X-ray super-cell crystallography of self-organized Co/Au(111) deposits

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We report for the first time *in situ* Grazing Incidence Small Angle X-ray Scattering (GISAXS), performed on self-organized Co/Au(111) deposits during growth with deep sub-atomic layer sensitivity. We observed surface super-diffraction peaks associated with the dots periodicity ($\sim 10\,\mathrm{nm}$). We show how the dots size and order can be inferred from a quantitative peak intensity analysis similar to that of conventional crystallography, and how the combination of GISAXS with STM can yield information about the percolation process and the buried microstructure of a film.

The fabrication of new materials often triggers the development of new probing techniques. In the past ten years much attention in the field of thin films has been drawn to self-organization, a procedure consisting of the epitaxial growth atop naturally patterned surfaces, yielding spontaneously-ordered nanometer-period arrays of nearly monodisperse objects such as stripes [1], wires [2] or dots [3]. Incidentally it was reported recently that the high lateral order of self-organization gives rise to satellite patterns in conventional crystallography [4,5]. Concerning scattering, Grazing Incidence Small Angle X-ray Scattering (GISAXS) is a recent technique that has been applied *ex situ* to layers or multilayers of dots [6] or clusters [7] showing a tendency to vertical alignment, but always with short range lateral order. In this Letter we report GISAXS experiments performed *in situ* on a single layer of Co/Au(111) laterally self-organized dots. This experiment can be viewed as surface super-cell diffraction (*i.e.* scattering over the lateral periodicity of the dot array), which allowed us from the far sub-Atomic-Layer (AL) range to gain in real time during growth various information on the dots such as size, size distribution, long-range order, coalescence process, etc.

Our GISAXS experiments were performed *in situ* on a fully dedicated experimental set-up built on the ID32 beamline at ESRF. No window is placed before the sample and the beam is defined by two successive pairs of motorized slits, thus minimizing background scattering. The beam($\lambda = 1.2096\,\text{Å}$) is shone under total reflection angle on the sample. Diffusion patterns were collected 1.2 m behind the sample on a 16-bit X-ray CCD detector placed just after an exit beryllium window and a Ta beam-stop. The combination of high flux, grazing incidence, on-surface structures, low background and before-growth background subtraction are mandatory to achieve a high signal-to-noise ratio well below one atomic layer (all GISAXS patterns shown this Letter are background-subtracted). To demonstrate the power of GISAXS performed under such conditions, we report here a study of the growth of Co on the herringbone-reconstructed Au(111) surface, from below 0.1 AL to 15 AL. Below coverage $\tau \lesssim 2\,\mathrm{AL}$ Co grows as a regular array of parallel rows of 2 AL-high dots [period ($\Lambda \sim 7\,\mathrm{nm}$) × ($2\kappa \sim 20\,\mathrm{nm}$)] [3](Fig.1a), whereas coalescence progressively occurs for higher coverages [8]. The recording time was varied from 30 s for 0.1 AL to (**XXX**) for 15 AL. Co was evaporated by steps from an ebeam-heated rod onto a Au(111) single crystal held at 300 K, with stops of a few minutes during GISAXS measurements. The pressure in the chamber was kept below (**XXX**) (**Mettre mot sur impédance pression ?**).

We first describe experimental results, and then proceed to discussion. Fig.1b-c shows GISAXS patterns of a $\tau = 1\,\mathrm{AL}$ deposit with the incident X-ray beam respectively perpendicular and parallel to the rows of dots. Let us

