X-ray diffraction line broadening in thin layers of quaterphenyl on C-covered gold(111)

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Thin films of crystalline organic semiconductors (conjugated molecules) offer promising prospects for future developments in electronic and opto-electronic devices. Defined interfaces, the specific molecular orientation within a crystalline film and large domain sizes are required to enhance the performance of such devices [1-3]. As it is well-known that various conjugated molecules form highly regular structures on metal surfaces, the role of the organic/substrate interactions in determining the final interface- and film-structure is very important and influences the resulting microstructure of the film.

X-ray diffraction line profile analysis is a powerful method to obtain microstructural characteristics [4,5]. Usually applied to thin films of inorganic materials like high  $T_c$  superconductors, Indium Tin Oxide (ITO) or coating materials (e.g. see [6]), line profile analysis on organic thin films is a difficult task. The problem is that diffraction peaks of sufficient intensity can only be observed at high d-values (low 2 $\theta$ -angles), and that no standards for the determination of the instrumental broadening are available in this region. Another problem is the low diffracted intensity of thin films, especially as the organic material consists of matter with low atomic mass which have low scattering cross sections.

In this study we concentrate on the system *para*-quaterphenyl ( $C_{24}H_{18}$ , 4P) on C-covered Au(111). The films were prepared at room temperature with a rate of 0.3 nm/min with a thickness of about 30 nm. The mean film thickness was monitored by a water-cooled quartz crystal microbalance during the evaporation process [7-9]. The diffraction pattern were collected with a Siemens D501 diffractometer with copper  $K_{\alpha}$  radiation and a secondary graphite monochromator in Bragg-Brentano geometry. Only reflections of net planes parallel to the surface of the substrate can be detected in this geometry. The line profile analysis of these recorded pattern reveal size and strain information perpendicular to the substrate surface. The morphology of the films is studied by atomic-force microscopy (AFM) using a Nanoscope IIIa system (Digital Instruments, Santa Barbara, CA) in tapping mode. Both, the x-ray and the AFM measurements were performed *ex situ* under ambient conditions.

The accuracy of the line profile analysis depends crucially on the separation of the instrumental broadening from the intrinsic sample generated broadening. Lanthanum hexaboride (LaB<sub>6</sub> - NIST, Standard Reference Material 660a) was used to determine the instrumental broadening. For an analytical expression of the broadening the Caglioti *et. al.* model [10] was adopted to the LaB<sub>6</sub> reference material. The instrumental broadening is taken into account in order to obtain the pure fraction of the investigated sample. This remaining broadening consists of two different contributions: size and strain. To separate them the Williamson-Hall analysis [11] is applied:

$$b(s) = \frac{1}{\langle l \rangle_{V}} + \sqrt{2\pi \langle \mathcal{E}^{2} \rangle} \cdot s \tag{1}$$

With: s the length of the scattering vector, b(s) the integral breadth of the peak.  $\langle l \rangle_V$  the volume weighted column length, which is in this case the volume weighted crystal size perpendicular to the surface.  $\langle \varepsilon^2 \rangle$  is the mean square (local) strain, whereas the whole root expression is the root mean square strain (rms strain).

Figure 1 shows the x-ray diffraction pattern of the sample. Scattered intensity is detected for the net plane (001) and its higher order reflections. All single peaks are fitted with pseudo-Voight shaped profile functions and the instrumental broadening is considered (for more details see e.g. [12,13]), as this task is essential for this method. Figure 2 is a Williamson-Hall plot of all (001) peaks with reasonable intensity. The results of the Williamson-Hall analysis are:  $1/\langle l \rangle_V = (0.011 \pm 0.001)$  nm and  $\sqrt{2\pi \langle \varepsilon^2 \rangle} = 0.006 \pm 0.001$ . This results in a volume weighted crystal size of around 90 nm. The value for the rms strain is typical for vapour deposited organic films [4,5].

4P forms a layer-like, continuous film with a granular morphology (see Figure 2). The grain structures have lateral dimensions in the length scale of 1 µm. These AFM images give us a hint towards the lateral surface dimension of the 4P structures that is not the true lateral dimension of the crystallites. Comparing the mean film thickness of 30 nm (obtained by the microbalance measurement) and the vertical roughness of the surface, it can be concluded that the local thickness of the film can range from several nm up to a few hundred nm. These values match the value obtained from the Williamson-Hall analysis, because the 90 nm are volume weighted crystal sizes, where the contribution of bigger crystallites is more pronounced than smaller crystallites. As AFM is a pure surface technique it is impossible to decide if the crystallites extend down to the substrate, but on the other side there can only be very few crystallites on top of each other. In this context the value of 90 nm seems representative for the investigated film and shows the applicability of this method for organic thin layers.



Figure 1: Left panel:  $\theta/2\theta$  scan of the 4P film deposited on C-covered Au(111). Right panel: Williamson-Hall plot of the (001)peaks. Only the peaks (001) to (004) could provide enough intensity for a peak shape analysis. The line is a linear least squares fit.



Figure 2: AFM results: The left image is a magnification of the overview scan shown at the right side. The morphological structure seems to be uniform over a large area of the sample.

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