EXPERIMENTAL REPORT

Title : Depth resolved structure of highly oriented hybrid films based on poly(3-hexyl-thiophene) and CdSe nanocrystals.

Experiment number: HS4498
Instrument ID10B
From 26/08/2011 to 30/08/2011
Local contact: A. Vorobiev.

Purpose of the proposal:
The in-plane and out-of-plane structures of highly oriented and crystallized thin layers (80-150 nm in thickness) of pure poly(3-hexylthiophene) and of the hybrid material made of poly(3-hexylthiophene) (P3HT) and CdSe nanocrystals have been studied by GIXRD for different values of the incidence angle in order to characterize the evolution of the structure of the material with depth. We have dealt with different types of samples:

1) Free defect low mass (5kDa) P3HT crystallized by slow Directional Epitaxial Crystallization (DEC) method [1] (sample name: P3HT 507 Cambridge).
2) A high mass (50kDa) P3HT provided by Merck and then prepared by slow DEC.
3) An intermediate mass (20 kDa) P3HT provided by Merck and then prepared by slow DEC.
4) A hybrid sample prepared with the 20kDa P3HT and spherical nanocrystals of CdSe of 5 nm in diameter in 1:1 proportion in mass.

In addition to the samples prepared by slow DEC, we have also studied pure polymer and hybrid samples prepared in the following way: the initial sample was first obtained by doctor blading on the substrate. Then the sample is rubbed by a roll whose rotation speed is controlled [2]. Several rubbing steps were typically applied to theses samples. The samples prepared following such a procedure were the following ones:

5) The low mass P3HT from the hexane fraction rubbed 2 times.
6) The 20 kDa P3HT from Merck rubbed 0 and 2 times.
7) A hybrid sample made with the 20 kDa P3HT and nanorods of CdSe 5nm in diameter and 25 nm in length in 1:1 proportion in mass and rubbed 0, 1, 2 and 3 times.

Measurements
The beamline was adjusted at the 21,22 keV incident energy (λ = 0,584 Å).
In-plane GIXRD measurements were systematically carried out by varying the incidence angle (from 0,01 to 0,06°) while the sample was rotated in the diffraction plane from 0 to 90° respectively to the incident beam. 2D images were recorded by using CCD camera.
Alternatively it was also possible to swap the CCD camera with a punctual detector. In such a case we could record in-plane diffractogramms at a given incidence angle (typically 0,06°) by positioning alternatively the sample at 0 and 90° respectively to the incident beam. The out-of-plane structure could also be probed by recording diffractogramms in reflection in symmetrical geometry.

Results
Several significant results could be obtained. It is difficult to show all of them in details in this report, we will just give a summary of the most significant ones:

1) concerning the “defect free” low mass P3HT crystallized by DEC, we could realize that several kinds of crystal types coexist in the sample. One set of crystals in which polymer

chains are placed flat-on on the substrate, very well aligned in the plane since their in plane signatures is lost when the sample is turned at 15°; a second set of crystals with the polymer chains lying edge-on on the substrate are then found at 45° in plane. Finally we also could detect a third set of crystals almost perpendicular in –plane to those with flat-on arrangement but these crystals exhibit a fibre symmetry… All this information could be obtained owing the omega in plane rotation of the sample.

2) By contrast, the same set of measurements performed on a high mass P3HT proved that in such a case we are exclusively dealing with crystals with fibre symmetry. The long axis of these fibres is well aligned in the plane giving a gain a mosaic around 15°.

The most significant results concern now the rubbed samples.

3) The clearest situation has been obtained with the 20 kDa P3HT sample. We have changed the incidence angle from 0,01° to 0,06° to probe the in depth structure of the layer. When the sample is not rubbed, we find 100% of the sample with crystals lying with chains edge-on on the substrate. After rubbing one time, at an incidence angle of 0,01°, we obtained a signature of crystals with a flat-on configuration while at 0,06° we found still crystals with edge-on configuration. After rubbing 2 times all the crystals have been rotated to a flat-on configuration. Thus it is a real experimental proof of what we had only speculated previously on results the only based on TEM.
4) For low mass P3HT the situation is the same but in such a case we still see some crystals with fibre symmetry which are not modified by rubbing.
5) Finally the other very good result concerns the hybrid material made of 20 kDa P3HT with nanorods of CdSe. When the sample is not rubbed, most of the polymer crystals are edge-on while the majority of nanorods are lying e with their long axis in the plane and showing the typical biaxial symmetry in te plane perpendicular to the substrate. When such a sample has been rubbed Two times, all te polymer crystals have been rotated again to the flat-on configuration and moreover, we can check that the in-plane organization gives the same orientation distribution of long axis of chains and long axis of nanorods (app. 30° of spread).

In conclusion, this experiment has been extremely fruitful and these significant results will come to complete the thesis of Lucia Hartmann (defended probably on early April). Morever these results will be published soon.

However, me must remark that we could not differentiate in any hybrid sample different layers with different electronic densities which could result in the depth of the sample in a “sandwich” structure which has been deduced from electron tomography analysis performed on hybrid sample P3HT-CdSe spheres obtained by DEC. As we know that in such a structure we have in fact first a upper thin layer of CdSe, then P3HT layer, then hybrid layer P3HT+CdSe and then P3HT layer, taking into account the very effective scattering power of CdSe crystals compared to the polymer, we are not in the best situation to probe these differences with enough accuracy. Another reason may come from the difference of thickness of respective samples prepared for electronic tomography analysis and those we have studied at ESRF respectively.