Growth dynamics and modelling of organic semiconductor thin films subject to post-growth processes

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The ability to control and drive the growth of organic semiconductor thin films is crucial for improving thin film properties and, in turn, device performances. In this respect, many efforts have been devoted to the comprehension of film growth mechanisms and to the development of models providing a quantitative description of the growth process. Nonetheless, thin films may experience post-growth evolution, which may involve different processes such as wetting, dewetting or ripening, often causing a change in the film morphology and/or structure, thus, affecting device performances. For this reason, probing the occurrence of post-growth phenomena is fundamental also in view of finding a strategy to control and exploit them [1,2].

Among organic semiconductors, tetraphenylporphyrin films are chosen as model-systems due to their great potential for applications in the fields of light harvesting, gas and chemical sensing, biomedicine, spintronics or heterogeneous catalysis. Here, a study about the growth dynamics of Nickel-tetraphenylporphyrin (NiTPP) grown on highly oriented pyrolytic graphite (HOPG) by organic molecular beam epitaxy is presented. This specific molecule/substrate couple is a paradigmatic system exhibiting a remarkable post-growth morphology evolution as monitored ex-situ by atomic force microscopy (AFM). This evolution is mostly characterized by a mass redistribution, highlighted by the growth in size of some of the islands at the expense of the smaller and less stable ones (which display a rather different morphology and possible different structure) consistent with an Ostwald-like ripening effect. To quantitatively describe the growth, the height-height correlation function (HHCF) analysis of the AFM images of a set of films with different thickness is carried out and the scaling exponents are extracted. Importantly, the method is demonstrated to be reliable only when applied to the samples after their evolution, i.e. when they can be considered in their steady state, meaning that the post-growth evolution has to be intended as an integral part of the whole growth process. Right after the extraction, indeed, the stage of the post-growth evolution for each sample with different thickness is different, preventing the extraction of the scaling exponents. At the same time, at intermediate evolution stages, families of different aggregates coexist displaying different growth dynamics.

In conclusion, the set of scaling exponents obtained from the HHCF analysis of NiTPP on HOPG suggests that the growth is mainly driven by an interplay between diffusion and step-edge barrier effect, in agreement with the observed ripening. These results, together with the overall approach adopted, attest the reliability of the HHCF analysis in systems displaying post-growth evolution [3]. This is a rather general result, not limited to the organics, and open new perspectives in the study of the growth dynamics of thin films subject to post-growth evolution.

References

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