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analyse these patterns. The small angle reciprocal space arising from the periodicity of the array of flat Co dots consists of rods perpendicular to the surface, whose intercept with the high-radius Ewald sphere yields elongated streaks on the diffusion pattern. This geometry is similar to that of Reflection High Energy Electron Diffraction (RHEED), except that instead of diffracting on a crystalline array of atoms, here X-rays diffract on an array of dots, explaining the name of *super-cell crystallography*. Like with RHEED, the inter-streaks distance is proportional to the length of diffusion vectors $\mathbf{q}$ perpendicular to the beam. Thus, Fig.1b-c probe respectively the order of individual dots within rows, and the order of rows one with respect to others. The streaks in Fig.1b are extremely sharp: $\Delta q/q = 3\%$ with Δq the full width at half maximum. Δq is one order of magnitude higher than the estimated experimental broadening (sample and CCD pixel finite size, beam divergence and non-monochromaticity), from which we infer that dots display a long range order within rows with an average coherence length of 30 dots. The order is thus of crystalline type within rows. In contrast the streaks in Fig.1c are broad. This reveals that the order between rows is short ranged. A simple liquid-type analysis shows that the row-to-row nearest-neighbor distance fluctuates around a mean value of $\overline{\kappa} = 8.5\,\mathrm{nm}$ with standard deviation $\sigma_\kappa = 2.05 \pm 0.1\,\mathrm{nm}$.

Let us examine the super reciprocal space in more detail. Resulting from the threefold symmetry of Au(111), it is known that three types of domains of Au reconstructions and thus of Co dots arrays are found, rotated one with respect to each other by 120°. This is consistent here with the observation of alternating narrow and broad streaks every other 30° of sample azimuth. However additional narrow streaks are observed at other angles and $\mathbf{q}$ vectors length. The examination of GISAXS patterns for many azimuths allowed us to draw a cross-sectional sketch of the reciprocal space of the array of Co dots (Fig.2). Concerning the peak position this sketch is qualitatively similar to the Fourier Transform (see inset of Fig.2) of a large scale STM image ($1.5 \times 1.5\,\mu$m) displaying the three domain types (image not shown here). We observed that the position of the narrow peaks are essentially fixed, whereas surprisingly the position of the broad peak along $< 11-2 >$ azimuths may fluctuate significantly (of as much as 15%) from one experiment to another performed with identical experimental protocol. Concerning peak intensity we present a quantitative peak intensity analysis of GISAXS patterns from $\tau = 0.1\,\mathrm{AL}$ (well separated dots) to more than $\tau = 15\,\mathrm{AL}$ (presumably a coalesced film). We focus here on the integrated intensity of the cross-section performed at the foot of peaks probing the order of dots within rows, because the peak narrowness allows a clear separation from the residual background and thus small error bars to be achieved. Fig.3a-b shows the intensity $I_1(\tau)$ of the first order peak (with diffusion vector q) and the intensity ratio $I_2(\tau)/I_1(\tau)$ of the second order peak (with diffusion vector $2q$, not shown in Fig.1) with first order, respectively. The width and shape of the peaks remained unchanged over the entire range of thickness.

We now turn to the discussion. The narrowness and position reproducibility of peaks along $[1-10]$ azimuths is easily explained by the fact that the inter-dots distance within rows is directly related to the so-called $22 \times \sqrt{3}$ Au reconstruction [9]. This reconstruction, that yields a local uniaxial surface stress relaxation, is known to fluctuate very little. In contrast, the inter-row distance is related to the herringbone reconstruction, a superstructure of the $22 \times \sqrt{3}$ reconstruction that arises to achieve an isotropic surface stress relaxation on the average. The herringbone superstructure results from the balance of local anisotropic strain energy versus the cost of 120° turns of surface dislocation lines. This secondary energy balance is more subtle than that of the $22 \times \sqrt{3}$ basic reconstruction, so that it is not surprising to evidence significant row-to-row distance κ fluctuations within the same sample, explaining the liquid-type order. Incidentally this can be checked from published STM images that show a large spread of κ values ranging from 6.3 nm [10] to 17.4 nm [3]. However, our experiments also demonstrate that the energy balance is so subtle that the mean row-row distance may vary from one experiment to another under apparently identical protocols. This point had never been addressed so far. Examining experimental details of crystal preparation in the above papers and according to our own experience, this large spread does not seem to be controllable through annealing or quenching parameters, but rather is related to the vacuum quality, better conditions yielding higher κ.

