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Shifts: 18	Local contact(s): Jakub Drnec	<i>Received at ESRF:</i>
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Report:

1) Introduction: We recently developed a new approach for *in situ* and *operando* XRD studies of spatially heterogeneous solid-liquid interfaces using high photon energies (40 - 70 keV) and a transmission geometry with near vertical incidence. This technique termed *Transmission Surface Diffraction* (TSD) allows direct projection of the in-plane reciprocal space geometry onto a 2D detector and benefits from a small beam footprint on the sample, enabling spatially resolved studies with (currently) $10 \times 20 \mu\text{m}^2$ resolution. A proof-of-principle illustrating the potential of this new technique by *in situ* studies of electrochemical surface phase transitions and deposition processes performed at ID31 during beamtimes IHCH-1022 and IHCH-1063 has been published recently. [1]

In this work, TSD was employed in combination with a newly developed micro-fluidic flow cell to study the electrodeposition of Bi on Au(111) and Au(100) electrodes. We also investigated the behaviour of thin $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-d}$ films under OER, and the oxidation of an electrodeposited epitaxial Co layer on Au(111).

2a) Improvements to the TSD electrochemical cell: The proof-of-concept studies shown in [1] used an electrochemical cell in which the beam would pass through 4.0 mm of electrolyte as well as a 0.1 mm glass window. For this study, a newly manufactured micro-fluidic cell with an electrolyte flow channel of dimensions 8 mm \times 2 mm \times 0.5 mm and a 0.1 mm PEEK window was used, providing a 60 % reduction in water background intensity (Fig. 1) as well as more controlled electrodeposition conditions under laminar flow compared to the previously used cell.

b) Electrodeposition of Bi on Au(100) and Au(111): Bi electrodeposition onto Au(100) and Au(111) was performed from 0.1 M HClO_4 + 1 mM Bi^{3+} at potentials of $E = -0.25$ V and -0.20 V, respectively (vs. Ag/AgCl). We can show that orientation and epitaxy can be determined from a single image for films down to one monolayer.

For a 30 ML Bi film on Au(111), the in-plane scattering shows a six-fold arrangement of diffraction spots (Fig. 2a). From this image, the orientation of the film can be unambiguously identified as Bi(012) (using the hexagonal notation), with characteristic peaks at in-plane distances of 3.28 Å, 4.55 Å and 4.75 Å as a result of the rectangular Bi(012) surface unit cell. The deposition on a substrate with three-fold symmetry will result in six equivalent domains, giving rise to the observed diffraction pattern. From the same image, one can determine that the Bi[01-4] direction lies parallel to the Au[11-2] direction, i. e. the short edge of the Bi(012) surface unit cell lies parallel to the unit cell edge of the Au substrate. This epitaxy is in agreement with previous literature. [4] A rotational disorder with FWHM = 5° was observed.

For a Bi film on Au(100), a twelve-fold arrangement of diffraction spots is observed (Fig. 2b). Again, the structure can be clearly identified as Bi(012) from a single image by its visible reflections. Bi(012) domains were found at angles of 0°, ±28°, 90°, 90°±28° to the Au[100] direction, with the 0° and 90° domains being the most prominent. This agrees with available literature. [5] Previous experiments also reported the presence of ±15°, 45°, 90°±15°, 90°±45° growth directions for thin Bi films < 20 ML, which we could not confirm for any film thickness.

c) Microdiffraction of a Bi(110) deposit on Au(100): Bi(012) was electrodeposited onto Au(100) for 100 s at E = -0.25 V vs. Ag/AgCl by flowing 0.1 M HClO₄ + 1 mM Bi³⁺ through the cell's micro-fluidic channel at a speed of 10 μl/s. Under these conditions, Bi deposition is diffusion-limited and majorly effected by cell geometry and electrolyte exchange rate. A 10 × 20 μm² focused beam was used for spatially resolved investigation of the deposited film, revealing significant heterogeneities. As an example, Fig. 3a maps the intensity of an in-plane Bi(01-4) peak over the electrode surface, revealing a film thickness gradient along the direction of laminar electrolyte flow as well as from the centreline to the channel walls. While the film is unstrained in regions of thick Bi coverage, a slight strain of ~0.2 % can be observed in regions of thinner Bi coverage (Fig. 3b).

