	Experiment title: Structural development from sexiphenyl mono- to multilayers on Cu(110) p(2x1)O	Experiment number: SI 1536
Beamline: BM32	Date of experiment: from: 18.04.2007 to: 24.04.2007	Date of report: 30.8.2007 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Tobias U. Schüllli	
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Report:

Sexiphenyl (6P: $C_{36}H_{26}$) 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 conjugated organic molecules, including those mentioned above have been studied on clean Cu(110) and p(2x1) oxygen reconstructed Cu(110) (CuO) [1-3]. These measurements included in-situ (UHV) surface science techniques like ARUPS, STM, NEXAFS and LEED and followed the growth from (sub-) monolayer to multilayer thick films of device relevant dimensions. In addition the crystallographic structure and morphology of these in-situ prepared and characterised films has also been investigated ex-situ by laboratory XRD and AFM. Our controlled UHV experiments showed that epitaxial growth with unique crystallite/molecular orientation and morphology can be achieved on inorganic substrate templates.

The major aim of the experiments reported here was to study the transition from the initial monolayer growth to the bulk crystal structure (a), which is not accessible with conventional XRD. The initial stages of growth are particularly challenging, because of the large lattice mismatch of e.g. the bulk 6P structure (monoclinic with $a = 8.091\text{\AA}$, $b = 5.568\text{\AA}$, $c = 26.241\text{\AA}$ and $\beta = 98.17^\circ$) to the CuO substrate (rectangular unit cell $a = 5.1\text{\AA}$, $b = 3.6\text{\AA}$). It should be noted that despite the big lattice mismatch both crystalline monolayers on the one hand and highly crystalline thick films on the other hand have been found with our lab techniques.

A second focal point we have investigated is the epitaxial growth of organic heterostructures (b). The interfaces between organic layers have recently attracted considerable interest as modern organic devices tend to consist of multiple layers and the interfaces between these layers can dramatically influence their device performance. Therefore at this beamtime also heterostructures of 5A and 6P grown on Cu(110) and CuO have been investigated.

A third topic we have explored involved using the 2D-detector to perform “real-time” diffraction experiments (c). Here we have followed the evolution of the diffraction pattern of a 6P/5A heterostructure upon heating.

a) The 6P monolayer and the transition to the bulk crystal structure:

6P was stepwise deposited in-situ on an oxygen reconstructed Cu(110) substrate. GXID diffraction pattern have been measured for 6P films with different thicknesses from below one monolayer up to 300 \AA . All diffraction patterns confirm that the orientation of the molecules is the same in the monolayer as well as in the thick layers, i.e. the long molecular axis is always parallel to the CuO rows of the surface reconstruction. But the spacing of the molecules in this direction is larger for molecules in the first monolayer compared to

the lattice spacing of the bulk crystal, which was observed for all film thicknesses beyond one monolayer. This suggests an unexpected abrupt transition from the monolayer to the bulk structure.

The evaluation of the molecules periodicity in the direction perpendicular to the CuO-rows is difficult because in this direction the organic structure (6P(20-3)) is commensurate to the substrate surface reconstruction and thus buried in the much stronger signal of the CuO surface reconstruction. Therefore it was impossible to observe this packing in the monolayer. But again, for films thicker than one monolayer the 6P(20-3) bulk crystal structure was detected, also in this direction. To study this aspect of organic-inorganic-heteroepitaxy molecules that either do not have a rectangular surface unit cell or that are fully incommensurate to the substrate are better suited, e.g. pentacene or α -sexithiophene (6T).

