

Evolution of the surface morphology of rubrene under ambient conditions

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Evolution of the surface morphology and local conductivity on cleaved surfaces of rubrene single crystals is characterized with atomic force microscopy. The cleaved surface was found to exhibit molecular reorganization that results in the formation of nanoscale beads aligned along molecular step edges and fingers, narrow molecular structures, one molecule high, and in excess of 1 μm long. The beads show insulating behavior and a band bending effect on the surface nearby. Their formation has a strong environmental dependence, which has implications for the operation of rubrene field-effect transistors in the ambient environment. © 2011 American Institute of Physics. [doi:10.1063/1.3551624]

Organic semiconductors are known as a possible inexpensive alternative for use within electronic devices, and much research has focused on their charge transport properties.¹ Crystalline rubrene has been at the center of this research due to it having a reported field-effect mobility of 10–40 $\text{cm}^2/(\text{V s})$, extremely large for an organic semiconductor.^{2–4} Recently rubrene has also been suggested as a candidate for photovoltaic cells.⁵ Significant effort is now directed toward exploring the modification and control of electronic properties of rubrene; it has been shown that charge carrier concentration and mobility can be manipulated substantially through surface chemistry or interfacial effects.^{4–9} The mechanism controlling the variation of electrical properties is not completely understood, although it was suggested that surface oxidation plays a significant role.^{8–14} Most studies so far concentrated on the “as-grown” single-crystal rubrene surfaces, which exhibit increased carrier mobility in comparison to polycrystalline rubrene films.³ However the as-grown surfaces are less than ideal because postgrowth surface development is often unknown.¹⁰ As a consequence the electrical transport measurements can vary widely from surface to surface. Postgrowth development needs to be understood and a controllable way of preparing high quality contamination-free surfaces needs to be established.

In this letter we describe the evolution of the surface morphology of rubrene single crystals from its environmentally unexposed state and show how the electrical properties vary in the location of features developed over time. We investigated cleaved rubrene surfaces that provide two major benefits over the as-grown surfaces: The newly formed surface is unoxidized, allowing controllable studies of chemical doping processes, and large molecularly flat terraces can be reproducibly created, allowing reliable device fabrication. We show that after cleaving the rubrene surface undergoes molecular reorganization, under the influence of ambient environmental conditions, resulting in conductive properties which change with time and differ from that of as-grown

rubrene. The results shed light on the natural evolution of the surface of rubrene and suggest that these surface processes could have a significant impact on the performance of rubrene field-effect transistors and other electronic components. Furthermore, our detailed characterization of the molecular redistribution on the surface provides the data on which models of molecular surface dynamics can be tested, potentially leading to the development of a long-sought fabrication method for ordered rubrene thin films.

We start by describing the process by which we produce the unexposed rubrene surface using a simple cleaving technique. We used single-crystal rubrene samples grown by the vapor transport method.¹⁵ Sample preparation was performed by mounting the crystal (typical dimension of $2 \times 1 \times 0.3 \text{ mm}^3$ thick) onto a rigid conducting surface using a conductive silver epoxy (EPOTEK 410). More epoxy was then used to attach a rigid metal post to the *ab*-plane surface of the sample. Once the epoxy had cured, lateral force was applied to the post, causing the sample to cleave along the *ab*-plane and exposing a fresh sample surface located at least 50 μm below the original surface.

The topography and electronic properties of single-crystal rubrene surfaces were studied with atomic force microscopy (AFM) and conductive atomic force microscopy (C-AFM), respectively, using a Veeco Dimension 3100 system. Regular images were acquired for over 20 samples, over the course of 24 months. To facilitate C-AFM a conductive channel of graphite paint was made between the sample mount and the sample surface. To study the evolution of cleaved surfaces in the presence of an ambient environment, topographs of the same area of surface were obtained continuously for periods up to 3 days; these areas were regularly revisited over a period of more than 1 yr.

