Crystallinity of pn heterojunction has been an important problem for improving the performance of organic electronic devices. Particularly for organic solar cells, designing the structures in a size scale comparable to the exciton diffusion length (10-100 nm) is crucial [1,2]. As the pn heterojunctions of the organic solar cells consist of donor and acceptor-type molecular materials, thorough understanding in detailed mechanisms how the two molecular materials form these contact structures is needed for pursuing the efficient interfaces. However, since most of past works on the molecular interfaces used polycrystalline organic thin films as substrates, structural disordering and non-uniformity have prevented ones to clarify the molecular behaviours at the interface. In this work, growth mechanisms and crystallographic structures of well-defined organic semiconductor pn heterojunctions built on using the organic single crystal surfaces, namely epitaxial overlayers of a typical n-type molecular semiconductor fullerene (C$_{60}$) on the single crystals of pentacene (C$_{22}$H$_{14}$) or rubrene (C$_{42}$H$_{28}$), are examined by grazing incidence X-ray diffraction (GIXD).

Pentacene and rubrene single crystals used as the substrates were produced in a purified nitrogen stream, on which 20 nm-thick C$_{60}$ overlayers were grown at the growth temperature ranging from 130 to 370 K at the deposition rate of 0.03 nm/s. GIXD measurements were conducted at BL19B2 and BL46XU (Proposal Nos. 2015A1685, 2015B1624, 2016A1676, 2016B1612, 2017A1570).

The GIXD results indicated that C$_{60}$ forms fcc crystalline overlayers in the (111)-orientation on both single crystal substrates. Two-dimensional GIXD measurements revealed that the fcc-C$_{60}$ (220) diffraction spots on the single crystal pentacene appeared at every sixty degree of the sample azimuthal angle $\phi$ with respect to the X-ray. This means that the C$_{60}$ overlayers grow epitaxially on the pentacene single crystal [3]. In contrast, on the rubrene single crystal substrate, the fcc-C$_{60}$ (220) diffraction spots appeared at every thirty degree of $\phi$. This indicates that, whereas the C$_{60}$ overlayer grows epitaxially also on the rubrene single crystal, their in-plane orientation is not unique but two types of domains rotating their (111) hexagonal lattices by 90$^\circ$ each other are formed.

A mean crystallite size of C$_{60}$ for each sample is derived from widths of the C$_{60}$ (220) spot profiles assuming the Scherrer equation. At room temperature, the mean crystallite sizes of C$_{60}$ on the pentacene and rubrene single crystals are 130 nm and 150 nm, respectively. The former is clearly larger than the cases of C$_{60}$ grown on a pentacene thin film and Si wafer [4]. Wide variation of the mean crystallite size from 30 to 250 nm by changing the growth temperature from 130 to 370 K (Fig. 1) suggests fine controllability of these heterojunction structures. The possible mechanisms how the structural properties of the substrate molecules govern the heterojunction structures will also be discussed in this contribution.


Figure1. In-plane mean crystallite sizes of C$_{60}$ on the single crystals of pentacene and rubrene plotted as a function of the growth temperature.