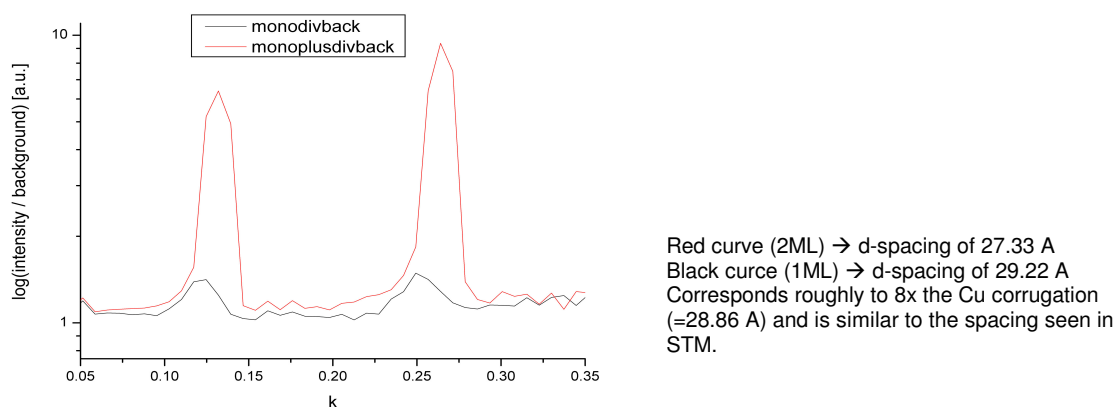


Figure 1: Shift of the (001) and (002) diffraction peaks from the first monolayer to the second.

b) 5A/6P heterostructures:

The epitaxy of 5A/6P heterostructures grown on Cu(110) and CuO have been studied by GIXD. The heterostructures have been prepared in Graz and were introduced to the BM32 vacuum system. GIXD measurements of the substrate and the two organic layers revealed the in-plane orientation of the films. For CuO the pentacene layer grows with a (022) plane parallel to the substrate and the azimuthal orientation is in such a way that the direction of the next neighbour molecules ([11-1] direction) is parallel to the CuO rows (see Fig. 2). As the CuO surface has a two-fold symmetric surface there were two symmetry equivalent orientations of the pentacene crystallites found. The consequence of this alignment is that the molecules' long axis is inclined by $\pm 6^\circ$ with respect to the CuO rows. This alignment is unexpected as previous experiments for 6P or 6T have determined a growth with the long molecular axis fully parallel to the surface oxygen rows. On top of the pentacene layer the 6P molecules align parallel to the long molecular axis of the pentacene molecules, although this alignment results in a totally incommensurate growth.

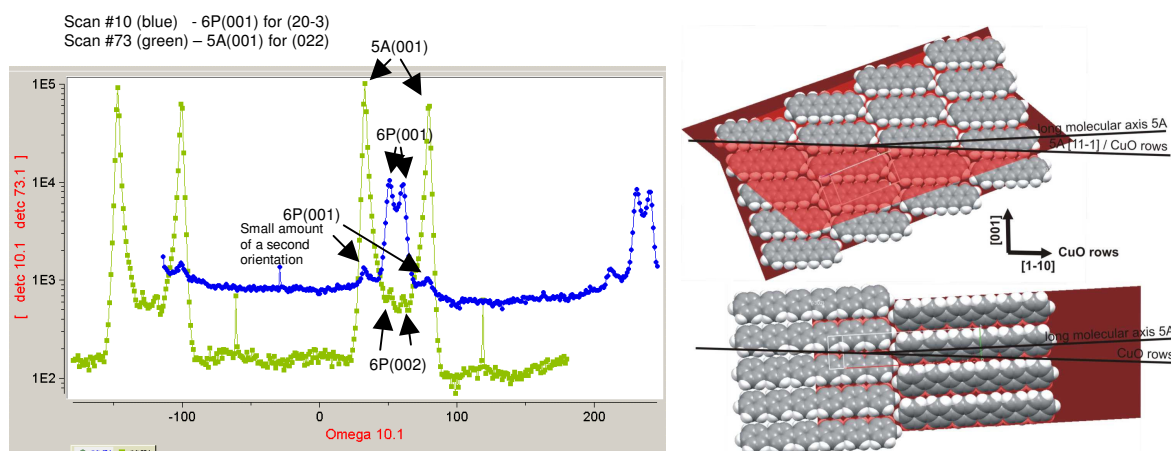


Figure 2: The left image shows diffraction pattern of a CuO-5A-6P heterostructure. The (001) diffraction peaks are symmetric around the direction of the CuO-rows. With the knowledge of the 5A single crystal structure the orientation of the molecules with respect to the CuO surface could be determined and results in an inclination of the long molecules axis of 6° with respect to the CuO-rows. The 6P orientation is shown below with their long molecular axes parallel to the 5A molecules axes.

