ESRF	**Experiment title:** **Search for mechanical strain in epitaxially grown thin films of sexiphenyl**	**Experiment number:** **SI-898**
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Shifts: **9**	**Local contact(s):** **Oleg Konovalov**	*Received at ESRF:*

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Report:

As in the proposal for the beamtime application suggested, epitaxial grown thin films of sexiphenyl on mica(001) substrates were investigated during nine shifts of beamtime at the surface diffraction beamline ID10B. It was our first beamtime at the ESRF and the first experience at the beamline ID10B, this beamtime gave us the possibility to get familiar with the experimental set-up of a '2+2' surface X-ray diffractometer. The applicability of this experimental set-up for structural research on epitaxial grown thin films of sexiphenyl was tested for out-of-plane scattering and for in-plane scattering (surface diffraction). The experimental parameters to investigate layers of sexiphenyl at this beamline have been determined, limiting parameters evaluated and first interesting results in direction of the goal of the proposal were obtained. In fact the performed experiments have brought us closer to the goal to understand the epitaxial order in thin films of sexiphenyl on mica(001) and to verify mechanical (or residual) strain in this type of epitaxial grown thin film. A detailed evidence for mechanical strain could not be reached finally.

1. DEGRADATION OF THE SEXIPHENYL LAYERS DUE TO BEAM DAMAGE

As generally known high intensity X-ray radiation can damage organic layers. Not directly the primary beam is responsible for the destruction of the organic material, but, secondary processes like photoelectrons or chemical reactive ozone are responsible for material degradation. To monitor the material degradation one single Bragg reflection was investigated by a series of scans performed continuously over a period of several hours. Figure 1 gives the first performed scan (filled circles) and the final scan after an exposure of four hours. The intensity decreases about one order of magnitude, however, the peak shape and the peak position remains constant.

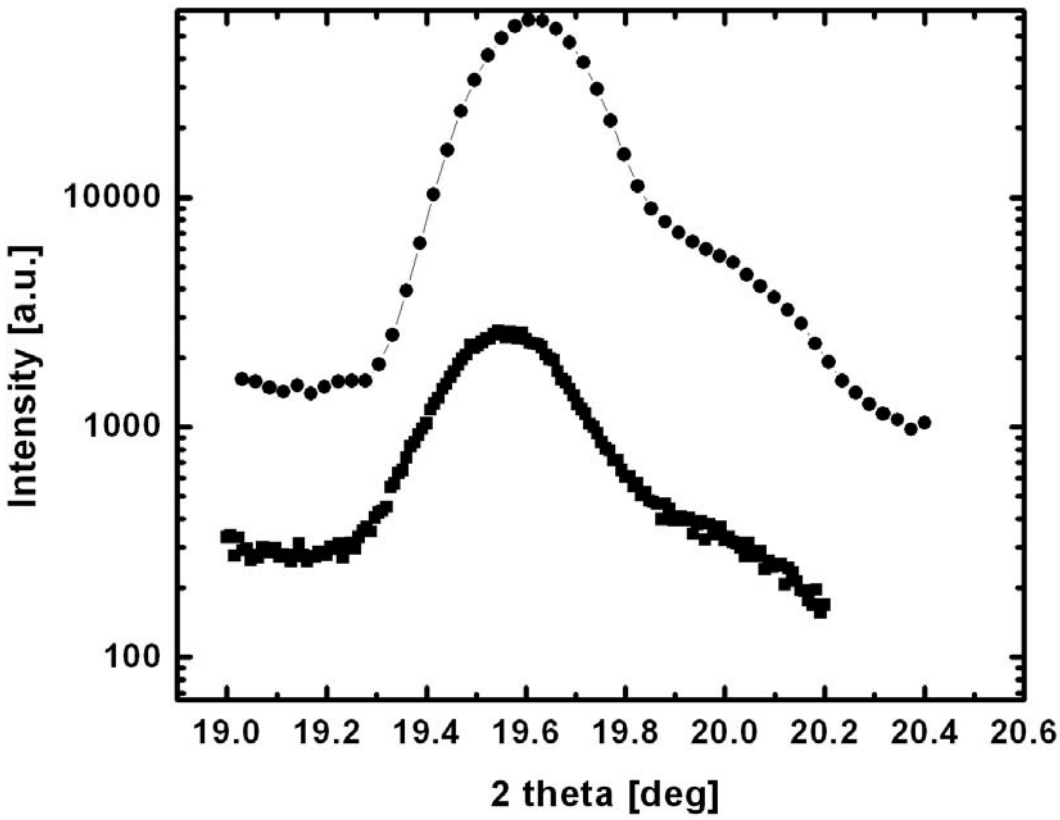

Fig.1: Radiation damage of the organic layer due to the high intensity primary beam with an energy of 8keV. Two scans on a single diffraction peak are shown; one gives the initial scan directly at the beginning of irradiation (filled circles), the second one gives the same scan after irradiation of four hours at the same area (filled squires). The experiments were performed on a sexiphenyl thin film grown on mica(001) with an average thickness of 7 nm.

