ESRF	**Experiment title:** GIXD studies of selectively adsorbed self-assembled organic monolayers on various faces of semiconductor single crystals.	**Experiment number**: SI-1547
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Octadecylamine (ODA, $C_{18}H_{39}N$) is an important surfactant, widely used as capping molecule for nanoparticle synthesis[1-5]. Despite the growing number of papers which describe ODA-assisted syntheses of nanostructures, the crystal structure of ODA remains currently unsolved. The aim of the current experiment was to study the crystal structure of ODA films on solid substrates of single crystals using grazing incidence synchrotron x-ray diffraction (GIXD) and x-ray reflectivity (XRR). The films were prepared by self-assembly or by casting of ODA molecules dissolved in ethanol. Unfortunately diffraction from self-assembled monolayers was not observed due to low signal-to-noise and/or lack of long range order in the monolayer films. Therefore, we hereby describe below the results obtained for casted films of ODA.

We have previously investigated the crystal structure of ODA in-house using powder x-ray diffraction (XRD). This study showed that ODA has two distinct lamellar phase structures, depending on the preparation conditions. The powder diffractogram of the anhydrous ODA phase is shown in Figure 1a(i) (black) and that of ODA exposed to methanol is shown in Figure 1a(ii) (red)[6]. The dotted green and red lines show the positions of the lamellar peaks of both phases, respectively.

For the synchrotron measurements, the samples were prepared by dissolving anhydrous ODA powder in ethanol, placing a droplet of the suspension onto a single crystal GaAs wafer and then

allowing for the ethanol to evaporate. Projections of the GIXD measured intensities onto q_{xy} and XRR measured intensities onto the q_z axis of the casted ODA film are shown in Figures 1b and c, respectively.

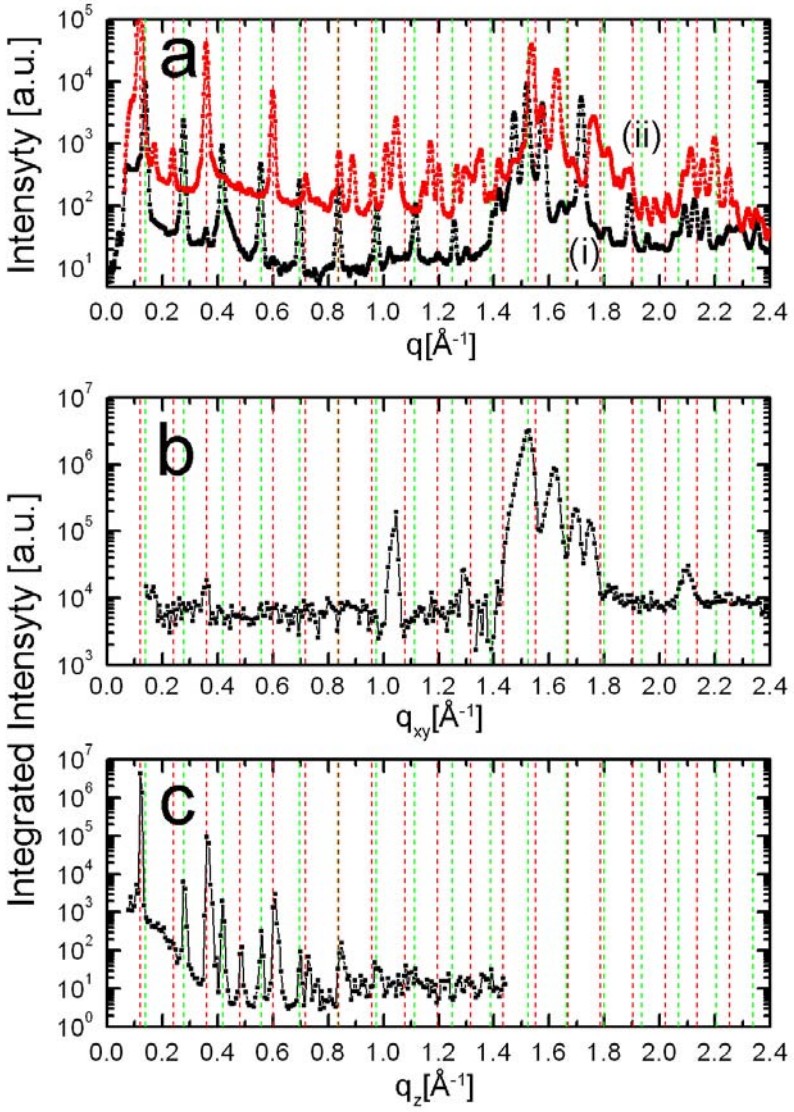

Figure 1: (a): Powder XRD diffractograms of (i) the anhydrous phase of ODA and of (ii) ODA exposed to methanol. (b): Projections of the GIXD measured intensities onto q_{xy} and (c): Simultaneously measured XRR intensities onto q_z of casted ODA film as observed in the linear PSD detector in the same geometry as (b).

The GIXD scan (Figure 1b) revealed mostly in-plane peaks that resulted from planes perpendicular to the subphase surface, and only one weak low-order lamellar peak from the methanol phase of ODA. Interestingly, the XRR data (Figure 1c) showed the presence of distinct

lamellar peaks in extended sequences corresponding to six orders of diffraction of the fundamental (001) reflection in both ODA phases, with periods of 45.04Å (for the anhydrous phase) and 52.34Å (for the methanol phase). This indicates that the ODA films are strongly oriented with the lamellar planes parallel to the substrate surface. The fully extended length of an ODA molecule is approximately (1.54+1.265×18)+3=27.31Å.[4, 7] Thus, the ODA structure is comprised of parallel bilayers of molecules that are tilted at $\phi_1 \approx 34^\circ$ and $\phi_2 \approx 15^\circ$ with respect to the surface normal, for the anhydrous and methanol phases, respectively. Notably, the peaks of the methanol phase are significantly stronger than the anhydrous phase. This is not surprising, since the sample was not held especially in dry condition. Furthermore, this points out the similar effect of water (humidity) and methanol molecules (both polar) on the structure of ODA.

Based on these results, we are currently focused on solving the unit cell structure of both phases of ODA.

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