The spontaneous amorphous-to-crystal transition in rubrene thin films: a combined morphological and photo-physical study

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Rubrene (RUB) is one of the most extensively investigated organic semiconductors, specifically for the high hole mobility and almost unit singlet fission (SF) and triplet fusion (TF) efficiencies in the solid state [1]. These properties make RUB attractive for application in transistors, light-emitting diodes, and light-harvesting devices leveraging either upconversion or downconversion of excitons.

The above-mentioned record properties, however, are specific of RUB crystalline solids, and most studies have so far focused on single crystalline RUB, in its orthorhombic polymorphic structure. However, for integration in devices, crystalline RUB thin films are required. A key issue with RUB is its tendency to grow naturally (at room temperature) in amorphous or spherulitic form on all substrates relevant for devices. In addition, RUB solids are susceptible to efficient photo-oxidation, particularly in the amorphous phase, which ultimately affects their electronic and optoelectronic properties.

In a previous study [2], we demonstrated a method to grow orthorhombic RUB thin films with unprecedented degree of crystallinity and controlled domain orientation via organic molecular beam epitaxy on organic single crystal substrates. We also showed that, in ambient conditions, these films benefit from the formation of an epitaxial native oxide layer, which protects the underlying RUB from further oxidation [3].

Here, we delve into the spontaneous transition from amorphous to crystalline RUB occurring in ultra-high vacuum (UHV) during the growth of such films. For this study, we propose an innovative approach, which combines an *ex-situ* analysis via atomic force microscopy and polarized optical spectroscopy, with a photoluminescence (PL) investigation carried out *in situ* (i.e., in UHV), to directly probe the kinetics of the amorphous-to-crystal transition. Then, we investigate the role of three crucial growth parameters, namely storage time in UHV, growth rate, and substrate temperature during the deposition. This enables us to rationalize the growth process and optimize the growth conditions, to ultimately improve the overall order and crystallinity of RUB films, as determined by X-ray diffraction, and indirectly assessed by PL spectroscopy.

References

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