The cleaving process routinely produces surfaces with large molecularly flat terraces, in some cases with sizes of up to approximately $100 \times 100 \mu\text{m}^2$, which is sufficient to allow device fabrications on a single terrace. Terraces on cleaved surfaces are intersected by straight step edge boundaries with regular orientations as seen in Fig. 1(a); this is in contrast to step edges on the as-grown surfaces which tend to be rough and meandering,^{16,17} such as those shown in Fig.

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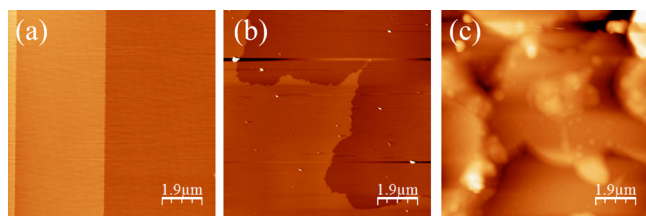


FIG. 1. (Color online) Topographic AFM images (tapping mode) of single-crystal rubrene surfaces; (a) a freshly cleaved sample showing three molecular terraces, (b) an as-grown sample 2 weeks after growth, and (c) an as-grown sample approximately 3 yr after growth. The color scale (black to white) is 10, 13, and 400 nm for (a), (b), and (c) respectively. The samples were all stored and imaged in ambient conditions.

1(b). Figure 1(c) shows an as-grown surface after storage for 3 yr, exemplifying the extreme of postgrowth development. The unknown nature and lack of controllability of the observed postgrowth development have implication for rubrene's suitability for device applications.

AFM allowed the topographic evolution to be monitored. Small surface “beads” of matter began to appear at the step edge boundaries as seen in Fig. 2(a). Beads were initially seen between 30 min and several hours after cleaving. When initially detected they had an average height of ~ 3 nm and a bead-to-bead spacing of 250–600 nm ranging

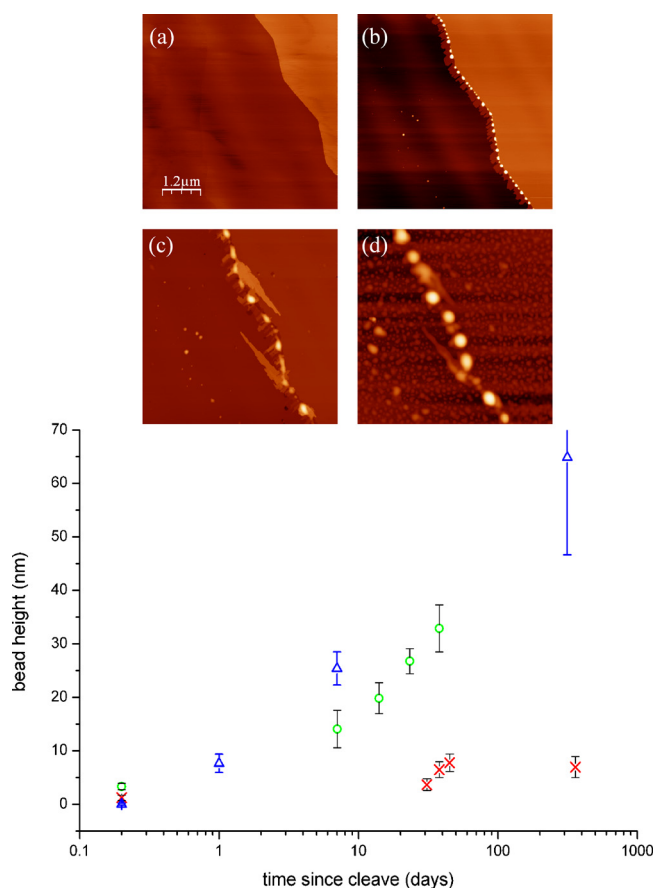


FIG. 2. (Color online) Bead formation after cleaving for several samples shown as the bead height vs time. Average bead height is evaluated using topographic AFM images; error bars show one standard deviation taken over a sample size of approximately 50. Blue triangles correspond to the sample shown in insets (a)–(d): (a) 1 h after cleaving, (b) 1 day after cleaving, (c) 7 days after cleaving, and (d) 11 months after cleaving. The color scale (black to white) is 10, 13, 45, and 150 nm for images (a), (b), (c), and (d), respectively.

