



	Experiment title: Structural development from sexithiophene and pentacene mono- to multilayers on Cu(110) and Cu(110) p(2x1)O	Experiment number: SI-1679
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Shifts: 18	Local contact(s): Andrea M. Resta	<i>Received at ESRF:</i>
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Report:

Sexithiophene (6T: $C_{24}S_6H_{14}$) and pentacene (5A: $C_{22}H_{14}$) are not only promising molecules for organic devices but they are also of interest as model molecules for basic growth studies. During the last years the growth of several organic molecules including the above mentioned ones on Cu(110) and Cu(110) p(2x1)O (CuO) have been studied by the experimentalists.[1-4] The measurements carried out include in-situ surface science techniques like ARUPS, STM, NEXAFS and LEED from monolayer to multilayer thick films. The crystallographic structure and morphology of in-situ (UHV) prepared and characterised films has also been investigated ex-situ by laboratory XRD techniques and AFM. These laboratory experiments showed that epitaxial growth with unique crystallite/molecular orientation and morphology can be achieved by carefully controlling the inorganic substrate properties. The aim of the experiments reported here was to study the transition of the initial monolayer growth to the bulk crystal structure. The initial stages of growth are particularly interesting because of the large lattice mismatch of e.g. the bulk 6T structure (monoclinic with $a = 44.71\text{\AA}$, $b = 7.85\text{\AA}$, $c = 6.03\text{\AA}$ and $\beta = 90.76^\circ$) to the reconstructed substrate CuO (rectangular with $a = 5.1\text{\AA}$, $b = 3.6\text{\AA}$). Although heaving this big lattice mismatch crystalline monolayers and highly crystalline thick films have been investigated with lab techniques [3,5].

Mainly two sets of experiments have been concentrated on: a) the monolayer structure of 6T on CuO and its change for thicker film, b) 5A grown on CuO, and desorption experiments during heating.

a) The monolayer of 6T:

6T was deposited in-situ on a oxygen reconstructed Cu(110) surface. GXID diffraction pattern have been measured for a monolayer thick and a about 300 Å thick film. The resulting diffraction pattern confirms that the orientation of the molecules is the same in the monolayer as well as in the thick layers. The long molecular axis is always parallel to the CuO rows of the surface reconstruction. The spacing of the molecules in this direction is larger for molecules in the first monolayer compared to the bulk crystal structure which was observed for all thicker films.

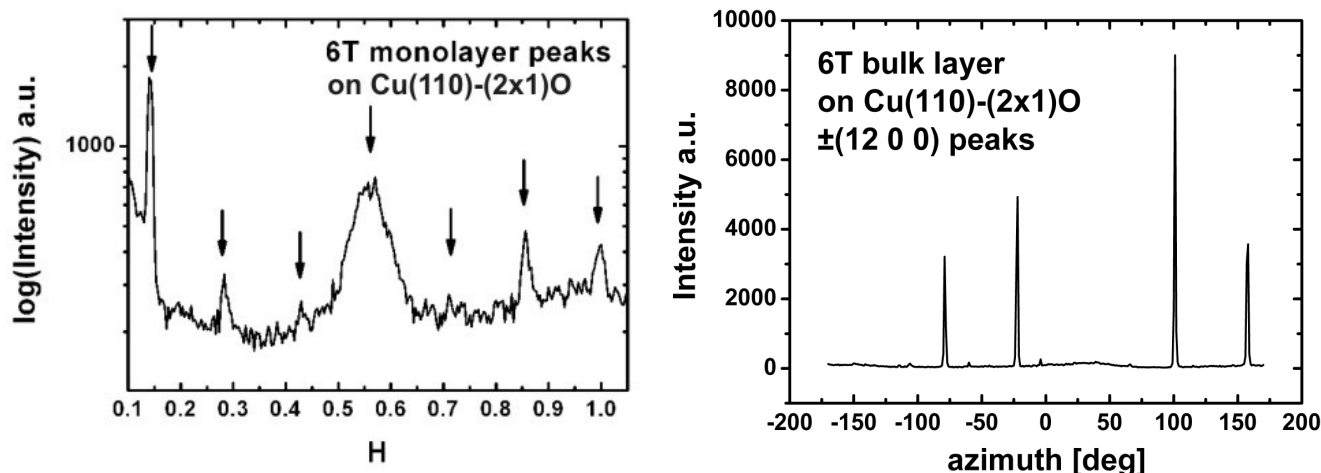


Figure 1: Peaks of the (h00) series of the 6T monolayer structure (left) and an azimuthal scan of the (12 00) peaks of the 6T bulk structure (right) are shown.

