Striped domains at the pentacene:C$_{60}$ interface

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Scanning tunneling microscopy observations of the initial growth stages of the first layer of pentacene on a monolayer film of C$_{60}$ on Ag(111) are presented. Pentacene films nucleate and grow with molecules standing up at the pentacene:C$_{60}$ interface similar to thin film phases observed on weakly interacting substrates such as SiO$_2$. Unlike reported thin film pentacene phases, those on 1 monolayer C$_{60}$/Ag(111) exhibit a striated morphology with domains of 4 nm nominal width. This long range pattern of periodic pentacene displacements relative to the substrate is the response to stress induced in the pentacene film by its interaction with the rigid C$_{60}$ support. © 2009 American Institute of Physics. [DOI: 10.1063/1.3046721]

A major motivation for the development of electronic devices using organic materials is their mechanical flexibility. This property is valuable for the design of durable devices, sometimes in unique formats such as “electronic paper.” Mechanical flexibility arises microscopically from interactions between the molecules that are weaker than covalent or ionic interactions in most inorganic materials. These weak interactions suggest that reconstructions of surfaces and interfaces may be common and potentially dramatic. Large numbers of low energy degrees of freedom can lead to complicated molecular structural motifs.

An example is found in recent x-ray diffraction measurements that indicated the restructuring of several layers of F$_{16}$CuPc induced by formation of an interface with di-indenoperylene. Such heterojunctions between different organic materials are increasingly technologically relevant in optoelectronic devices. In this paper we demonstrate a case where weak interactions facilitate the development of extended defect structures in nanoscale film morphology driven by interfacial stress. We describe scanning tunneling microscope (STM) studies of a donor-acceptor heterojunction formed by growing pentacene on top of a layer of C$_{60}$ on an Ag(111) surface. This approach illuminates the initial stages of growth of pentacene:C$_{60}$ junctions, as recently employed in organic photovoltaic cells. In these devices, the ability of an exciton to generate a photovoltage upon dissociation is related to the efficiency with which it can reach an interface and the efficiency of charge separation at the interface. Optimizing interface morphology for these processes is a necessary step in optimizing device performance.

Experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure of $3 \times 10^{-9}$ Pa) containing a commercial STM [Omicron VT-STM (Ref. 7)]. The Ag(111) surface was prepared by growing a thick epitaxial film of Ag on mica in a separate vacuum chamber (base pressure of $1 \times 10^{-5}$ Pa). This surface was transferred to the main UHV chamber where it was cleaned by sputtering with 1 keV Ar$^+$ ions and annealing at $\sim 500$ K. The surface was characterized by low energy electron diffraction and STM. A uniform single layer of C$_{60}$ was grown on the Ag(111) surface by depositing a multilayer film of C$_{60}$ from an effusion cell (Createc LTC-40) and then annealing to $\sim 500$ K. The result was a uniform (2,3,2,3)R30$^\circ$ overlayer of C$_{60}$. Pentacene was deposited onto the C$_{60}$ monolayer (held at room temperature) from a separate effusion cell (Createc SFC-40). To minimize damage to the pentacene films, local electronic properties were measured using constant current distance-voltage spectroscopy.

The STM image in Fig. 1(a) shows a pentacene island on a monolayer (ML) C$_{60}$/Ag(111). The butterfly shape island is typical for pentacene on C$_{60}$ reflecting its high mobility on the C$_{60}$. Images additionally show a triangular pattern arising from edge dislocations in the Ag(111) film. The apparent height of the pentacene islands above the surrounding C$_{60}$ was measured as 1.2 $\pm$ 0.2 nm based on an average of 19 different line profiles across different island edges on differ-

FIG. 1. (Color online) (a) STM image ($-0.84$ V, 38 pA, 1396 $\times$ 1670 nm$^2$) showing a pentacene island on top of 1 ML C$_{60}$/Ag(111). (b) Distance voltage characteristic (54 pA current, average of 13 sweeps measured at different locations) for a pentacene island. HOMO-derived structure is marked by the arrow. (c) STM image ($-0.84$ V, 38 pA, 502 $\times$ 502 nm$^2$) showing the edge of a pentacene island on 1 ML C$_{60}$. (d) Line profile across the point on the island edge indicated by the blue line in (c).

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ent days [e.g., Figs. 1(b) and 1(c)]. The variations in apparent height occur as a result of common (but unknown) variations in tip work function that influence the local tunneling barrier. Despite this minor effect, the correspondence between the physical length of the pentacene molecule and the apparent island height is a strong indication of a “standing up” layer of pentacene on C$_{60}$.

This height is slightly smaller than that typically reported for upright oriented pentacene films, possibly suggesting an increased tilt of the long axis away from the surface normal. However, electronic factors can also influence apparent height variations in STM measurements.

