Flux dependence of the morphology of a tetracene film on hydrogen-passivated Si(100)

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(Received 7 December 2005; revised manuscript received 8 February 2006; published 15 March 2006)

The initial stage of vacuum evaporated tetracene films on hydrogen-passivated Si(100) substrates has been investigated using ex situ atomic force microscopy. Three-dimensional (3D) islands and dendrites are obtained at low deposition rates near equilibrium growth conditions. By increasing the deposition rate to a proper range away from equilibrium conditions, terraced grains are formed with layers of standing molecules and good film connectivity. 3D grains with a high aspect ratio appear once the deposition rate is beyond the optimized range. These flux-dependent results indicate a kinetic path for the formation of uniform tetracene films. The initial growth patterns are discussed within the frame of the morphological instability theory.

DOI: 10.1103/PhysRevB.73.121303 PACS number(s): 68.55.−a, 81.15.Hi, 68.55.Ac

Organic thin films are attracting increasing attention because of their rich functionality in devices, such as field-effect transistors (FETs) and light-emitting diodes, where carrier transport and luminescent behaviors are primarily governed by the structural properties of the thin films. Understanding the film formation and optimizing the structural definition (e.g., molecular aggregation, packing, and orientation) are thus not only important in the fundamental research of organic thin films but also imperative to technological progress.

Among the π-conjugated small molecules, pentacene has been intensively studied because of the high carrier mobility in its FETs and because high-quality thin-film growth can be readily achieved. Tetracene consists of four fused benzene rings, with only one ring less than that of pentacene. The bulk crystalline structure of tetracene is similar to that of pentacene with herringbone molecular packing. However, for tetracene thin films, a significantly lower carrier mobility than that for pentacene films was found, and the corresponding thin film growth was reported in favor of island growth with a granular structure. On the other hand, tetracene showed impressive properties in organic light-emitting FETs. Despite these facts, research on tetracene film growth on solid substrates is far from extensive. The study of the initial film formation is particularly lacking, although it is generally accepted that the first few monolayers at the interface are crucial in determining the carrier mobility properties of the film. Also, the type of “layer-by-layer” growth reported in forming pentacene films has not been realized in tetracene case.

In this work, tetracene thin-film growths have been carried out on hydrogen-passivated Si(100) surfaces under ultrahigh vacuum. The deposition rate is used as a kinetic control to alter the tetracene film morphology and structure formation on this well-defined inert substrate surface. We show that high-quality tetracene films can be obtained within a proper range of deposition rate with a similar layer-by-layer growth mode to that for pentacene growth. Besides demonstrating a kinetic path to achieve large grains and good film connectivity of the material, these results also offer us opportunities to explore the thin-film growth mechanisms in light of the morphology instability theory.

Hydrogen-passivated Si(100) substrates were prepared ex situ following a chemical treatment procedure. Tetracene (98%, Sigma-Aldrich) was evaporated in a vacuum (base pressure \( <3 \times 10^{-9} \) Torr) from an alumina crucible heated by a tungsten basket, and the deposition rate was controlled by adjusting the temperature from 380 K to 430 K. A quartz crystal microbalance was used to monitor the nominal thickness and to estimate the deposition rate. Prior to the deposition, clean material was obtained by degassing the tetracene in the vacuum over 10 h at 333 K. All depositions were done with the substrate at room temperature. The nominal film thickness used is \( \pm 4 \) nm for flux rate dependence comparisons. Topographic images were obtained by an ex situ atomic force microscopy (Digital Instruments Dimension™ 3100) in tapping mode with Si tips, and the images were analyzed using software WSxM. The root-mean-square (RMS) roughness of as-prepared H/Si(100) substrates was measured with the atomic force microscopy (AFM) images as within the range of 0.8–1.0 nm.