In Figure 1 on the left side a GIXRD pattern of a monolayer thick film of 6T is depicted. It shows that in the direction of the long molecular axis, that is also the direction of the copper-oxygen rows (CuO), are commensurate to the substrate with a lattice constant seven times that of CuO. This means that the long unit cell axis is $7 \times 3.6 \text{ \AA} = 25.2 \text{ \AA}$ [6]. These results are in full agreement with previous STM measurements [5]. In addition this measurement proves that the monolayer structure remains even when growing thicker films upon it. The thicker films grown on this monolayer structure are (0 ± 10) oriented. Due to the monoclinic bulk crystal structure four different orientations are observed and can be clearly distinguished in the GIXRD pattern of Fig. 1 (right side). Unfortunately due to some problems during the beam time, no further details of the monolayer structure could be obtained.

Figure 2 shows two specular scans of the (020) peak of 6T. The higher intensity peak is the one of the film as deposited – the very same film as in Fig. 1 on the right side. The lower intensity peak was measured after annealing the film shortly above the desorption temperature. Clearly the crystallinity of the film was improved, as the peak width is considerably reduced.

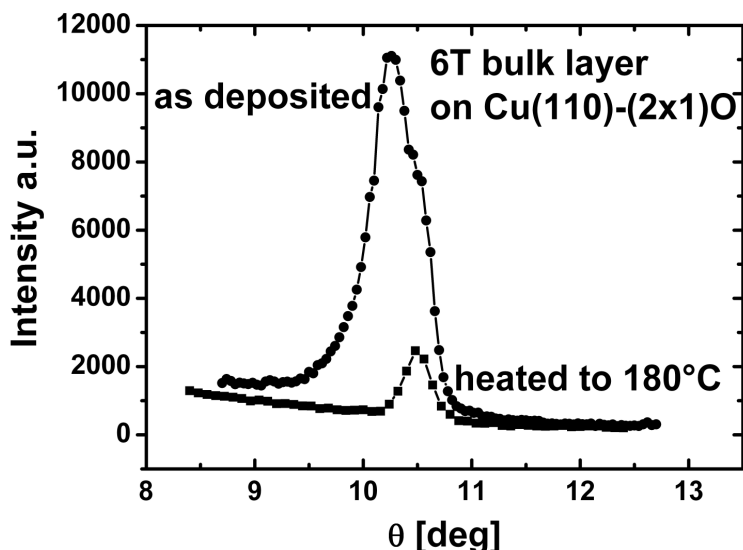


Figure 2: 6T(020) diffraction peak as deposited at room temperature and annealed to 180°C.

b) 5A on CuO:

Pentacene (5A) grows on Cu(110)-(2x1)O in an (022) orientation [7] where the individual molecules within this plane are tilted by around 5° with respect to the substrate corrugation. This tilt is expected to be absent in the first monolayer and emerging in later growth stages. To gain some insights in this expected behaviour we have tried to follow the deposition and desorption of very thin pentacene layers. Due to the low scattering cross section of this pure hydrocarbon material we have watched the evaporation at the position of the Yoneda wing (see Fig. 3 left panel). Even at a thickness where the Yoneda wing was clearly observed the specular intensity of the pentacene film was hardly measureable. Nevertheless the structure of the grown film could be measured in-plane for the (022) orientation of the pentacene films. This was also the position where the desorption of the organic layer was measured (Fig. 3 right panel). Due to lack of time only the feasibility of this procedure could be shown.