2. FIRST EXPERIENCE IN SURFACE DIFFRACTION

The field of surface diffraction is highly interesting and application relevant, since extremely thin films down to the monolayer regime can be investigated. Information about the lateral order in monolayers thickness can be obtained. Since the order in the first monolayers are crucial for the formation of epitaxial grown films (or crystallites within the film) and due to the fact that in several device applications of sexiphenyl (e.g. in case of organic field effect transistors) the interface and the charge transport within the first monolayers are crucial for the device performance, a detailed knowledge of the structural properties of the first monolayers are very important.

Therefore, the experimentalists of this project (Resel, Oehzelt, Haber, Andreev) were highly interested in performing surface diffraction on their samples. The beamline scientist (Konovalov) gave a nice introduction to the method and showed directly the performance of experiments. In fact, surface diffraction on the samples could be observed; reflections arising from epitaxial grown sexiphenyl as well as from the substrate material mica are verified. In-plane reflections of the epitaxial grown layer of sexiphenyl reveal the characteristic of the epitaxial growth of sexiphenyl on mica surfaces. In Figure 2 surface diffraction of the 21-3 reflection of bulk sexiphenyl is shown. The multifold observation of the 21-3 reflection is in fully agreement to the already known features of epitaxially grown sexiphenyl. However, the unexpected broad features of sexiphenyl reveal unexpected weak order within the film.