Figure 1(a) shows dendrites obtained at a low deposition rate of 0.1 nm/min with typical branch widths of a few microns. Long branches are straight about 20 µm in length. During the deposition, the surface structure is significantly improved. A close inspection reveals that the surface consists of terraced grains.
The terrace width (or spacing) tends to be equalized as further growth proceeds, suggesting the existence of Ehrlich–Schwoebel barrier at the terrace edges. A line profile in Fig. 1 shows a typical step height of ~1.4 nm, close to 1.34 nm (the length of tetracene molecule), indicating a “standing” molecule configuration. The film morphology is very similar to that of typical pentacene films reported in literature. The film formed by these admolecules has experienced significant relaxation (both lateral and vertical edge diffusions) before being incorporated. Paired triangle symbols in Fig. 1(a) mark the parallel contour edges, the correlated edge orientations indicate that the branch consists of highly crystallized segments. Therefore, the near-equilibrium relaxation appears to be effective within the range of branch width. Compared with the typical length of a dendrite branch, the branch width is much shorter [i.e., a few microns in Fig. 1(a)]. Beyond this shorter length scale, the near-equilibrium mass transport rate at the growth front is no longer sufficient for keeping the overall structure in compact shape, the point effect of diffusion would then cause admolecules accumulated at structure protrusions to develop branches, leading to the dendrite formation. The appearance of the outer kink sites of the dendrite contour [Fig. 1(a)] suggests the existence of point effect of diffusion: They are noticeably thicker than the other parts on the contour, and they are indeed the starting points for the development of further structures when the growth continues.

At higher deposition rates [Figs. 1(d) and 1(e)], the growth deviates from the near-equilibrium process discussed above. The higher impingement rate at growth front leaves the admolecules less time to fully relax to reach equilibrium incorporation sites. The observed layered morphology is presumably related to more suppression of the vertical edge dif-
fusion than that of the lateral edge diffusion. The different suppression level of the vertical and lateral edge diffusions is likely due to the difference in the activation thresholds, with the vertical edge diffusion being more costly in energy. In addition, the increased nucleation density [or the reduced spacing between two-dimensional (2D) islands] would increase the chances of 2D islands coalescence before the second layer nucleation,\textsuperscript{16} also in favor of 2D growth.

At sufficiently high flux rates (Fig. 2), the 3D grain morphology indicates\textsuperscript{16} that the rapid deposition causes multilayer-island growth before effective island coalescence takes place. In addition, the significant overlapping of the diffusion fields of islands associated with the high nucleation density would disturb the diffusion processes and slow down the lateral growth of an island toward its neighbors,\textsuperscript{11} consistent with the morphology of the high-aspect-ratio 3D grains. There are exposed substrate regions (dark area in Fig. 2) coexisting with these 3D grains, which seems to indicate a small sticking coefficient of the admolecules on H/Si(100). Theoretical results show a weak molecule-substrate interaction for pentacene on H/Si(100).\textsuperscript{17} Given the similar molecular structures for pentacene and tetracene, a similar weak interaction between tetracene and H/Si(100) substrate could be expected.