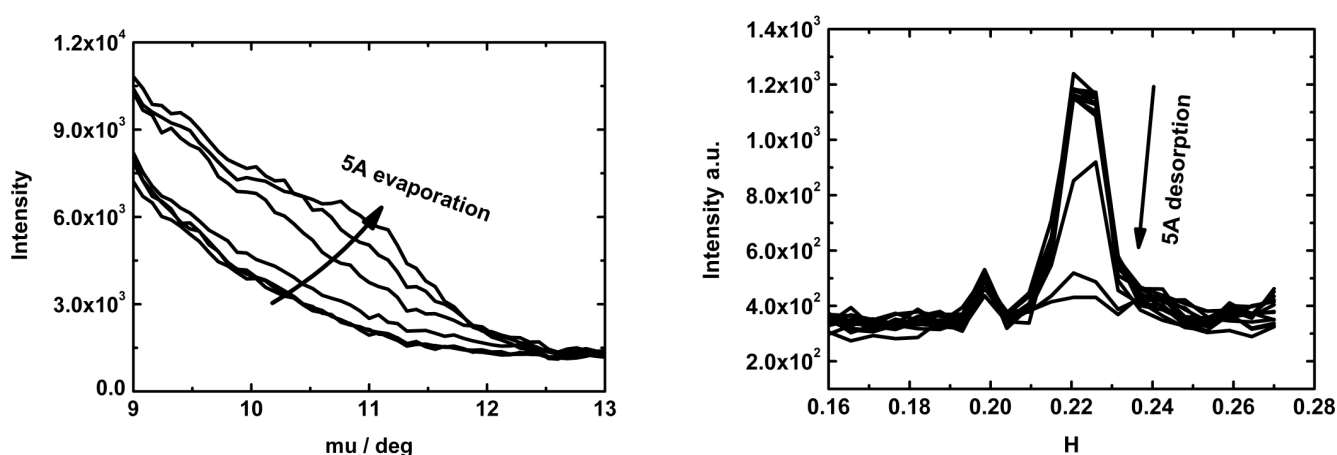


Fig. 3: Pentacene deposition watched at the Yoneda-wing (left) and pentacene desorption followed at (001) peak of the (022) orientation (right).

- [1] *Intra- and intermolecular band dispersion in an organic crystal*, G. Koller, S. Berkebile, M. Oehzelt, P. Puschnig, C. Ambrosch-Draxl, F.P. Netzer, M.G. Ramsey, *Science* 317, 5836 (2007).
- [2] *Organic Heteroepitaxy: p-Sexiphenyl on Uniaxially Oriented α -Sexithiophene*, M. Oehzelt, G. Koller, J. Ivanco, S. Berkebile, T. Haber, R. Resel, F.P. Netzer, M.G. Ramsey, *Adv. Mater.* 18, 2466 (2006).
- [3] *The molecular orientation of para-Sexiphenyl on Cu(110) and Cu(110) p(2x1)O*, M. Oehzelt, L. Grill, S. Berkebile, G. Koller, F.P. Netzer, M.G. Ramsey, *ChemPhysChem* 8, 1707 (2007).
- [4] *Surface induced crystallographic order in sexiphenyl thin films*, R. Resel, *J. Physics: Cond. Matter*, 20, 184009 (2008).
- [5] *α -sexithiophene on Cu(110) and Cu(110)-(2x1)O: an STM and NEXAFS study*, M. Oehzelt, S. Berkebile, G. Koller, J. Ivanco, S. Surnev, M.G. Ramsey, *Surf. Sci.* 603, 412 (2009).
- [6] *α -sexithiophene films grown on Cu(110)-(2x1)O: from monolayer to multilayers*, M. Oehzelt, S. Berkebile, G. Koller, T. Haber, M. Koini, O. Werzer, R. Resel, and M.G. Ramsey, *Springer Proceedings in Physics*, in print.
- [7] *Epitaxial order of pentacene on Cu(110)-(2x1)O: One dimensional alignment induced by surface corrugation*, M. Koini, T. Haber, O. Werzer, S. Berkebile, G. Koller, M. Oehzelt, M.G. Ramsey, R. Resel, *Thin Solid Films* 517, 483 (2008).