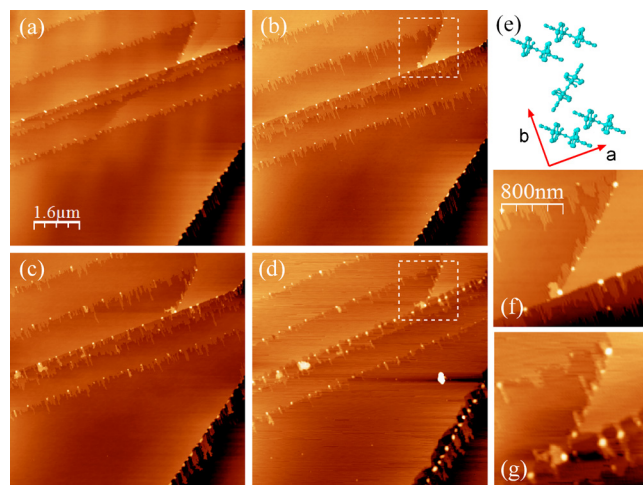


FIG. 3. (Color online) Topographic AFM images (tapping mode) showing the change in surface morphology of a rubrene surface (a) 4.5, (b) 5.5, and (c) 6.5 weeks and (d) 11 months after cleaving. Images (f) and (g) are enlargements of the same area indicated in (b) and (d), respectively. The color scale (black to white) for images (a) and (b) is 13 nm, that for (c) and (d) is 17 nm, and that for (f) and (g) is 20 nm. Schematic (e) shows the crystallographic directions *a* and *b* and the orientation of rubrene molecules.

from sample to sample. Continual growth of these beads occurred as clearly seen in Fig. 2: 1 h after cleaving [Fig. 2(a)] rubrene shows a clean surface; 1 day after cleaving [Fig. 2(b)] the edge is decorated with beads and has finger elongations growing from it onto the lower terrace; after 7 days and 11 months [Figs. 2(c) and 2(d)] the step edge shows substantial overgrowth, some beads have merged, and large features are seen to grow from the step edge. The growth occurred in both illuminated and unilluminated conditions. The average height of beads for several samples is plotted in Fig. 2. The growth rate reduces over time and in some samples the beads reach a maximum height (Fig. 2, red crosses).

After the initial bead formation their development was accompanied by the formation of narrow one molecule high features, “fingers,” as seen in Fig. 3. Fingers were seen to appear several hours after cleaving, and their growth originated from the base of step edges. The fingers had an anisotropic growth preferring to grow along the *b*-axis with a length to width ratio of up to 7:1 and growing to lengths in excess of 1 μm . As seen in Figs. 3(a)–3(d) the fingers are molecularly flat and have a height of 1.4 nm, equal to the height of a single rubrene molecular layer. The height of the fingers implies that they are constructed of either rubrene or a rubrene species, such as rubrene peroxide, where the perturbation of the structure is of such a small degree that it is not resolvable using AFM. Fingers have also been seen to grow from the base of beads as seen in Fig. 2, and a reduction in the bead height was observed in some cases indicating that material from the beads can migrate to form the fingers. This in turn infers that the beads are composed of the same material as the fingers, although, unlike the fingers, there is no evidence that the structure of the beads exhibits crystalline ordering.