d) Investigation of thin Pr_{0.5}Ba_{0.5}CoO_{3-d} films on NdGaO₃ under OER conditions in 1 M KOH: The structure of a 40 nm film of Pr_{0.5}Ba_{0.5}CoO_{3-d} deposited by PLD on a 1 mm NdGaO₃ substrate was investigated in 1 M KOH during successive potential stepping from 0.5 V up to 1.2 V and during cyclic voltammetry between 0 V and 1.0 V (all potentials vs. Ag/AgCl). The data analysis for this part of the experiment is still in progress at the time this report.

e) Investigation of Co₃O₄ under OER conditions: Using the procedure described in [2], 30 ML of epitaxial Co(001) were grown on a substrate of 60 ML Au(111) on Si(111) (manufactured as per [3]). The Co layer was then (partially) oxidised to Co₃O₄ by stepping to a potential of E = 0.4 V vs. Ag/AgCl. A decrease in intensity at the Co Bragg peak positions could be observed, corresponding to the oxidation of approximately 1.5 ML of Co. However, we were not able to identify any Co₃O₄ diffraction peaks. The experiment was later repeated in traditional GID geometry at ID03 as part of beamtime MA-3074, where no Co₃O₄ diffraction peaks could be identified either. This suggests that the Co oxide formed *in situ* may be disordered.

3) Conclusion: We have shown that TSD allows structure and epitaxy determination from a single image, even for incommensurate deposits with many domains such as Bi on Au(111) and Au(100). Using a focused beam, spatially resolved studies of an electrodeposited Bi(012) layer on Au(100) could be performed, revealing heterogeneities associated with diffusion-limited deposition under laminar flow. This is important as many different electrochemical conditions can be probed in one experiment, significantly decreasing the time needed for the optimization of the deposition process.

References:

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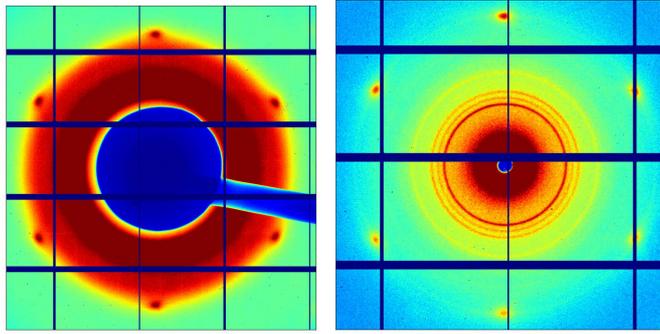


Fig. 1: Scattering from 0.6 mm Si(111) ($E = 70$ keV, vertical incidence) with the beam passing through 4.0 mm (left) and 0.5 mm (right) of electrolyte. Intensities are normalised to the Si 1st order peaks.