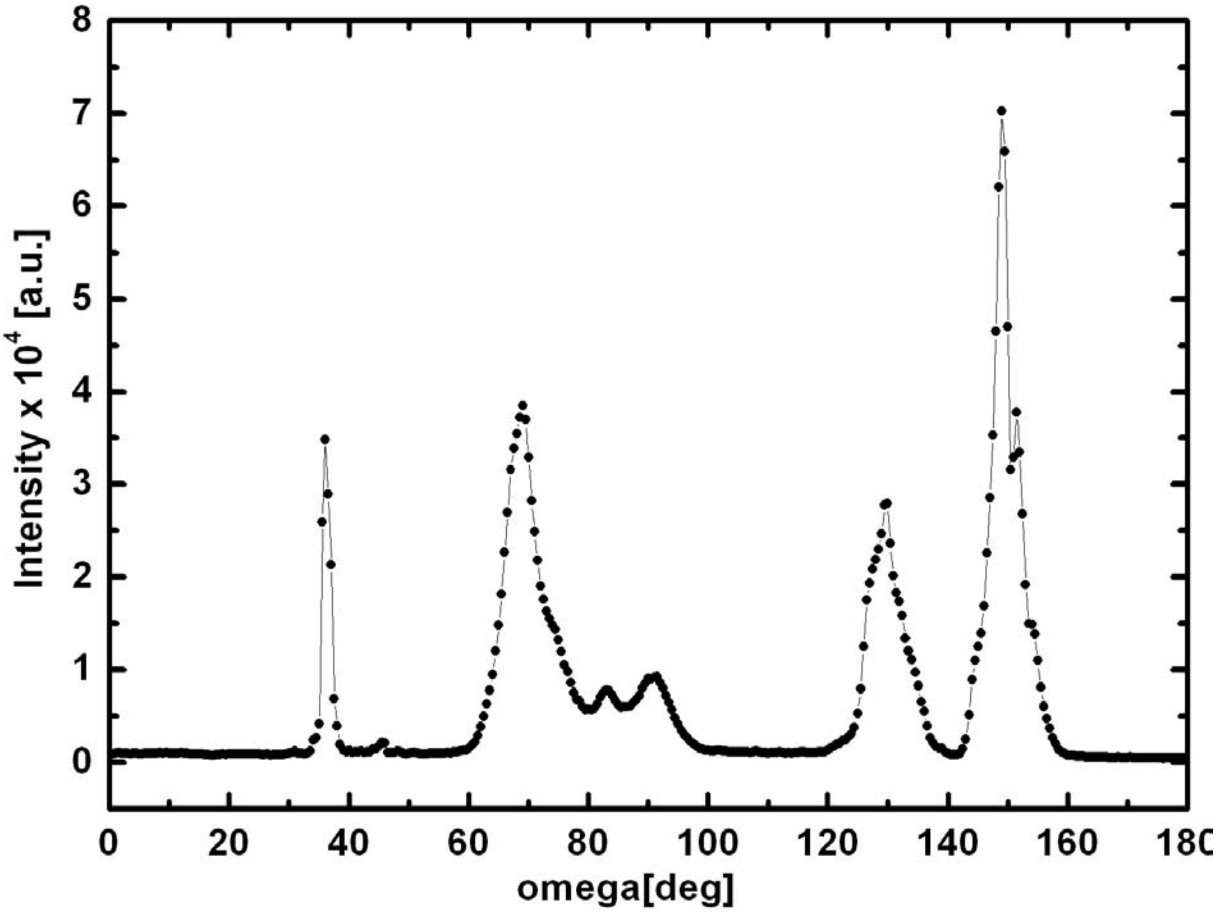

Fig. 2: Grazing incidence diffraction of the 21-3 reflection of epitaxially grown sexiphenyl crystallites. As expected the reflection is observed at six different rotation angles, this corresponds to the six different epitaxial relationships of epitaxially grown sexiphenyl on mica(001). The experiment was performed on a sample with an average thickness of 68 nm.

3. SEARCH FOR OUT-OF-PLANE REFLECTIONS

The vertical configuration of the '2+2' goniometer uses the angles *om* and *th* for sample movement and the angles *gam* and *del* for movement of the detector. Using the angle *om* for sample movement and the detector angle *gam*, in-plane reflections can be observed by surface diffraction (grazing incidence diffraction), by this method reflections with the scattering vectors parallel to the surface of the sample are accessible. On the other hand by using only the angle *th* for sample movement and the detector angle *del*, the widely used geometry for powder diffraction with scattering vectors perpendicular (and close to the perpendicular direction) to the surface of the thin films are accessible.

Examples for reflections of both types are depicted above in Fig.1 (scattering vector perpendicular to the surface of the sample) and in Fig.2 (scattering vector parallel to the surface of the sample). However, the activation of defined reflections with scattering vectors in intermediate directions (in the whole orientation space) orientations was not possible for the experimentalists.

A partial overcome of this problem was reached by using additional circles of the goniometer (the *chi* - and the *phi* – circle). Special macro-routines of the SPEC software were developed, and even with this solution only a limited number of out-of-plane reflections of the epitaxially grown sexiphenyl layer were accessible. However, the limited access to the reflections of the epitaxially grown sexiphenyl film made an exact performance of the initial beam time proposal impossible. Nevertheless, additional two reflections of the epitaxially grown sexiphenyl could be investigated in detail.

In principle a full solution of this problem would be possible. The goniometer angles *om* and *th* and the two detector angles *gam* and *del* have to be specially combined in order to get an Eulerian geometry (2Θ, ω, ψ, φ) of the goniometer. The connection between the goniometer angles of the "2+2"-geometry to the four angles of an Eulerian geometry are determined after returning home from the ESRF-beamtime. Starting from the knowledge of the four Eulerian angles the corresponding angles *om, th, gam, del c*an be determined by following equations:

$$\psi = \arccos\left(\frac{2}{\sqrt{\left(1+\frac{1+\cos 2\Theta}{\sin del}\right)^2\left((\cos 2\Theta - 1)^2 + \left(1-\frac{\cos 2\Theta}{\cos del}\right)^2 + (\sin del)^2\right)}}\right)$$

$$gam = \arccos\left(\frac{\cos 2\Theta}{\cos del}\right)$$

$$om = \varphi + \arccos\left(\frac{\left(\cos\left(\frac{del}{2}\right)\right)(1+\cos 2\Theta) + \left(\sin\left(\frac{del}{2}\right)\right)(\sin del)}{\sqrt{(1+\cos 2\Theta)^2 + (\sin gam)^2 + (\sin del)^2}}\right)$$

$$th = \frac{del}{2} + \omega - \frac{2\Theta}{2}$$

Unfortunately an analytical solution for obtaining the "2+2" goniometer angles (*om, th, del, gam*) for given Eulerian angles (2Θ, ω, ψ, φ) is impossible. Therefore the goniometer angle *del* has to be determined by numerical methods from the first equation by using 2Θ and ψ as input parameters.

4. RECIPROCAL SPACE MAPS

The highly collimated beam at the beamline ID10B makes a mapping of reciprocal lattice points possible. The mappings give information about the degree of orientation of the epitaxially grown sexiphenyl crystallites and it reveals also the structural perfection of the substrate. In principle, signs of mechanical strain in the lattice of the sexiphenyl crystallites should be possible to observe by reciprocal space maps.

Figure 3 gives one example of a reciprocal space map of the 11-1 reflection of sexiphenyl. The obtained reciprocal space maps are first data, and it seems that the obtained data at the current stage are not sufficient for a detailed characterisation of the epitaxial layer. The amount of data is too limited for publication. Further experimental series on the system have to be performed.