We now analyse peak intensity data, with a view to extracting quantitative information on the growth. To do this we propose an analytical model of the reciprocal space. The direction perpendicular to rows is named x in the following, while y rows are parallel to y. We divide the total scattered amplitude arising from individual Co atoms before percolation into three embedded summations: the first one is over a single dot giving rise to a smoothly varying envelop (the mean form factor F_{dot}), the second one F_{row} over one perfectly ordered row of dots yielding a series of narrow peaks for $q_y = 2\pi/\Lambda$, and the third one F_{liq} over the origin of the rows characterized by a liquid-type order along x. The total diffracted intensity can then be written

$$I = |F_{\mathrm{dot}}|^2 \times |F_{\mathrm{row}}|^2 \times |F_{\mathrm{liq}}|^2 \tag{1}$$

Assuming disk-shaped 2 AL-high dots before percolation we find

$$|F_{\rm dot}(\mathbf{q})|^2 = \frac{2\pi\Lambda\kappa\tau}{q^2} J_1^2\left(q\sqrt{(\Lambda\kappa\tau/2\pi)}\right) \quad (2)$$

where J_1 is the first Bessel function and τ is expressed in AL. For $F_{\rm row}$ we used a Lorentz-based function mimicking the incoherent superposition of rows with approximately 30 dots along y. The evaluation of $|F_{\rm liq}|^2$ requires some calculation. Due to the short-range order along q_x, $|F_{\rm liq}|^2$ is conveniently expressed as the Fourier transform of the Patterson function of the origin of the rows, related to the origins nearest-neighbors distribution function [11]. The calculation is not as straightforward as that of a 1d-liquid as the average unit cell of the array, a rectangle of size $\Lambda\times 2\kappa$, holds two dots (rows'origin). Besides the location of the central dot is not simply that of the first dot translated along the $\pi/6$ direction of the double-line Au(111) reconstruction, because the two nucleation sites are not equivalent [9]. The central dot is thus displaced along y by a quantity ϵ that may vary during growth, for the two types of dots growth proceeds in opposite directions along y [12]. The right first neighbor distribution function of the central and left-hand corner dot are thus respectively

$$h^{\pm}(x,y) = \frac{1}{\sqrt{2\pi\sigma_\kappa^2}} \exp\left[-\frac{(x-\kappa)^2}{2\sigma_\kappa^2}\right] \delta(y \pm \frac{1}{2}x \pm \epsilon) \quad (3)$$

Using these two functions and after some calculation we find

$$|F_{\rm liq}(\mathbf{q})|^2 = (\sinh c\cosh c + \cos a\cos b\sinh c\cosh d + \sin a\sin b\cosh c\sinh d)/(\sinh^2 c + \sin^2 a) \quad (4)$$

with $a = q_x\kappa$, $b = q_y(\frac{1}{2}\kappa + \epsilon)$, $c = (q_x^2 + \frac{1}{4}q_y^2)\sigma_\kappa^2/2$ and $d = q_xq_y\sigma_\kappa^2/2$. Finally we checked that the Ewald sphere curvature and the sample azimuthal misalignment can be neglected in the intensity calculation, because the large value of σ_κ induces a large spread of peak intensity along the q_x direction.

For numerical evaluation we used the Λ, κ and σ_κ values deduced above from experimental data. The analysis of the data with the more rigorous Eq.(1) does not change these three figures. Let us also stress that the liquid-type peak fit used to extract κ and σ_κ must be performed at low coverage ($\tau \lesssim 1$ Å) so that the variation of $F_{\rm dot}(\kappa)$ does not yet play a role in Eq.(1). During growth the evolution of $I_n(\tau)$ is connected with $F_{\rm dot}(\tau)$, while $F_{\rm row}$ and $F_{\rm liq}$ remain unchanged. We can thus predict the evolution of $I_1(\tau)$ and $I_2(\tau)/I_1(\tau)$ (Fig.3c-d). The cancellation of $I_2(\tau)/I_1(\tau)$ close to $\tau = 0.5$ AL results from the overlap of the second order peak of $F_{\rm row}$ with the first zero of J_1. Encouragingly the experimental $I_2(\tau)/I_1(\tau)$ curve experiences a clear minimum, indicating the relevance of the model and the limited distribution of dots shape and size. Most importantly as one single minimum is expected, the model allows us to calibrate precisely the experimental coverage rate τ, which is of importance for the analyses reported hereafter.

