In Situ Study of the Growth of Nanodots in Organic Heteroepitaxy

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We report the self-organization of organic nanodots with high crystallinity during the growth of organic heterostructures of Di-indenoperylene (DIP) onto copper-hexadecafluorophthalocyanine (F_{16}CuPc), donor and acceptor molecules, respectively. The process is related to the Stranski-Krastanov growth mode, which is accompanied by a novel type of structural reconstruction of the underlying organic film. This reconstruction affects three monolayers adjacent to the organic interface. In spite of the close resemblance to the formation of semiconductor nanostructures for inorganic heteroepitaxy, the present results conclusively demonstrate a distinctly different growth mechanism for organic heteroepitaxy whose understanding demands further theoretical studies.

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The last decade has witnessed an increased emphasis on the development of devices based on organic semiconducting materials. Among the different explored materials, small aromatic molecules have been recognized as promising candidates for future applications, because they can be grown in films of high crystalline order, thus fulfilling one of the important requirements to obtain high charge carrier mobility. Perhaps, the most compelling reason for the efforts of trying to understand the growth mechanisms of organic films (and beyond its academic interest) is the demand for controlled structures. Organic thin film growth is definitively more complex than that of inorganic materials. Although the state-of-the-art of organic thin film growth is still far from being a well-established paradigm, considerable progress has been achieved in their growth on inorganic substrates whereby different modes of epitaxy have been described [1–4] and atomistic theories of nucleation could be successfully applied for some systems [5].

The growth of organic-organic heterostructures [6–17] is by far less understood in spite of the fact that organic interfaces are a key element for many electronic devices such as organic light emitting diodes, organic ambipolar transistors or organic solar cells. In contrast to inorganic systems, whose physical principles of heteroepitaxy have been solidly established and successfully exploited to control the fabrication of nanostructures, the present day knowledge of the mechanisms of ordering and growth in organic structures is almost lacking. Because of the different properties inherent to organic materials, i.e., large size, anisotropy, and relatively weak intermolecular interaction (van der Waals), issues like "strain" or "epitaxy" are expected to lessen in significance with respect to their role in heteroepitaxy of inorganic semiconductors. Yet their role on the emerging morphology, as well as other issues like molecular interdiffusion and structure at the organic-organic interface, remain largely unexplored, mainly due to the difficulty in accessing the structure at the organic-organic interface.

In this Letter, by combining atomic force microscopy with *in situ* surface-sensitive x-ray diffraction, we demonstrate the self-organization of well-ordered organic nanodots with high crystallinity and show that their growth is intimately related to a novel type of reconstruction of the underlying organic film which affects three monolayers adjacent to the organic interface. We have studied the growth of Di-indenoperylene (DIP) onto a film of copper-hexadecafluorophthalocyanine (F_{16}CuPc), which are two aromatic molecules typically used as donor and acceptor materials for heterojunctions [Fig. 1(a)]. The molecules have been evaporated in ultrahigh vacuum onto Si(100) wafers covered by their native oxide at a substrate temperature of 120 °C.

The spontaneous emergence of well-defined DIP dots during DIP deposition on F_{16}CuPc at elevated temperature (120 °C) can directly be observed by atomic force microscopy (AFM) measurements. Figure 1(b) shows a topographical image obtained by AFM after deposition of 2.4 monolayers (ML) DIP (40 Å) onto an ultrathin F_{16}CuPc thin film of 2.2 ML (31 Å). The morphology evidences a rather well-ordered nanostructure composed out of DIP nanodots, which exhibit an average size of 100 nm(lateral) × 7 nm(vertical), as well as a very flat and smooth surface [Fig. 1(c)]. The dot-dot autocorrelation function [Fig. 1(d)] discloses a decaying oscillatory behavior with a mean distance of 270 nm between the

