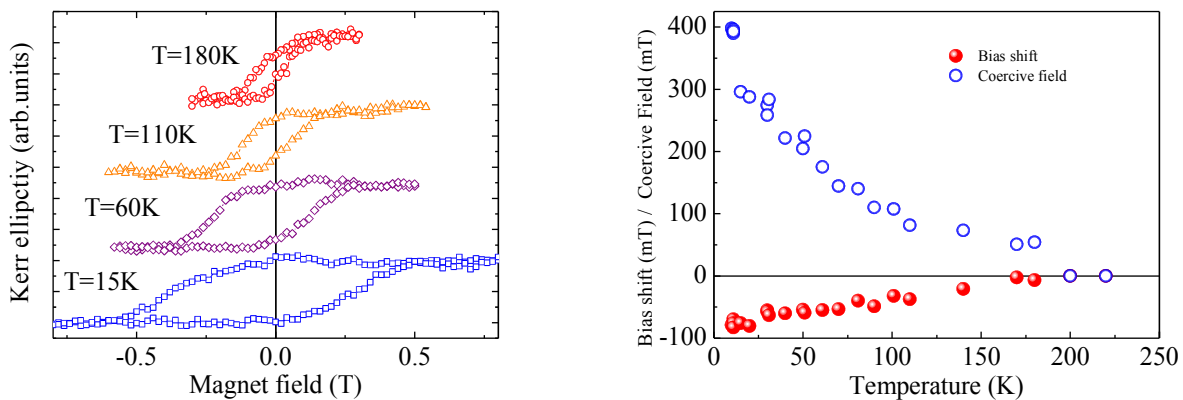

Figure 4: Polar MOKE measurements on the S7 sample: (left) hysteresis loops at different temperatures; (right) exchange bias shift and coercive field as function of temperature, after field cooling under an applied magnetic field of 1Tesla perpendicular to the sample surface.

In figure 4, we present the study of the magnetic properties by polar MOKE measurements. The hysteresis loops were measured after magnetic field cooling under 1 Tesla applied perpendicular to the sample surface from room temperature down to 10 K. The loops were measured also perpendicular to the surface by increasing temperature. As can be seen in figure 3-left there is a large increase in the coercive field and exchange bias shift at low temperatures. We observed that the out-of-plane anisotropy of the system is maintained up to 180K. After that the out-of-plane anisotropy is lost and spins reorient in-plane. For temperatures above 180K both the out-of-plane coercive field and exchange bias vanishes. In figure 4-left, the Kerr ellipticity is given in arbitrary units but the average value was about 100 to 150 μrad up to about 140K, and then dropped to about 70 μrad close to 180 K.

A magnetic field cooling parallel to the surface - with a 1 Tesla field - was performed to verify if the out-of-plane anisotropy was indeed due to the exchange coupling with the CoO. After this procedure, the hysteresis loops were measured with the magnetic field perpendicular to the surface, as done previously. We observed that there were no more perpendicular loops indicating that the system was no longer with an out-of-plane easy axis.

The magnetic properties show clearly that this system, which should have in-plane magnetic anisotropy, presents an out-of-plane magnetic anisotropy (after a MFC perpendicular) due to the exchange coupling with the antiferromagnetic oxide layer. However, it seems that the coupling does not occurs between the Fe layer and CoO, but between the ferrimagnetic phase of Fe3O4 and CoO. It turns out that the relevant interface is the Fe3O4/CoO one, which deserves a more deep study.