Despite displaying similar shapes, the $I_2(\tau)/I_1(\tau)$ curve estimated from $F_{\rm dot}$ solely lies nearly one order of magnitude higher than the experimental curve. Using Eq.(1) this can be ascribed to the already numerically determined disorder σ_κ and to the unit cell structure factor, and thus yields an estimation for the only remaining parameter $\epsilon = 2.5 \pm 1.5$ nm. From this we infer that the unit cell is nearly rectangular side-centered for low coverage, again in agreement with STM data [13]. This said, let us show that GISAXS quantitative analysis can also yield new information, not accessible by STM. $I_1(\tau)$ is predicted to decrease sharply above 2 Å (Fig.3), and should vanish upon percolation to a continuous film above 2 AL. To the contrary the experimental $I_1(\tau)$ reaches its maximum around 6 Å and some significant intensity is found up to at least 30 Å. A series of high-quality STM pictures taken at high coverage (from samples grown in different setups) confirms that although the dots percolate above 1.5 AL some residual roughness in exact registry with the periodic nucleation array remains, as already reported [8]. These images were digitalized in a step-like fashion to minimize convolution effects with the STM tip, and then used to compute the $I_1(\tau)(\tau)$ intensity arising from the Co deposit topographyFig.4. This revealed that above approximately 1 AL the topographic residual roughness is much too small to account for the experimental $I_1(\tau)(\tau)$. The extra intensity most probably arises from a periodic stress of the Au underlayer in contact with the Co array. Keeping in mind the high Z ratio of Au over Co, and that the close-to-q_z-origin cross-section GISAXS intensity scales with the squared thickness of the scattering structure, a simple elastic calculation shows that a residual Co/Au epitaxial misfit of a few tens of percent is enough to account for the observed intensity. Surface stress effects may also play a role [14]. Incidentally diffraction satellites on distorsions induced by dots on a matrix [4] or surface adsorbate arrays [5] have already been reported. Finally $I_1(\tau)(\tau)$ is still significant for $\tau > 6$ AL, whereas all periodic residual roughness has vanished (Fig.4). This shows that Au is still periodically stressed, revealing the persistence of a buried microstructure in the Co film (whose nature is not known a priori: voids, wetting Au atoms, grain boundaries etc.) despite a perfect surface percolation.

To conclude we have performed *in situ* GISAXS on self-organized Co/Au(111) deposits with deep sub-monolayer sensitivity, and studied the super-reciprocal-space of the dot array super-cell during growth. The quantitative analysis

of three diffraction peaks allowed us in particular to demonstrate that a periodic microstructure remains buried in the film after the surface percolation conventionally observed by STM. This raises hope that GISAXS may in the future complement STM and that the analysis of a larger number of peaks will allow one to unravel undestructively intimate buried details of deposits, the organization being used not as a goal for achieving physical properties, but as a tool, like crystals are used in conventional crystallography.

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FIG. 1. (a) 150 nm STM picture of Co/Au(111) ($\tau = 0.4$ AL) (b-c) Experimental GISAXS patterns for two perpendicular sample azimuths

FIG. 2. (a) sketch of the dots' array reciprocal space within the camera window, and the Ewald sphere. β and χ show intersects of Fig.Fig.1(b-c), respectively (b) FFT of STM picture with a different κ/Λ ratio.

FIG. 3. Experimental (a) $I1(e)$ and (b) $I2(e)/I1(e)$. Curves for the growth model are shown in inset. For (a) the intensity computed from STM images is shown (different symbols stand for different setups)

FIG. 4. 100 nm STM images of 4 AL Co/Au(111). Raw (a) and discretized (b) images.