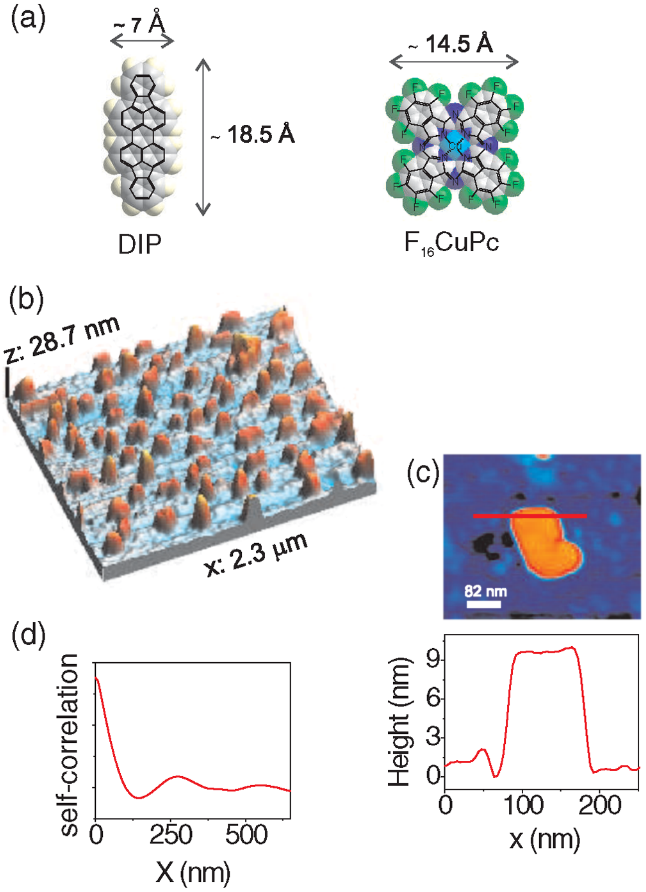

FIG. 1 (color online). (a) Scheme of the DIP and $F_{16}CuPc$ molecules (b) AFM topographic image illustrating the self-assembling of DIP nanodots of uniform size by evaporation of 2.4 ML of DIP (40 Å) onto 2.2 ML of $F_{16}CuPc$ (31 Å) (substrate temperature ~120 °C). (c) AFM topographic image of one of the DIP nanodots and a topographical profile showing the dimensions of the nanodot (100 nm(lateral) × 7 nm(vertical). (d) Self-correlation function showing a correlation length of 270 nm.

organic dots. Larger and higher DIP dots are found for higher coverage, thereby maintaining their narrow size distribution.

In order to shed light onto the growth processes, which finally lead to such self-organized organic structures, we have carried out an *in situ* x-ray study of the microscopic structure which evolves at the DIP-$F_{16}CuPc$ interface during DIP deposition. The measurements were carried out at the ID-10B beam line in the ESRF (Grenoble) with a wavelength of $\lambda = 0.95452$ Å in a portable UHV chamber. The experimental findings from an extended x-ray reflectivity study during the initial deposition of DIP (1 to 8 ML) onto $F_{16}CuPc$ are summarized in Fig. 2. By a routine fitting algorithm [18] the x-ray reflectivity intensity profile can be converted into an absolute electron density profile ρ (z) along the surface normal [right part of Fig. 2(b)].

