Effect of a Gold Overlayer Contamination on the Growth and Magnetic Properties of Au/Co/Au(111)*

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The presence of chlorine in gold is found to modified drastically the growth mode of Au on a Au(111) substrate. Whereas pure gold can grow layer by layer by step flow, contaminated gold is found to make random and/or vacancy islands and to modify the Au(111) herringbone reconstruction structure. The influence of a contaminated gold capping on the magnetic properties of cobalt ultrathin films has been investigated by in situ Magneto Optical Kerr Effect measurements. Surprisingly, the interface anisotropy is found to be of opposite sign as compared to the one of pure gold and thus favoring an in-plane magnetization. [DOI: 10.1380/ejssnt.2010.21]

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I. INTRODUCTION

In the elaboration of self-organized nanostructured materials, impurities and defects are involved in the growth process and often affect significantly the morphology and properties of the fabricated materials. A very careful surface preparation and high purity elements are always compulsory to achieve a convincing experiment and trust the conclusions. The presence of a chemical contaminant, even in limited quantities, can change drastically the growth mode and/or the magnetic properties. This strong dependency on the chemical composition can also be used as a powerful tool to taylor the physical properties.

Au(111) is one of the most used terminal surface to create self-organized nanostructures. In contrast to all other (111) faces of noble metals, the Au(111) surface exhibits a peculiar reconstruction which is based on a uniaxial compression of the topmost atomic layer along one of the three [110] directions. This results in a characteristic pattern consisting of segments of dislocations lines forming a zigzag-type pattern. This so-called “herringbone” Au(111) reconstruction [1] gives birth to a regular array of preferential nucleation centers which play a key role in the achievement of self organized nanostructures.

Scanning Tunneling Microscopy (STM) is a very powerful technique to determine the early stages of the growth of nanostructures. For example, the Co/Au(111) system have been extensively characterized from a structural point of view in the submonolayer range [2, 3]. This system is also one of the most studied in which a Spin Reorientation Transition (SRT) occurs. While increasing the film thickness, the SRT manifests itself by a change of the direction of the Easy Magnetisation Direction (EMD) from a perpendicular to an in–plane direction [4–6]. This change in the magnetic anisotropy essentially results from the interplay between the surface and inter-

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II. EXPERIMENTAL

The investigations of the growth modes have been performed by means of a variable temperature Scanning Tunneling Microscope (VT STM-Xa Omicron Nanotechnol ogy ©), operating in a UHV chamber. The base pressure is always better than 3×10−10 mbar including during the evaporations of cobalt and gold.

The substrate consists of a Au(111) oriented single crystal previously cleaned by Ar ion bombardment and annealed at 800 K for few minutes. Cobalt was evaporated at room temperature by electron bombardment from a rod (99.99 % purity – Goodfellow) and deposited at a fixe rate of 0.2 ML.min−1 (ML: atomic layer). Gold was also deposited at room temperature by the same technic but using a gold wire (99.99 % purity [As specified by the supplier] – Goodfellow) inserted in a Molybdenum crucible. The deposition rate for each materials was determined thanks to STM images. It was estimated from the area of the surface covered with the deposited materials on a calibration sample. Good reproducibility in the deposition rate was observed. For the gold capping layer, a standard 3 ML thickness was used. Magnetic hysteresis loops were recorded in situ during the film growth at room temperature by using po-
lar Magneto Optical Kerr Effect (MOKE) configurations with maximum applied magnetic fields up to 500 Oe.

Rutherford Backscattering Spectrometry (RBS) using a 2.00 MeV He\(^+\) ion beam have been performed at the SAFIR Van de Graaff accelerator at the Institut des NanoSciences de Paris (INSP). The total dose was set to be 20 \(\mu\)C. The measured RBS data were analysed and reconstructed using the RUMP software [12]. Further details can be found elsewhere; see for example [13].

III. RESULTS AND DISCUSSION

The growth mode of clean gold on Au(111) has been studied previously by Chambliss et al. [10]. They have demonstrated that most of the gold atoms sticks preferentially at the step edges. This feature is confirmed in Fig. 1 where 0.2 ML of gold has been deposited on Au(111). The gold used for this specific deposition was proved to have the composition given by the supplier. The typical herringbone structure of the Au(111) substrate can still be seen on the terraces. However, the shape of the mono-atomic edges are found to be modified upon gold deposition. Gold clusters have grown originating at the step edges. It is similar to a step flow like model for the growth but with a non perfect row-by-row growth. It corroborates that, at room temperature, the diffusion length of the gold deposited atoms is larger than the size of the terraces (an average of 100 nm on this sample) and that the deposited atoms tend to aggregate at the step edge rather than stick to nucleation centers [10].

