ESRF	**Experiment title:** **Evolution of epitaxial order in sexithiophene films grown on TiO_2(110)**	**Experiment number**: **SI-1160**
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Shifts: **17**	**Local contact(s)**: **Sean O'Flaherty**	*Received at ESRF:*

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Report:

INTRODUCION

Sexithiophene (6T) is a frequently used molecule for fundamental research as well as for device physics. During the last year the experimental team has investigated the epitaxial growth of sexiphenyl on TiO2(110) surfaces: Surface science techniques STM, NEXAFS, UPS and ARUPS investigations are carried out on films with monolayer thickness up to the multilayer regime. The film morphology 0f 0.5 to 5nm thick films is investigated by AFM. The crystallographic structure is investigated by laboratory XRD probing films with a thickness of 100nm.

EXPERIMENTAL STUDY

The aim of the present experiment is to perform structural studies on epitaxially grown films of 6T. Three different types of surfaces are used within this study: a reconstructed TiO2(110) surface, a non-reconstructed TiO2(110) surface and an organic template of sexiphenyl (6P) grown epitaxially on TiO2(110). Films with nominal thicknesses between 0.5nm (monolayer coverage) and 5nm are studied. The films are investigated by specular diffraction, grazing incidence in-plane diffraction (surface diffraction) and grazing incidence out-of-plane diffraction.

Epitaxial order of 6T on reconstructed TiO2(110) surface:

By specular scans the 020 reflection of the low temperature phase of 6T (LT-6T) is observed at $2\delta = 16.48°$. In case of in-plane diffraction the peak series h00 with h = 2, 4, 6, 8, 10 and 12 is observed. The analyses of the h00 peaks (surface diffraction) in combination with the reflection peaks of the substrate lead to the epitaxial relationships with high angular precision. Figure 1 shows an AFM micrograph together with a ω–scan via 200 reflections and the resulting orientations of the molecules within the epitaxially grown crystallites. The specific morphology of 6T shows elongated islands with a characteristic tilt angle of 43° relative to each other. This morphologhy can be explained by two facts: i) the molecules are aligned along the oxygen rows of the TiO2(110) surface and ii) based on these specifically aligned molecules the crystal

structure of 6T is formed which results in molecular rows of 6T molecules. Arrows are dawn along the molecular layers. Different epitaxially aligned crystallites show an inclination angle of 43° relative to each other which is reflected within the XRD pattern and also in the AFM micrograph. The observed 3° tilt of the long molecular axes relative to the oxygen rows are not well understood yet.

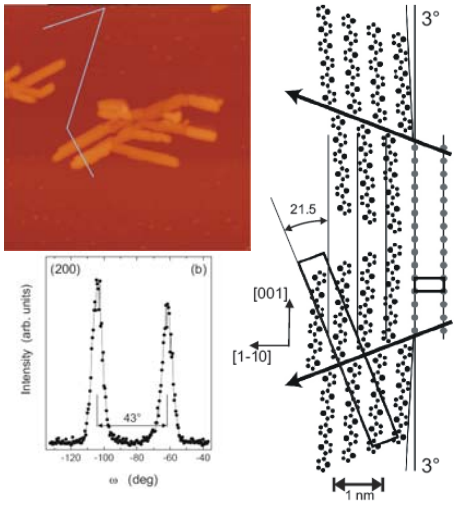

Figure 1: An AFM micrograph of a 5nm thick film of sexithiophene grown on a reconstructed TiO2(110) surface (top left). An in-plane rocking curve (ω - scan) of the 200 peak of the sexithiophene low temperature phase revealing two differently oriented crystalline domains (bottom left) and the resulting alignment of the molecules relative to the TiO2(110) oxygen rows drawn by vertical lines (from J. Ivanco et al. Surf. Sci. submitted)

The investigation of a 0.5nm thick film (monolayer thickness) does not reveal any result, although the expected intensity should be high enough to be detected. Neither specular scans nor in-plane scans lead to any hints of the expected peaks. This result has some correlation with the morphology studies of this monolayer film. Instead of aggregated elongated islands (as depicted in Fig.1) a structureless morphology is observed. Weak order within the first monolayer can be suggested.

A detailed analysis of the diffraction peaks is performed on samples with thicknesses of 1.6nm and 5nm. Out-of-plane rocking curves are performed on the 020 reflection and in-plane rocking curves are measured on the 200 and $\underline{12}00$ reflection. It turns out that with increasing film thickness the rocking curve width decreases. This is observed for in-plane as well as for out-of-plane rocking curves.

Structure of 6T films on non-reconstructed TiO2(110) surface:
The growth morphologies on the non-reconstructed TiO2(110) surface shows completely different features. A typical terrace like growth is observed. Unfortunately only a single diffraction peak is observed by specular diffraction, which cannot be assigned to any of the known crystal structures of 6T. No peak could be found by in-plane diffraction. This experimental fact suggests that this film is also epitaxially grown. However, it seems that a polymorph phase with unknown crystal structure is mediated by the TiO2(110) surface.

