



	<b>Experiment title:</b> Structure of Self-Assembled Monolayers (SAMs) from Thiol-Functionalized Oligothiophenes	<b>Experiment number:</b> SC-693
<b>Beamline:</b> ID10B	<b>Date of experiment:</b> from:23/02/2000 to: 29/02/2000	<b>Date of report:</b> 29/02/2000
<b>Shifts:</b> 18	<b>Local contact(s):</b> B. Struth	<i>Received at ESRF:</i>
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### Report:

The experiments have just finished the last week on the line ID10B with B. Struth and D. Smilgies . So , we just give here only a brief report of data .

The purpose of our measurements was to study the crystalline structure of thiol monolayers mainly functionalized by oligothiophenes (C12SH,  $\alpha$ -3T C6 SH,  $\alpha$ -4T C12SH) and grafted on metal . The monolayers adsorbed from solutions were adsorbed onto gold substrates. Gold was evaporated on glass covered with a thin chromium layer . The substrates were annealed in a hydrogen flame taking care to control the metal temperature . This flaming induces the formation of (111) terraces as shown by electrochemistry and STM.

The first X-ray measurements were focused on the substrate structure . They are polycrystalline with many (111) terraces . The substrates behaves as a 2D powder with a mosaic of grains .

Concerning the organic layers , we have carried out Specular Reflection (SR) measurements and Grazing Incidence Diffraction (GID; incidence angle  $0.4^\circ$ ; out of incident plane angle  $\gamma$ ) . These experiments have required very fine adjustments of the beam line because the quality of the gold substrate . One sample has been discarded because of its large roughness and/or lack of planarity.

The SR measurements have given evidence of interferences due to the organic layer . We have never got data indicating any layer damage . We expect to determine from these data the thickness of the layers and hence the molecule tilt angle.

Concerning the GID , we did not observed diffraction peaks for both the alkylthiol C12SH and the shorter functionalized thiol 3TC6SH . This could be due to difficulties of adjustments in regard with the quite poor quality of substrates . Concerning the 3TC6SH, no evidence has been given in the literature of crystallinity for such layers whereas the self assembling has been proved .

Fortunately, the last experiments of GID with  $\alpha$ -4T C12SH have shown very interesting diffraction peaks at  $d= 5.35\text{\AA}$  and  $4.2\text{\AA}$  . The first one was observed both at  $\gamma= 0$  and  $3.8^\circ$  and the second one only at  $\gamma=3.8^\circ$ . Hence , we conclude that the oligothiophene functionalized thiol monolayer is crystallized. Detailed analysis of data is now required notably for the assignment of the peaks to chains and/or to thiophene moieties crystallinity. The large width of the peaks should indicate rather small grain size, or large variation of molecular orientation.

In conclusion, in spite of the quite poor quality of substrates , very promising data have been obtained since it is the first time that crystallinity of oligothiophene functionalized thiol monolayers is reported . Others techniques such as IR spectroscopy have only given evidence of the self assembling of the molecules . Further investigations are now required with substrates of best quality in order to improve crystallographic data .

Proposal for further experiments

We shall study the crystallinity of these self assembled layers with the same gold substrates after optimizing the preparation and annealing technique in order to i) improve the optical and structural properties of gold surface ii) increase the organic grain domain size and homogeneity . Single crystals of Platinum and gold will also be used.

We also intend to investigate the structure of thiols layers prepared through an electrochemical way : short molecules such as  $\alpha$ -3T-C6 (without thiol function ) can be electrochemically grafted on the previously studied monolayers of  $\alpha$ -4TC12-SH . Finally , we will study the structure of thiol monolayers formed from mixture of alkyl and functionalized thiols.

For the next six months , the same beam time as for the first study (18 shifts ) is at least required .