For the heterostructure grown on clean Cu(110) the situation is different but yet not fully understood. Here the long molecular axis of the pentacene layer is around 5° off the Cu[001] direction (but in the opposite direction compared to the CuO-5A-6P heterostructure). The 6P molecules grown on top of this pentacene layer adopt no characteristic feature of the pentacene layer but the long molecular axis is oriented along the Cu[001] surface direction. A possible explanation of this behaviour could be that the pentacene does not cover the whole metal surface and that the subsequent growing 6P molecules still interact with the substrate.

c) “real-time” measurement of the desorption kinetic of a 5A/6P heterostructure upon heating:

The heterostructures discussed in the last paragraphs were heated, while measuring their diffraction pattern using a 2D detector. This organic–organic heterostructure was grown such that the molecules with the higher desorption temperature (6P) cover a molecular film of a lower desorption temperature (5A). Figure 3 shows a sequence of diffraction images taken for the heterostructure grown on Cu(110) as deposited (a), and subsequently heated up to 220°C (b-d). Figure 3 clearly shows that the pentacene molecules desorb first, leaving the 6P layer behind. Interestingly no significant changes in the 6P diffraction peaks could be observed upon desorption of the underlying pentacene layer. Qualitatively the same behaviour was observed for the CuO-5A-6P film. Here again the pentacene molecules desorb at a lower temperature than the 6P molecules although the pentacene was completely covered by a thick 6P layer. Again no change in the position of the diffraction peaks could be measured. This is surprising since the 6P molecules definitely grow on top of the pentacene crystallites as evidenced by the clear epitaxial relationship between the 5A and the 6P layer.

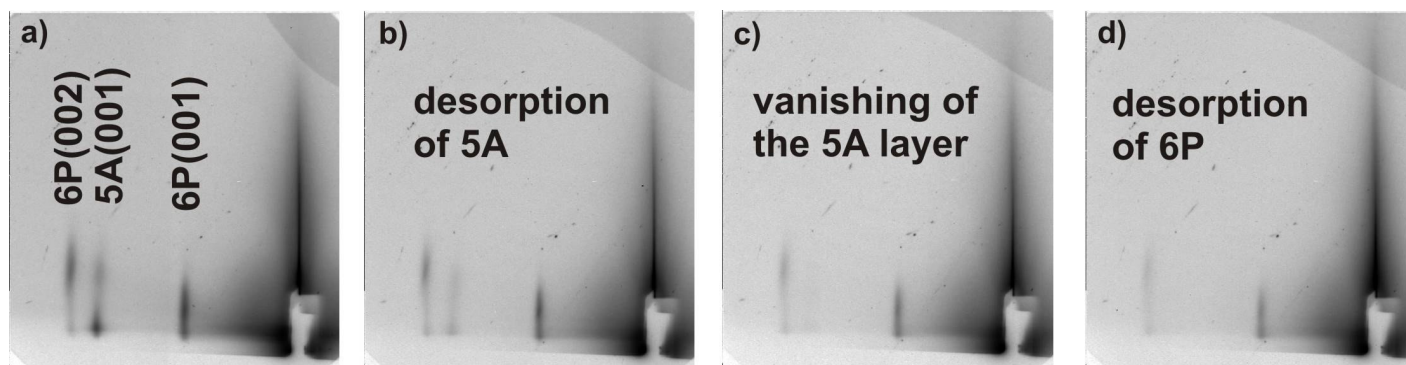


Figure 3: 2D diffraction pattern of a 5A/6P heterostructure grown on Cu(110). a) shows the diffraction from the heterostructure as grown. 1st and 2nd order diffraction peaks of the (001) net plane of 6P is labeled as well as the (001) peak of 5A. In b) the desorption of 5A is already clearly visible, while in c) the 5A layer is not seen any more. Note that the sequence of the organic layers with respect to the surface is 5A and 6P grown on top of it. Further heating results in the desorption of the 6P layer as well.

References:

- [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).