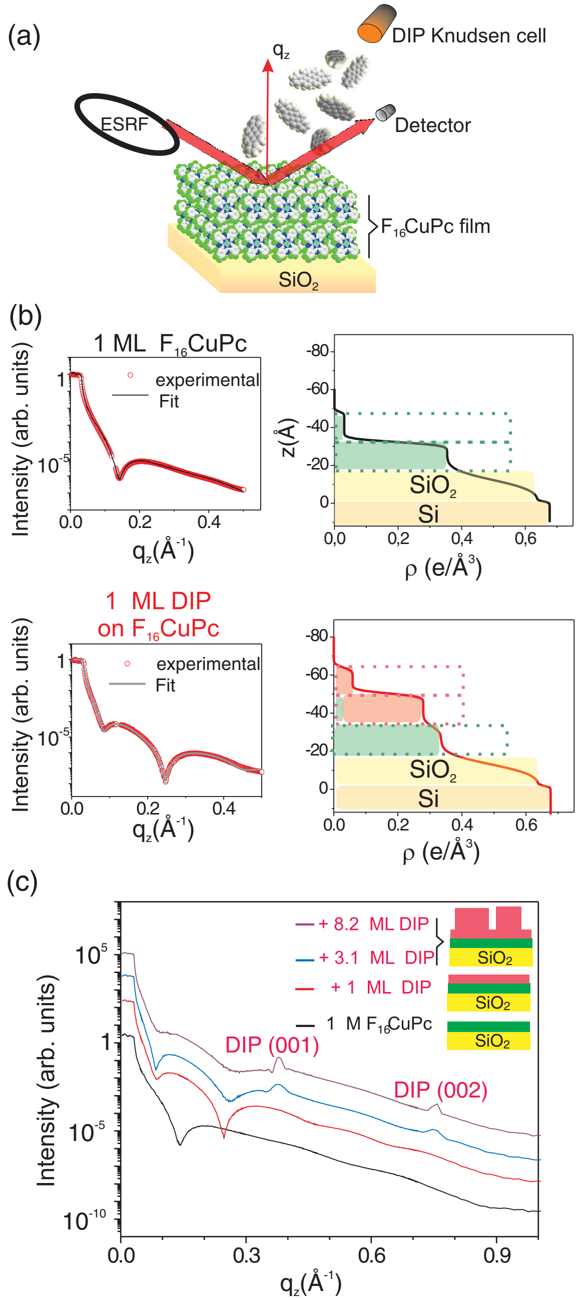

FIG. 2 (color). (a) Scheme of the x-ray experiment performed *in situ* during the growth of DIP onto $F_{16}CuPc$. (b) On the left: measured and fitted x-ray reflectivity data for 1 ML (14 Å) of $F_{16}CuPc$ on SiO_2 (top) and after deposition of 1 ML of DIP (17 Å) onto the $F_{16}CuPc$ (bottom). On the right: deduced electron density profiles. As a guide for the eyes, boxes in different colors mark the layers of different materials (the dashed boxes denote full coverage). (c) X-ray reflectivity for further DIP coverage. The inset depicts the deposition situation.

After deposition of 1 ML $F_{16}CuPc$ (14 Å), an almost complete $F_{16}CuPc$ monolayer of standing molecules forms with a partial nucleation of the second layer. This can directly be deduced from the *in situ* x-ray reflectivity and the fitted electron density profile (Fig. 2, top right). The subsequent evaporation of 1 ML of DIP (17 Å) leads to the formation of a DIP wetting layer with a very well-defined organic-organic interface [Fig. 2(b), bottom right]. We find that the DIP molecules complete the second layer and start the growth of the third layer. The electronic density of the underlying F_{16}CuPc remains unchanged upon DIP deposition, implying that molecular interdiffusion does not occur.

X-ray signals from the internal crystal structure of the DIP nanodots emerge, as soon as the nominal DIP coverage exceeds 3 MLs: The two Bragg reflections in Fig. 2(c) are identified as the DIP(001) and DIP(002) reflections associated with a spacing of $d = 16.6$ Å between adjacent molecular layers. This coincides with the ordered structure of upright standing molecules observed on SiO_2 [19]. From the narrow width of the (001) rocking curves, of only 0.0076°, we deduce an excellent microscopic alignment of the DIP dots with respect to the surface normal.

Our x-ray results thus reveal the formation of a wetting layer of 1 ML of DIP, followed by the formation of crystalline 3D islands upon further DIP coverage. This growth scenario, referred as Stranski-Krastanov (SK) growth, is well known in inorganic semiconductor heteroepitaxy and is held responsible for the self-organization of quantum dots [20]. The remarkable observation in our case is that the SK growth of DIP onto F_{16}CuPc involves a reconstruction of the underlying F_{16}CuPc film adjacent to the organic *p*-*n* interface.