Structure of 6T/6P organic heterostructures on reconstructed TiO2(110) surfaces:
Organic heterostructures of 6T / 6P on TiO2(110) reveal interesting growth aspects of both materials side by side and on top of each other. It could be shown that the out-of-plane rocking curves of this system are anisotropic, probably due to the anisotropic film morphology. Moreover, it could be demonstrated that the crystallisation of 6T can follow the orientation of 6P molecules.

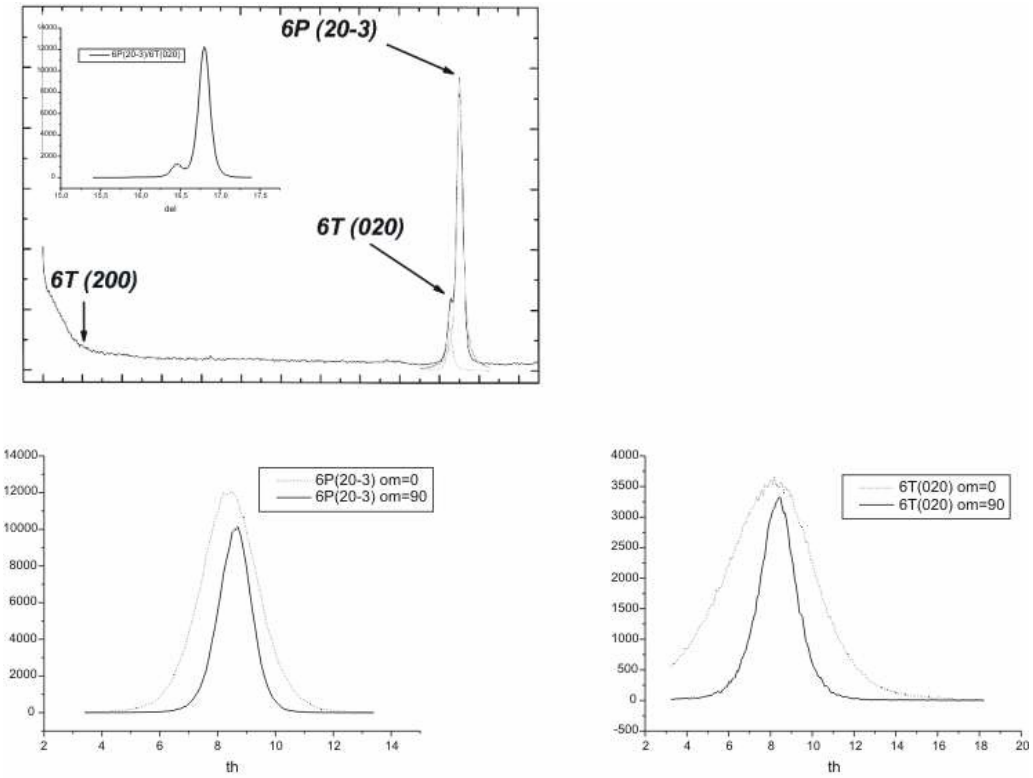

Figure 2: A specular scan of an epitaxially grown organic heterostructure of 5nm sexithiophene on 5nm sexiphenyl on TiO2(110) (above). Out-of-plane rocking curves of the 20-3 reflection of sexiphenyl (bottom, left) and of the 020 reflection of sexithiophene (bottom, right). Due to the anisotropic shape of the crystallites, two different types rocking curves in specular geometry can be observed (from G. Koller, Adv. Mater. submitted)

CONCLUSION

- The TiO2(110) single crystal surface is an excellent substrate for surface diffraction studies.
- No detectable beam damage of the 6T material at 11keV radiation under vacuum conditions.
- The epitaxial order of 6T-films with thicknesses of 1.6nm and 5nm (nominal film thickness) could be easily detected.
- The orientation of the 6T molecules within the epitaxial order could be determined with an accuracy ± 1°, with the result that the long axes of the 6T molecules are tilted 3° away from the oxygen rows of the TiO2(110) surface.
- There is a clear correlation between epitaxial order / crystallographic structure and thin film morphology
- The rocking widths of the in-plane peaks 200 and of out-of-plane peaks 020 are several degrees broad. Both rocking widths decrease drastically with increasing film thickness, which implies that the degree of epitaxial order enhances with film thickness.
- There are anisotropic rocking widths in the 6P / 6T heterostructure
- The epitaxial order in the film with a thickness of 0.5nm (nominal film thickness of one monolayer) could not be observed. The totally different film morphology suggests weak or no epitaxial order in the first monolayer.

PUBLICATIONS:

J. Ivanco, T. Haber, J. R. Krenn, F. P. Netzer, M. G. Ramsey, R. Resel
Sexithiophene films on reconstructed and unreconstructed TiO2(110) surfaces: electronic, structural and morphological properties
Surface Science, submitted

G. Koller, S. Berkebile, J. R. Krenn, F. P. Netzer, M. Oehzelt, T. Haber, R. Resel, M. G. Ramsey
Tuning the molecular organisation in organic / organic heterostructures
Advanced Materials, submitted