Oral presentation

Searching for new polymorphs by epitaxial growth

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The formation of unknown polymorphs due to the crystallization at a substrate surface is frequently observed. This phenomenon is much less studied for epitaxially grown molecular crystals, since the unambiguous proof of a new polymorph is a challenging task. The existence of multiple epitaxial alignments of the crystallites together with the simultaneous presence of different polymorphs do not allow simple phase identification.

We present grazing incidence X-ray diffraction (GIXD) studies with sample rotation on epitaxially grown film (with thicknesses from 10 to 30 nm) on conjugated molecules like PTCDA, 6,13-pentacenequinone (P2O), 1,2;8,9-dibenzopentacene (trans-DBPen) and dicyanovinyl-quaterthiophene (DCV4T-Et2) grown by physical vapour deposition on Ag(111) and Cu(111) single crystals. A new method for indexing the observed Bragg peaks allows the determination of the crystallographic unit cells so that the type of crystallographic phase can be clearly identified [1]. This approach even works when several polymorphs are simultaneously present within a single sample as shown for DCV4T-Et2 on Ag(111) (see Fig. 1) [2]. Additionally, epitaxial relationships between the epitaxially grown crystallites and the single crystalline surfaces are determined.

The origin of new polymorphs is due to nucleation on single crystal surfaces. The first monolayer is only accessible by surface sensitive methods that allow the determination of a two-dimensional lattice like low-energy electron diffraction (LEED). Therefore, we compare our results on the three-dimensional lattice with LEED experiments on molecular monolayers of the same conjugated molecules. A correlation between the first monolayer and the epitaxial growth of three-dimensional crystals together with lattice distortions and re-alignment of molecules can be observed. The selected examples show three possible scenarios of crystal growth on top of an ordered monolayer: (i) growth of a single polymorph, (ii) growth of three different polymorphs; in both cases the first monolayer serves as template. In the third case (iii) strong lattice distortion and distinct molecular re-alignments from the monolayer to epitaxially grown crystals are found [3].

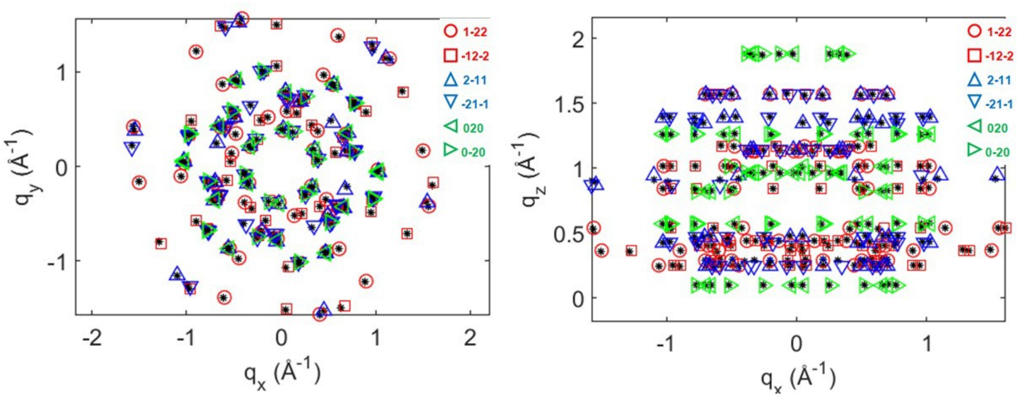

Figure 1. Positions of experimentally determined X-ray diffraction peaks (black) of DCV4T-Et2 crystals grown on Ag(111), obtained from rotating GIXD experiments. q_y/q_x position of the diffraction peaks (left); q_z/q_x positions of the diffraction peaks (right). Indexing of three epitaxially oriented polymorphs grown with the (1 -2 2) and (-1 2 -2) plane (red), (2 -1 1) and (-2 1 -1) plane (blue) and (0 2 0) and (0 -2 0) plane (green), respectively parallel to the substrate surface.

[1] Simbrunner, J., Schrode, B., Domke, J., Fritz, T, Salzmann, I. & Resel,, R. (2020). *Acta Cryst.* **A76**, 345.

[2] Simbrunner, J., Schrode, B., Hofer, S., Domke, J., Fritz, T, Forker, R. & Resel,, R. (2021). *J. Phys. Chem.* **C125**, 618.

[3] Simbrunner, J., Domke, J., Sojka, F., Jeindl, A., Otto, F., Gruenewald, M., Hofmann, O. T., Fritz, T., Resel, R. & Forker, R. (2022). *Acta Cryst.* **A78**, 272