Additional support for an upright molecular orientation for pentacene is found in the fractal shape of the pentacene islands on C$_{60}$ [Fig. 1(a)]. The island shape is similar to that observed for pentacene thin film growth on SiO$_2$. The common nucleation behavior and island shape occur on substrates that interact relatively weakly with the π electrons in pentacene. Based on the large scale similarities between Fig. 1(a) and pentacene island shapes observed for other weakly interacting substrates, it can be inferred that the microscopic pentacene-pentacene interactions within the island and arrangement of pentacene molecules are very similar to the thin film structure on SiO$_2$. Final support for upright pentacene comes from constant current distance-voltage spectra [Fig. 1(b)] that show a shoulder at about 0.5 eV below the Fermi level. This corresponds to the onset of the pentacene highest occupied molecular orbital (HOMO) observed for other standing pentacene layers.

As shown in Figs. 2(a) and 2(b), the pentacene layer exhibits a unique mesoscale surface pattern of striped domains on top of C$_{60}$. Here extended bright regions meander on the surface, nearly parallel to one another. They are separated by wider regions with an apparent height that is $0.04-0.06$ nm lower than the bright regions. The spacing between bright domains has been measured to be $8 \pm 1$ nm based on an average of 100 measurements of the spacings between parallel bright domains on different surface regions. Similarly, the width of the bright domains is measured as $3.6 \pm 0.6$ nm. The striped domains are not strongly affected by the morphology of the Ag(111) substrate, as shown by the STM image in Fig. 2(b). Stripes (diagonal ripples) extend for distances $>500$ nm crossing Ag steps and triangular dislocations without interruption. The bright regions may be viewed as defective regions of pentacene, while the darker regions represent ideal ordering as described below.

Regions with ideal pentacene ordering are examined with higher resolution in Fig. 3. In the inset we superimpose markers for the C$_{60}$ sublayer (green circles) and the pentacene standing phase (blue lines). Pentacene positions are taken as the standing phase $ab$ parameters reported for pentacene/SiO$_2$.

The molecular scale contrast in the STM image reflects the mismatch in the C$_{60}$ sublayer and the pentacene $ab$ plane. Tunneling conductance along the pentacene axis is low and dominated by the local pentacene-C$_{60}$ “contacts,” introducing topographic variations even in the ideal pentacene-C$_{60}$ regions. Bright spots represent good contacts and therefore have the symmetry of the C$_{60}$ sublayer. Such contrast is reminiscent of other standing organic monolayer phases.

It is instructive to compare the bright striped domains for pentacene/C$_{60}$ films to the localized “sliding defects” reported by Kang et al. for pentacene on a benzenethiol self-assembled monolayer (BT-SAM). The apparent height difference in STM in both cases is about 0.05 nm. The localized defects for pentacene on BT were attributed to vertical displacement of pentacene molecules compared to their surroundings. This could arise from a rigid motion of a pentacene molecule or a change in the angle that the molecular long axis makes with the surface normal. Interpreting the apparent height difference between different domains as the result of such a rotation implies a change in angle of about 3°. This is consistent with angular changes observed in semi-empirical energy minimization calculations of the restructuring of C$_{60}$-pentacene interfaces. Figure 3(b) shows a schematic of the long range modulation in the pentacene layer on C$_{60}$.
ture indicates a spatially correlated condensation of defects. While both interfaces contain vertically displaced pentacene, the displacement propagates only on C$_{60}$.

Defect features at the pentacene:C$_{60}$ interface may impact electrical transport in the pentacene layer or charge separation at the interface. Theoretical calculations have suggested that sliding defects for pentacene on BT would introduce shallow trap states broadened by about 0.1 eV compared to states in the defect free regions. Within the resolution of the tunneling spectra [Fig. 1(b)], there are no significant differences in the electronic spectrum over the ideal regions compared to the defective regions of the pentacene film. This is consistent with distortions within the film that produce only minor (~0.1 eV) modifications to the electronic structure.

The likely origin of the extended defect domains for pentacene grown on C$_{60}$/Ag(111) is stress in the pentacene film due to interactions with the C$_{60}$ sublayer. Spontaneous formation of striped stress domains has been predicted based on elasticity theory and observed for a number of systems. These include Pb–Cu(111) surface alloys and the p(2 × 1)–O–Cu(110) added row reconstruction. The latter case shares the feature in common with pentacene/C$_{60}$ that stripes along one direction and/or anisotropic elastic constants in the pentacene. This will lead to facile domain wall formation at the interface. Theoretical calculations have suggested that a facile route to exerting control over nanoscale interface morphology is to carefully engineer stress relief patterns at soft interfaces.

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