

**Experiment title:**

GIXD investigation of homo- and hetero- epitaxial films of oligothiophenes grown on top of oligothiophene single crystals by Organic Molecular Beam Deposition

Experiment number:

SI-1410

Beamline:

ID03

Date of experiment:

from: 20-sept-06 08:00 to: 26-sept-06 08:00

Date of report:

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Shifts:

18

Local contact(s):

Roberto Felici

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

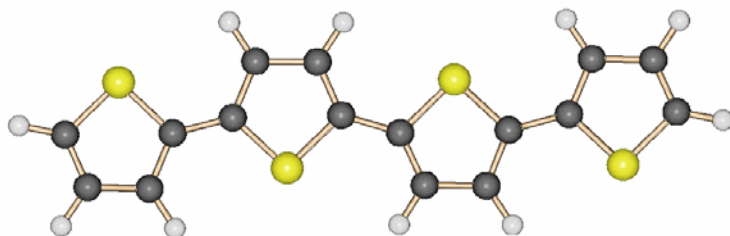
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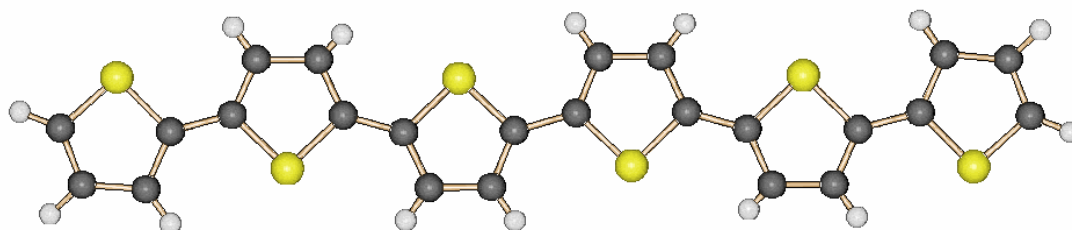
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Report:

Single crystals of the low and high temperature polymorphs of α -hexathiophene and α -quaterthiophene have been grown in our labs by vapour phase techniques. They appear as thin flakes, some hundreds of nm thick and several mm² large. Crystalline samples were placed on a glass plate 1x1 cm² in size contacting their (001) face. The surface diffraction experiment have been carried out by putting these samples in a custom chamber ensuring dry nitrogen atmosphere. The beam energy was 19 keV and the incidence angle was set to 0.3°. No X-ray beam shutter in front of the sample was available during experiment dead times as it was required in our proposal



α -quaterthiophene



α -hexathiophene

The aim of the experiment was the study of surface relaxation/reconstruction phenomena of molecular organic materials by the collection of fractional order scattered intensity (Crystal Truncation Rods) along a direction orthogonal to the surface plane exposed by the samples. In general, surface reconstruction for molecular solids is a phenomenon seldom studied and recognized. Of course, in the case of these films, studied for their exploitation in electronic devices, a detailed knowledge of their surface structure is required. In the last years we invested a lot of time on investigating oligothiophenes as single crystals and thin films, and some indications of possible surface reconstruction emerged from detailed Atomic Force Microscopy characterization of these systems.

After an accurate alignment of the samples, L-scans have been performed for three relevant rods for each sample. For low temperature α -hexathiophene single crystals these were $(-1\ 1\ L)$, $(-1\ 3\ L)$, $(0\ 3\ L)$. Then, for each rod, data were collected performing a small theta-scan for each fractional value of L. The integrated intensity of the $(-1\ 1\ L)$ rod performed with the ANA program (downloaded from the ESRF web site) is shown in Figure A. Work in progress consists in the refinement of the surface structure of the crystal by means of the program ROD through simulation of the rod diffraction patterns. Figure B reports the diffracted intensities calculated for the unrelaxed structure of the (001) surface of α -hexathiophene indicating there are relevant structural differences between the real structure and the truncated bulk structure. Unfortunately, molecular complexity, and therefore the number of structural parameters to be refined, poses harsh problems to the refinement. Since collected CTR data alone are not sufficient to refine an unconstrained structure, constrained refinement (bond length and angles fixed) by modifying programme ROD will be flanked and aided by molecular dynamics simulations with improved potentials specifically developed for oligothiophenes.

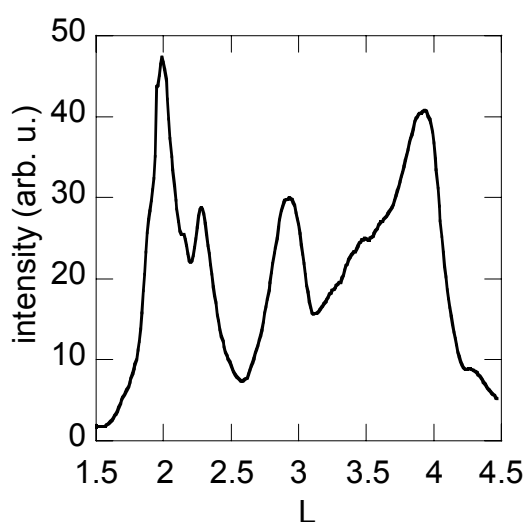


Figure A. $(-1\ 1\ L)$ rod diffraction collected on a α -hexathiophene (low temperature polymorph) single crystal.

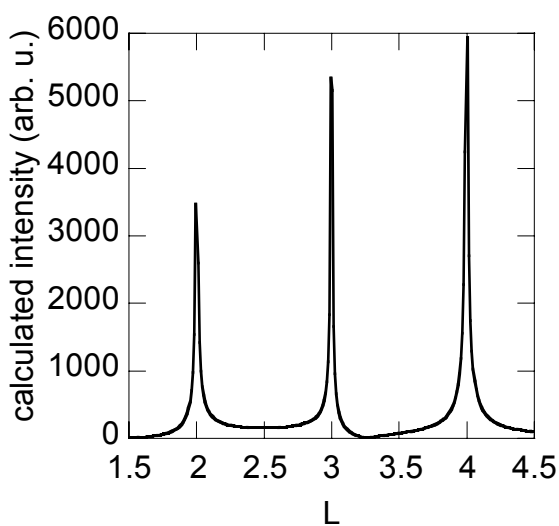


Figure B. $(-1\ 1\ L)$ rod calculated on the basis of the unrelaxed structure of α -hexathiophene as single crystal

The same procedure has been adopted for single crystals of α -quaterthiophene and for films deposited on these single crystals: one sample with a 10 nm deposit of α -quaterthiophene on the low temperature polymorph of α -hexathiophene, and another one with a 2 nm deposit of α -quaterthiophene on the high temperature polymorph of α -hexathiophene. Unfortunately, due to the continuous exposure to the X-ray beam, a progressive transition of the high temperature polymorphs of both α -quaterthiophene and α -hexathiophene to their corresponding low temperature polymorphs has been observed during measurements induced by X-ray photons; this is particularly evident and serious for α -quaterthiophene single crystals. Hence, we believe that data collected on α -quaterthiophene are not reliable being a mixture of contributions arising from different crystal structures.