Figure 2 (upper part) shows an STM image where 0.05 ML of contaminated gold was deposited on Au(111). A complete different feature can be observed for this contaminated material. The growth mode is characterized by the nucleation of gold clusters with a rather large size distribution ranging from 50 to 1000 atoms. No significant organisation of these clusters, in particular with a link to the reconstruction of the Au(111), can be seen. Furthermore, the presence of gold clusters influences seriously the herringbone structure of Au(111). As shown in figure 2 (upper part), the parts of the sample where no gold has been deposited still exhibit the typical herringbone with well characterized elbows. On the contrary, this regular organisation is clearly destroyed by the gold cluster and no regular zigzagging lines can be observed. Furthermore, no identical set of elbows can be found in the vicinity of the gold clusters. This feature is typical of the Au(111) surfaces with random or vacancy islands [11].
Figure 2 (bottom part) corresponds to a deposition of approximately 0.5 ML of contaminated gold. New features can be observed. The gold clusters are found to significantly increase in size but still a rather large range of clusters size can be seen. For this coverage, a statistical second layer is found on top of the larger gold clusters. A close look at the STM images reveals that the discommensuration lines are still visible underneath the gold clusters. The gold clusters all exhibit a shape of 6-side type while regular hexagons can only be found seldom. A new phenomenon is observed for this highest gold content. Holes in the surface (black dots) are clearly seen all around the gold clusters. As shown in the depth profile of Fig. 3, the depth of these holes is close to a monoatomic step height. This indicates that the deposition of contaminated gold induce an exchange of atoms with the surface and results in the creation of vacancies islands. The growth mode observed for the gold deposited clearly indicates that the quality of the gold can not be as pure it was claimed by the supplier and it tends to demonstrate the presence of a significant amount of contaminant in the starting material. While pure gold grows on a step flow like type, contaminated gold creates gold clusters and significantly affect the Au(111) reconstruction.

In order to confirm the presence of an impurity, a sample of approximately 80 monolayers of contaminated gold was grown in the same chamber on polished pyrolitic graphite substrate. This sample was analysed thanks to RBS measurements. The experimental and refined RBS spectra are shown in Fig. 4. Two major structures can be identified in the spectrum corresponding to the carbon substrate (low energy) and the gold top layer (high energy). A good agreement was found between the gold layer thickness as determined in the reconstructed RBS spectra.
FIG. 5: (Upper part) MOKE hysteresis loop obtained in the polar configuration for a 5 ML Co film. (Bottom part) MOKE hysteresis loop obtained in the polar configuration for a 5 ML Co film capped with clean Au (3 ML).

FIG. 6: Typical MOKE hysteresis loops obtained in the polar configuration for films of 0.4, 1.2 and 3 ML (A, B, C respectively) and with an additive Au capping layer on the 3 ML one (D).
spectrum and the one estimated using the deposition rate (approximatively 18 nm). A close look at the experimental RBS spectra reveals the presence of a relatively small peak located at approximatively 1.32 MeV. Thanks to the refinement of the RBS spectrum, this structure was identified as the presence of chlorine located through the whole depth of the gold layer (see the inset of figure 4). Furthermore, the quantity of Cl was estimated to be roughly 10 ± 2 at.% with a constant ratio through the whole film. It clearly outlines the occurrence of an impurity that was not referenced in the purity test sheet of the manufacturer. Indeed, Chlorine gas (in particular to remove the Ag atoms present in mine extracted gold) or Chlorine solution are known to be rather extensively used in the gold refinement process [14].

Since the presence of the contaminant plays a major role in the growth mechanism, it is of interest to investigate the effect of the use of contaminated gold on the magnetic properties. For example, it is known from in situ polar Magneto-Optical Kerr Effect [15–17], in situ torsion magnetometry [18] and relativistic spin-polarized local spin density calculations [19] that the thickness of the cap influences the magnetic surface anisotropy in Au/Co/Au sandwiches. Figure 5 shows the influence of the clean Au capping layer on a 5 ML thick cobalt film. On the upper part of Fig. 5, a typical MOKE hysteresis loop recorded in the polar configuration is presented. It demonstrates that for this thickness, the EMD lies in the plane of the film. These results are in good agreement with Allenspach et al. [5] which have reported a SRT from the out of plane to the in plane direction around 4.5 ML. While capping the sample with clean gold, a change in the EMD is observed. The EMD appears to be out of the plane and the coercive field \( H_c \) can be estimated to 70 Oe. The effect of the gold capping layer can be interpreted in term of change of the surface anisotropy coefficient \( K_s \) which is part of the total energy [7]. In the expression of the free energy, the volume term which is dominated by the shape anisotropy is always positive and thus it favors an in plane magnetisation. As a conclusion, the effect of a gold capping layer can be interpreted by a change of \( K_s \) which becomes strongly negative after capping [15].

As the deposition of clean gold was shown to favor an orientation of the EMD out of the plane, we have studied the influence of the deposition of contaminated gold on a cobalt film which exhibits an out of plane EMD. A 3 ML cobalt film was chosen which corresponds to a thickness located far below the critical thickness for the SRT [5]. Our results (see Fig. 6 A, B and C) confirm that while increasing the Co thickness, a magnetic signal appears and the EMD of a 3 ML Co film is out of the plane with a \( H_c \) of roughly 30 Oe. One would expect that a clean gold capping layer would not modify the EMD of the sample and increase the coercive field. As shown in Fig. 6 D, the effect of a contaminated gold capping is to change the EMD from a direction out of plane to an in plane orientation. This is completely in disagreement with the case of pure gold which was demonstrated to favors a negative value for \( K_s \) and should not change the EMD of a 3 ML cobalt film. This results demonstrates that the presence of a limited amount of Chlorine dramatically changes the influence of a capping layer presumably through the value of the surface anisotropy constant. It highlights the extreme sensitivity of the anisotropy constants to the chemical nature of the interface.

### IV. CONCLUSION

We have shown that an unexpected growth mode of gold on Au(111) can reveal the presence of an impurity in the evaporated material. While a step flow like growth was observed using pure gold, the formation of gold and/or vacancy islands is seen with gold contaminated with chlorine. We have measured by ion beam analysis that 10 at.% of Cl in the deposited gold was at the origin of this complete different behavior.

From a magnetic point of view, we have shown that the contaminant in the gold capping layer had a drastic effect on the surface anisotropy of a cobalt film, favoring an in plane magnetization in contrary to the standard Co/Au interface anisotropy.

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