This phenomenon has been disclosed by grazing incidence x-ray diffraction (GIXD), which allows us to access the in-plane crystal structure of F_{16}CuPc and DIP during the growth [Fig. 3(a)]. As illustrated schematically in Fig. 4, F_{16}CuPc stands upright, adopting a columnar stacking of cofacially oriented molecules with a distance between molecular columns of $d(100) = 14.59$ Å and a intermolecular distance of $d(010) = 3.20$ Å [black curve in Fig. 3(a)] [21]. Most interestingly, we observe a clear shift of the F_{16}CuPc in-plane reflections upon the evaporation of 1 ML of DIP, which is highlighted by the arrows in Fig. 3(a). This shift reveals the reconstruction of the underlying F_{16}CuPc film which adopts new lateral lattice spacings, being $d(100) = 11.83$ Å and $d(010) = 3.32$ Å. This change in $d(100)$ (by 14%) points to the formation of a columnar stacking with an average tilt of the F_{16}CuPc molecular plane relative to the [100] direction of about 35° (see Fig. 4). Such a F_{16}CuPc structure has never been observed before and is, according to our experimental observations, induced by the deposition of a DIP monolayer which assumes its characteristic herringbone structure with two molecules per unit cell (the lattice parameters are $a = 8.45$ Å, $b = 7.08$ Å, and $\gamma = 90°$) [22,23]. In contrast to the rather large reconstruction of the underlying F_{16}CuPc, the DIP wetting layer shows no apparent structural changes, i.e., same structure than that exhibited on SiO_2.