In order to understand the origin of beads and fingers, we investigated effects of atmospheric conditions on the surface development. Several rubrene samples were prepared for cleaving and then placed into an argon environment 3 mbar above ambient pressure. The samples were then cleaved within the argon atmosphere and either removed im-

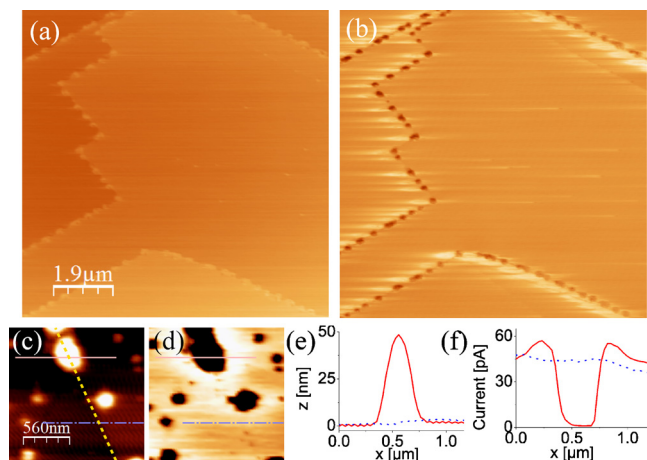


FIG. 4. (Color online) Rubrene surface 2 months after cleaving: (a) topographic AFM image (contact mode) with a color scale (black to white) of 100 nm, (b) C-AFM image of the same area as (a) with a color scale (black to white) range of 200 pA. (c) and (d) show a topographic image and a C-AFM map, respectively, near a step edge, highlighted in (c) for ease of identification. (e) and (f) show topographic and conduction profiles, respectively, of the indicated paths in (c) and (d).

mediately or left in the argon atmosphere for several days after cleaving. On immediate removal from the argon atmosphere the cleaved samples showed no difference to samples cleaved in normal atmospheric conditions, as expected. The samples that were removed 1 week after cleaving showed no surface developments while being in the argon atmosphere. This result shows that the growth of beads is initiated by the presence of an atmospheric component.

In order to probe how the electrical characteristics of the cleaved surface vary from that of an as-grown surface, and how these effects vary with the development of the surface, conductive AFM was used. Figure 4 shows a topographic image and a current map of a rubrene surface, 2 months after cleaving. The beads have a much reduced conductivity in comparison to the adjacent flat terraces. The data presented in Fig. 4 were recorded while the sample was under illumination; the effect is also observed when the sample is probed in the absence of light, although the current is reduced.

Close inspection of the conduction map reveals that conduction is uniform over terraces and step edges as previously seen on as-grown surfaces,⁷ and suggests that no molecular reorganization occurs on the terraces.¹⁸ However in close proximity to the beads conduction increases, instantaneously decreasing at the location of the bead. This is clearly shown in the conduction maps [Figs. 4(b) and 4(d)] and in the conduction profiles [Fig. 4(f)]. Note that the conduction map in Fig. 4(b) shows some streaking which can be avoided by using a lower scan speed as in Fig. 4(d). The reduced conductivity within the beads may be due to a lack of a crystallographic structure that prevents the overlap of π -orbitals between molecules, inhibiting bandlike charge transport.^{3,19} The increase of conductivity in close proximity to the bead is an intriguing observation and could imply that the bead causes band bending on the surface directly below the bead, either as a result of an interfacial effect or due to the bead being charged by the AFM tip.

The exact structure and composition of the beads remain unknown. It is obvious however that step edge boundaries play an important role in the formation of both beads and fingers. They (i) offer a different chemical environment to

terraces and (ii) allow a degree of molecular steric deformation, both of which can make reaction of rubrene with the environment more favorable. The formation of beads in particular must be taken into account when considering the surface area for device fabrication and the continually evolving step edges should be avoided. Further study is being undertaken to clarify the composition of beads.

The data presented in this letter show the morphological changes of the cleaved rubrene surface and how they affect the local conductivity. The surface reorganization consists of two distinct processes: the formation and three-dimensional growth of nanoscale beads, and the formation and two-dimensional growth of narrow one molecule high fingers. These processes are shown to have an environmental dependence and occur in atmospheric conditions implying the incorporation of an atmospheric component, likely oxygen or water, into the material. The observed morphological changes to the surface of rubrene are important considering that exposed surfaces are used in rubrene-based devices. Further controllable studies of the environmental effects performed on cleaved rubrene surfaces can help understand the mechanisms controlling the variation of electronic properties of rubrene.

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