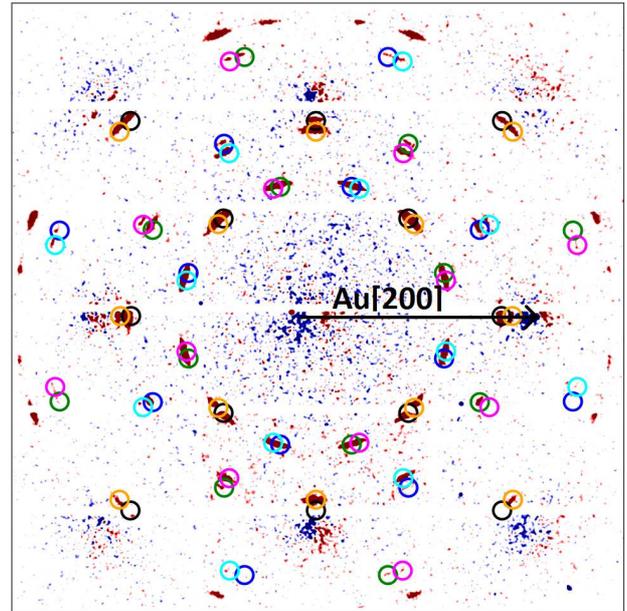
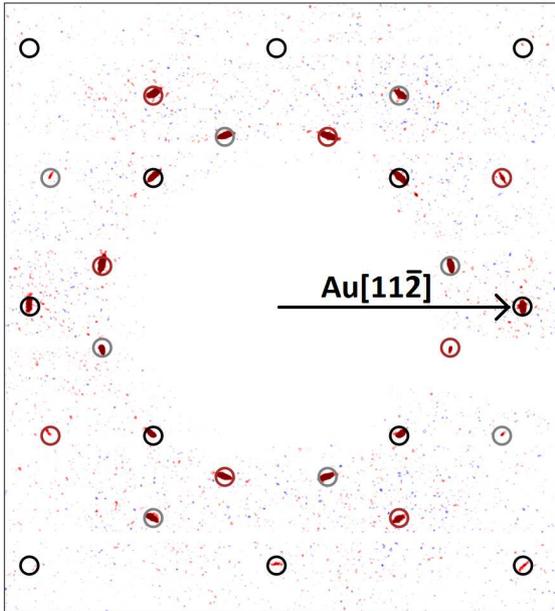


Fig. 2: Scattering ($E = 70$ keV, vertical incidence) from 30 ML Bi(012) electrodeposited on (a) Au(111) and (b) Au(100), displayed as intensity difference between scattering from the bare electrode and after deposition. Bi(012) peaks marked in the same colour belong (per image) to the same rotational domain. Some peaks are obscured by detector tile edges.

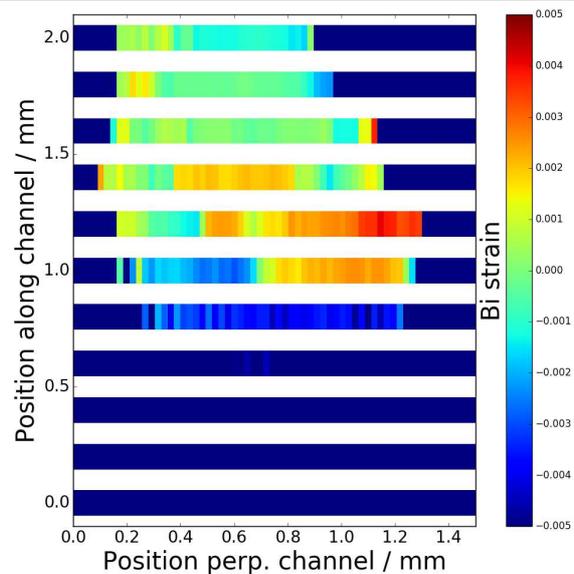
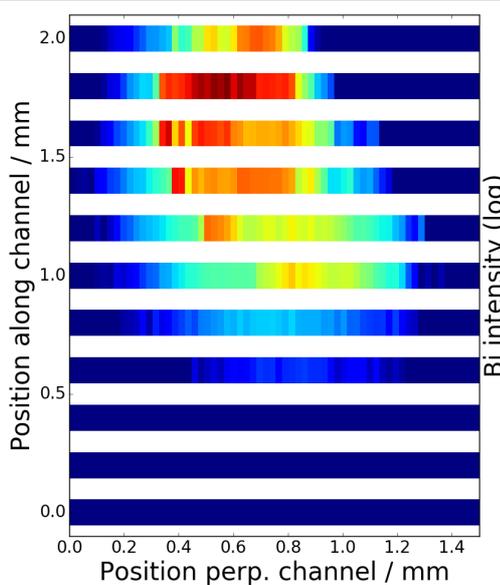


Fig. 3: TSD surface microdiffraction studies of a Bi(012) film on Au(100), demonstrating the extraction of structural properties. (a) Intensity (logarithmic scale) of an in-plane Bi(01-4) peak, corresponding with film thickness (b) Strain calculated from shifts in peak position. The electrolyte flow was along the up-down direction.