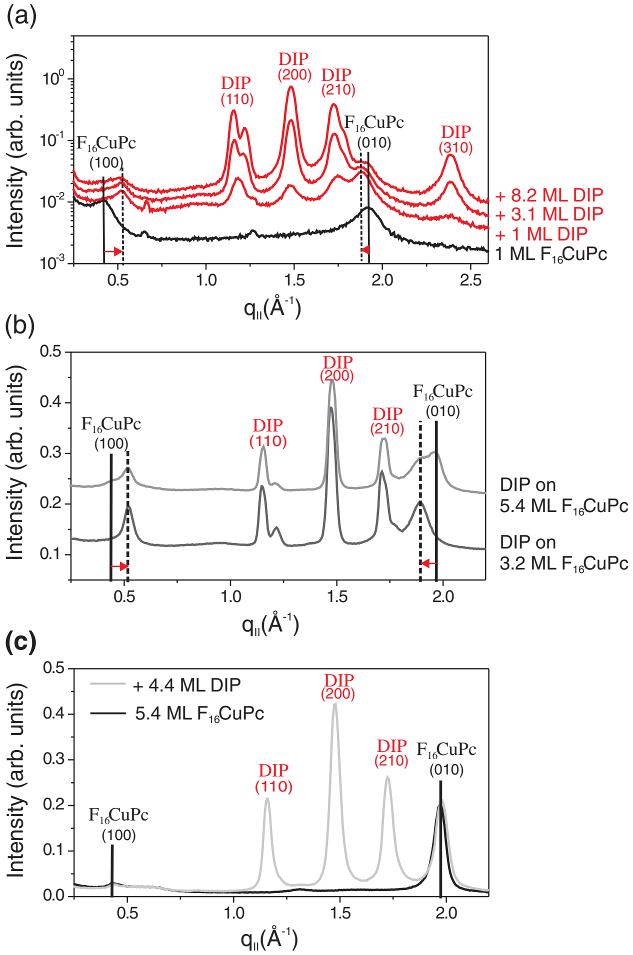

FIG. 3 (color online). (a) GIXD data for DIP (from 1 to 8.2 ML) grown on top of 1 ML of F_{16}CuPc obtained for the same sample as in Fig. 2 (substrate temperature ∼120 °C). The deposition of 1 ML of DIP onto the F_{16}CuPc film results in a shift of the F_{16}CuPc in-plane reflections (dashed bars) evidencing a reconstruction of the F_{16}CuPc film. (b) GIXD data for the deposition of ∼5 ML DIP onto a 3.2 ML F_{16}CuPc film and onto a 5.4 F_{16}CuPc films (substrate temperature ∼120 °C). The thin F_{16}CuPc film undergoes a total reconstruction. In the thicker F_{16}CuPc film, we estimate from the integrated intensities that 3 ML of F_{16}CuPc close to the organic-organic interface reconstruct. (c) 4.4 ML DIP deposited onto 5.4 ML of F_{16}CuPc for a substrate temperature of ∼35 °C (room temperature).

This reconstruction of the underlying F_{16}CuPc film and the subsequent formation of DIP nanodots on top of the DIP wetting layer also occur for thicker F_{16}CuPc films, as confirmed experimentally up to a F_{16}CuPc film thickness of 17 ML. We find from a detailed analysis of the diffraction data [summarized in Fig. 3(b)] that the reconstruction of F_{16}CuPc is limited to three layers adjacent to the organic-organic interface.

A key question now is whether or not the observed DIP-induced interface reconstruction of the underlying F_{16}CuPc film is prerequisite for the formation of the DIP nanodot array. The clue to answer this question is found in

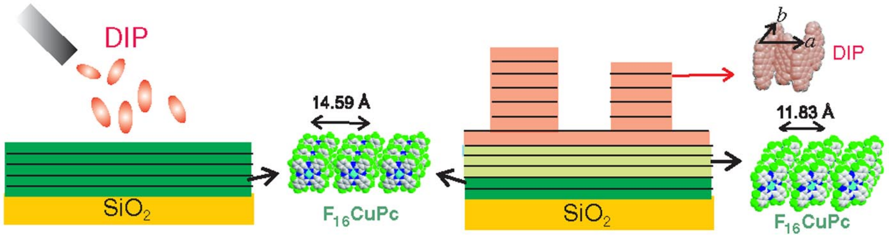

FIG. 4 (color online). General scheme of Stranski-Krastanov growth of DIP nanodots onto F_{16}CuPc thin films.

growth experiments performed for substrate temperatures of -10 °C and 35 °C [Fig. 3(c)]. At these (low) temperatures, DIP deposition does not lead to the rearrangement of the underlying F_{16}CuPc film (most likely because of kinetic barriers). Most interestingly, we also find that no formation of DIP nanodots takes place; instead, we observe the growth of a smooth layered heterostructure. [24] This clearly shows that it is the interface reconstruction of the F_{16}CuPc film which apparently modifies the energy landscape of the organic heterojunction such that SK growth of the DIP sets in, and that other factors which could be associated with the SK growth, such as intermixing or strain in the DIP wetting layer (in the form of in-plane lattice distortion) play no role.

In conclusion, we demonstrate the self-organization of well-ordered DIP nanodots with high crystallinity by Stranski-Krastanov growth of organic-organic DIP-F_{16}CuPc heterostructures. We provide strong evidence that their growth is intimately related to a novel type of interface reconstruction of the underlying F_{16}CuPc film which affects three monolayers adjacent to the organic-organic interface (with changes in the lateral lattice parameter by 14%). In spite of the close resemblance with the formation of inorganic semiconductor nanostructures, the present results conclusively demonstrate a distinctly different growth mechanism for these organic systems. Which kind of heteroepitaxy drives to the observed structural reconstruction and how this leads to the Stranski-Krastanov growth of the organic adlayer are open questions whose understanding clearly demands more experimental and theoretical efforts.

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[24] Neither the DIP nanodots' growth nor the F_{16}CuPc reconstruction occurs upon a postannealing treatment at ~120 °C.