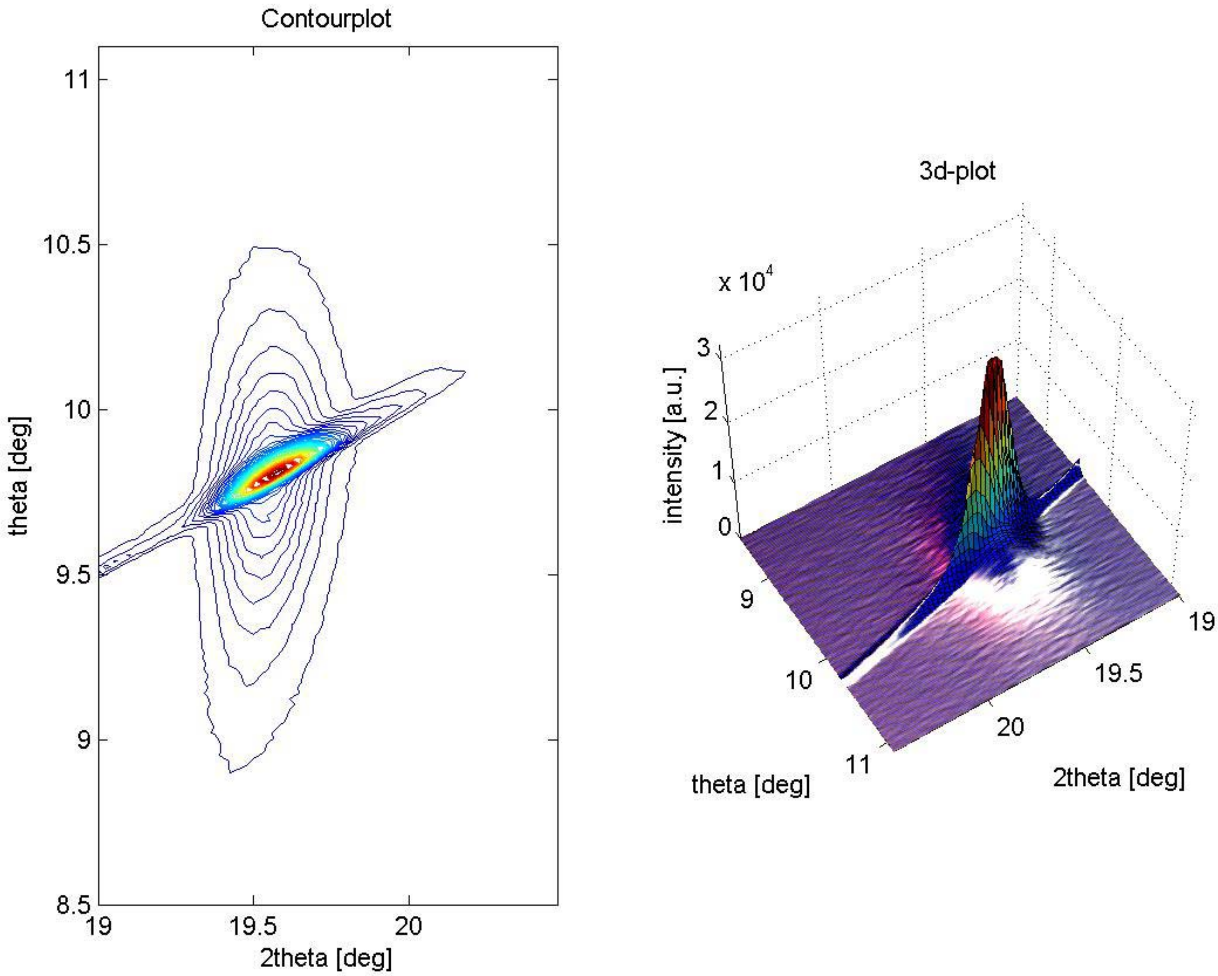

Fig.3: Reciprocal space map of the (11-1) reflection of sexiphenyl. The map was taken from a sample with an average thickness of 7 nm, the degradation of the organic layer during the experiment was corrected.

5. CONCLUSION

The beamline ID10B at the ESRF fits excellent for the structural characterisation of epitaxially grown organic films. The typical scattering angles of the organic materials are in the easy accessible range of the detector movement. Interesting scientific work on the epitaxial growth of organic molecules down to the monolayer regime can be performed.

For a detailed investigation of epitaxially grown organic films the control system of the goniometer has to be extended in a way so that investigations under an Eulerian geometry are possible. Additional new routines within the SPEC control software should solve this problem.

The degradation of the organic samples has to be taken careful into account. Experimental precautions like a domed sample chamber can minimize this effect. However, a careful observation of the sample degradation during the experiment would be always necessary.

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