ESRF	**Experiment title:** In-situ studies of the structure and heteroepitaxial growth of electrodeposited bismuth films on Au(111)	**Experiment number**: **SI-1640**
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Shifts: 18	**Local contact(s)**: Mr Jerome ROY (e-mail: jerome.roy@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

F. Golks, K. Krug*, D. Kaminski*, J. Stettner, H. Zheng*, S. Morin* and O.M. Magnussen**

Report:

In this work in situ surface x-ray scattering (SXS) studies in transmission geometry on the heteroepitaxial electrodeposition of bismuth on Au(111) and Au(001) electrode surfaces were performed, using the "hanging mensicus" electrochemical cell employed in our previous experiments on homoexpitaxial electrodeposition [1]. Bismuth thin films exhibit interesting physical properties such as a very large magneto-resistance and electrochromic effects; Bi deposits in the submonolayer regime formed by underpotential deposition (UPD) have very good catalytic properties for important electrode reactions, e.g. oxygen reduction. The group of Prof. Morin has performed extensive studies on electrodeposited Bi films on Au, including in situ STM and ex situ x-ray diffraction studies with a laboratory source [2,3].

The potential-dependent structure of Bi adlayers in the UPD regime was studied by in situ grazing-incidence surface x-ray diffraction (GIXD). For Bi UPD layers on Au(111) a (2×2) followed by a (p×√3) structure at more negative potentials was found, which is in perfect agreement with results obtained in a previous SXS study employing a thin layer cell [4]. Bi UPD on Au(001) was previously studied only in an in situ STM investigation, where a sequence of three Bi adlayer structures of increasing packing density – a (3×3), a (√2×3√2)R45°, and a c(4×2) superstructure - were reported with decreasing potential [5]. The presence of the first two structures could be confirmed by in situ GIXD measurements, which also allowed to derive detailed models of these commensurate adlayer structures. In particular, the quantitative crystallographic analysis gave strong support for the unusual arrangement of Bi in tetramers within the (3×3) phase, proposed in the STM study (Fig. 1a). Furthermore, the higher resolution of SXS as compared to STM allowed to identify the c(4×2) superstructure as an uniaxial incommensurate c(√2×p√2)R45° phase with substantial potential-dependent electrocompression that increases linearly with decreasing potential (Fig. 1b and c).

The structure of thin bismuth films on Au(111) and Au(001) was studied by in situ GIXD and out-of-plane x-ray measurements. By deposition at potentials 10 to 20 mV more negative than the Nernst potential (i.e. at low Bi deposition rates) films of defined thicknesses between 3 and 36 monolayers were created. Subsequently, the crystalline structure of these Bi films was characterized at the Nernst potential, where the films are stable. On both substrates (012)-oriented Bi films were observed. For Au(111) the measurements revealed the same epitaxial arrangement, reported in the previous ex situ studies of much thicker films (≈200 ML) [3]. The Bi(012) deposits on Au(001) were found to exhibit two different epitaxial orientations with the [100] axis parallel or ±28° rotated relative to the [001] direction of the Au substrate lattice. In the early stage of film growth (3 ML) the Bi unit cell is significantly expanded compared to bulk Bi crystals. This is most noticeable along the surface-normal direction, where a lattice expansion by 10% was observed, while the in-plane lattice was expanded by only 2 to 3%. With increasing film thickness the bismuth lattice structure contracts. Measurements at 36 monolayers thick films are in perfect agreement with literature values for Bi

crystallographic parameters. At all film thicknesses the peaks of the c(√2×p√2)R45° UPD phase were observed parallel to those of the bulk Bi lattice, suggesting that the surface either is only partly covered by a 3D Bi deposit or that the UPD layer structure is maintained even underneath thicker Bi films.

In summary, these measurements allowed to in situ follow the structural evolution of bismuth films formed by heteroepitaxial electrodeposition on Au(111) and Au(001) from the monolayer regime up to a film thickness of 36 layers. The obtained data confirmed and refined previous structural data on Bi adlayers and allowed to determine the epitaxial arrangement and structural relaxation of the Bi multilayer films.

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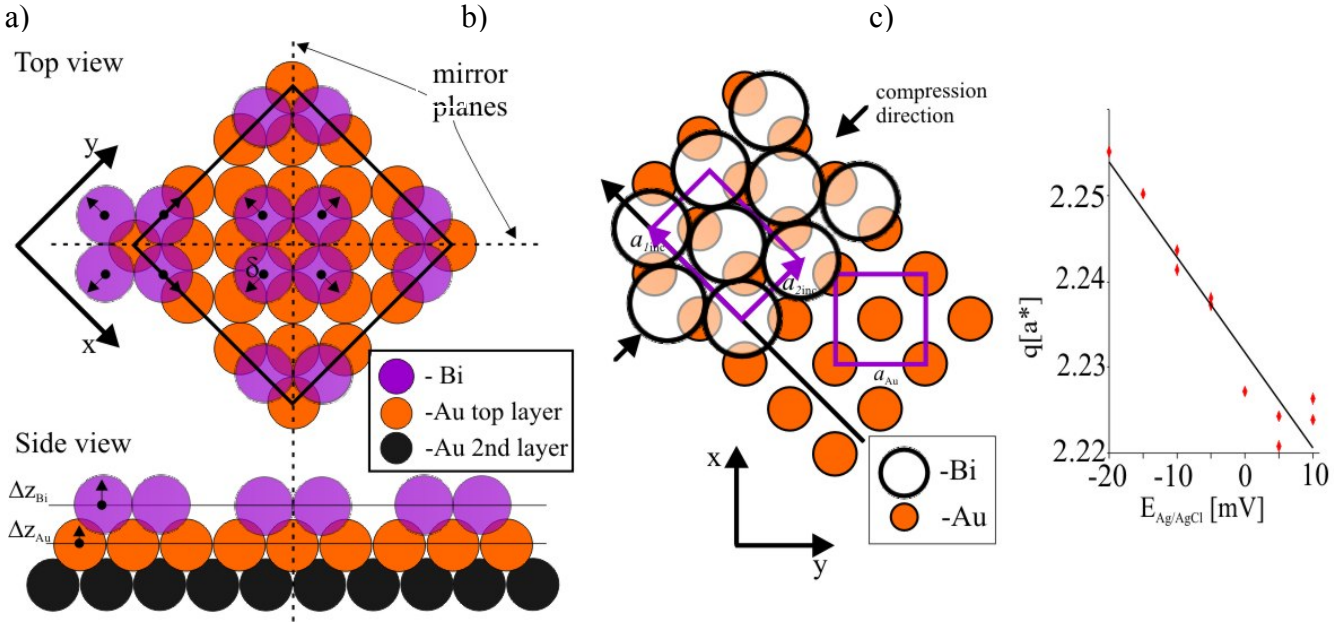

Figure 1. Schematic illustration of **(a)** the (3x3)-Bi UPD adlayer (arrows indicate the allowed Bi relaxation directions in the fitted model) and **(b)** c(√2×p√2)R45° adlayer. **(c)** Shift of the (q·√2, q·√2, 0.1) reflection with potential, showing the electrocompression of the incommensurate c(√2×p√2)R45° phase.