The formation of layered morphology [Fig. 1(e)] is explored in more detail when the coverage is varied in growth under the same flux rate of 1 nm/min. Figure 3 shows different stages of the submonolayer growth. The monolayer height is measured as $\sim 1.4$ nm, in agreement with the standing molecule structure and a weak molecule-substrate interaction.\textsuperscript{9,18,19} Branch splitting has taken place at the early stage [Fig. 3(a)], which is a clear indication of an isotropic (fractal) growth in contrast to the previous anisotropic (dendrite) growth [Fig. 1(b)]. Similar to the pentacene fractals reported previously,\textsuperscript{3} the 2D tetracene patterns in Fig. 3(a) if described by the diffusion-limited-aggregation (DLA) (Ref. 20) model (hit-and-stick model), have a fractal dimension of $\sim 1.67$.\textsuperscript{21} However, the limited branch width in Fig. 3(a) implies the existence of lateral edge diffusion, as was also the case for pentacene fractals.\textsuperscript{3} In the frame of the morphological instability theory, the growth-shape-formation mechanism for the fractals [Fig. 3(a)] is similar to that for the dendrites [Fig. 1(b)]. The fractal growth involves 2D edge diffusion and more isotropic branch development (essentially based on accidental protrusions) as compared to that of dendrites. With increasing coverage, the branches become wider [Fig. 3(b)], and a second layer nucleates [arrow in Fig. 3(c)] while the first layer is at a coverage of $\sim 60\%$ (Fig. 4). Similarly, when the coverage of the second layer approaches 60\%, the third layer growth starts noticeably (Fig. 4). This growth sequence is nearly identical to the “steady-state layer-by-layer growth” for pentacene on silicon surface.\textsuperscript{3} The corresponding coverage-related mechanisms proposed for pentacene case (Ref. 3) (e.g., islands coalescence, and second layer nucleation)\textsuperscript{16} are thus likely to be applicable to the tetracene case.

It has been shown that cohesive energy for any polycrystalline crystals approximately scale with the molecular length or the number of benzene rings,\textsuperscript{18} so that intralayer molecule-molecule interaction for tetracene is relatively weaker than that for pentacene. Consequently, tetracene mass-transport (diffusion) barriers at its island edges are lower, making tetracene 3D island growth easier to be activated, which is consistent with the fact that in pentacene film growth the 3D crystalline structures require an elevated temperature to form.\textsuperscript{9} Similarly, at room temperature, layered morphology is obtained\textsuperscript{14} for pentacene growth on the same substrate at the flux rate that tetracene would form dendrites, also consistent with above energetic consideration.

We have shown that tetracene growth on H-passivated Si(100) substrate at room temperature is a rich source of

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**FIG. 3.** (Color online) AFM images (20 $\mu$m $\times$ 20 $\mu$m) of tetracene submonolayer growth with deposition rate of $\sim 1$ nm/min for three samples at coverage of (a) 0.15 ML, (b) 0.3 ML, and (c) $\sim 0.65$ ML, respectively. Phase image (a) shows tetracene fractals (dark features). Topographic image (b) and (c) show the development of the 2D film growth with the arrow in (c) indicating the initial second layer.

**FIG. 4.** Fractional layer coverage vs integral coverage for tetracene growth on H/Si(100). Each integral coverage involves an independent sample.
information on the molecular diffusion and aggregation processes. By increasing the deposition rate, the growth morphology can be successively altered to have 3D dendrites, terraced grains with layers of standing molecules and high-aspect-ratio 3D grains. While the 3D structures cause either poor film connectivity or high density of grain boundaries, the terraced grains form a layered morphology with good film connectivity and significantly improved grain size. The layered morphology is obtainable only within an optimized range of deposition rate, where the growth kinetics comprises both suppressed 3D edge diffusion and adequate lateral diffusion on the surface. Under the optimized deposition rate, not only the layered morphology is similar to that reported for a typical pentacene film, but also the terraced-grain formation follows the same layer-by-layer fashion, which has not been achieved for tetracene prior to this study.

We thank John R. Dutcher for his kind support with the AFM instrument for this study. This work was supported by Natural Science and Engineering Research Council of Canada (NSERC), and by Canada Foundation for Innovation (CFI) and Ontario Innovation Trust (OIT).

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10Hydrogen passivation of the surface is used to avoid high density of dangling bonds on the substrate, see, for example: J. J. Boland, Phys. Rev. Lett. 67, 1539 (1991); J. Vac. Sci. Technol. A 10, 2458 (1992).
13WSxM©; http://www.nanotec.es
21Fractal dimension is calculated for relatively isolated fractals [e.g., the upper-left one in Fig. 3(a)] with box counting: W. S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA (http://rsb.info.nih.gov/ij/) 1997–2005.