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Nucleation and growth of tetracene films on silicon oxide

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Tetracene film growth on SiO_2 at room temperature via vacuum evaporation has been studied using *ex situ* atomic force microscopy. We demonstrate that tetracene films of layered morphology and good connectivity can be achieved on SiO_2 under favorable growth conditions. Island size distribution analysis shows that tetracene nucleation in the optimal growth is diffusion mediated with a smallest stable cluster consisting of four molecules (i.e., the critical island size $i=3$). The film stability is sensitive to the film thickness. Postgrowth film structural evolution occurs on the time scale of minutes for the films at coverage less than three monolayers, while stable films become evident at coverage higher than three monolayers.

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I. INTRODUCTION

Conjugated semiconducting oligomers such as polyacenes have shown great potentials as materials for organic electronic devices.[1–4] In particular, for devices such as emerging organic light-emitting field-effect transistors,[4,5] tetracene ($C_{18}H_{12}$) is regarded as a promising candidate. Because the molecular films serve as the device active layers, their structural properties primarily govern the carrier transport and luminescent behaviors.[1–4] Especially, in an organic field-effect transistor, the field-induced carriers are located mostly within a few monolayers (MLs) of the organic film above the molecule-dielectric interface;[6] therefore, understanding of the thin-film properties and the film structure formation in growth is of fundamental importance.

Tetracene ($C_{18}H_{12}$) consists of four fused benzene rings—just one ring less than the most studied polyacene pentacene. Although a high carrier-mobility value was reported in tetracene single-crystal form,[7] the mobility values for tetracene thin films on SiO_2 have been found about an order of magnitude lower.[8,9] Reports show that the tetracene films are largely dominated by granular growth structures.[8–10] However, compared with efforts in pentacene film studies,[11–14] research on tetracene films is far from being extensive. In particular, a layered film morphology in tetracene growth has not been realized on SiO_2, the archetypical gate oxide material in thin-film transistors, despite the recent progress in quasi- "layer-by-layer" growth for tetracene on hydrogen-terminated Si(001).[15,16] Also, the initial tetracene island formation and the factors that influence the film structural properties on SiO_2 have not been fully explored.

In this paper, we report that tetracene films of layered morphology and good connectivity can be realized on thermally grown SiO_2 using proper kinetic conditions in growth. Quantitative analysis of atomic force microscopy (AFM) data shows that tetracene nucleation is diffusion mediated with a smallest stable cluster consisting of four molecules (i.e., the critical island size $i=3$), as in the case of pentacene growth on SiO_2.[17] Under ambient conditions, pronounced postgrowth film evolution occurs on the time scale of minutes for the tetracene islands with less than three molecular layers in thickness and continuous deposition leads to a stable tetracene film at coverage higher than three MLs. Possible factors to cause the film morphology evolutions have been discussed.

II. EXPERIMENTAL DETAILS

Tetracene (98%, Sigma-Aldrich) was deposited from a homemade evaporator with an alumina crucible covered with tantalum screen. The crucible was heated by a tungsten basket under ultrahigh vacuum with a base pressure below 3×10^{-9} Torr. The deposition rate was monitored by a quartz-crystal microbalance. All the film growth was done with the substrate at room temperature. Silicon wafer substrate cleaning procedures prior to oxidation included ultrasonic agitation in acetone, 45 min boiling in $H_2SO_4(98\%):H_2O_2(30\%)=1:3$, and ~1.5 min etching in 1% HF to remove the native oxide from silicon wafers. A 30-nm-thick SiO_2 substrate was then thermally grown on Si(001) substrates at 950 °C in dry oxygen at the ambient pressure.[18] The as-grown SiO_2 substrates with root-mean-square roughness ~0.4 nm were used without any further treatment. After film deposition, samples were taken out of the growth chamber immediately (within ~5 min) and investigated with an atomic force microscopy (Digital Instruments Dimension™ 3100) operated in air in tapping mode with Si tips.

III. RESULTS AND DISCUSSIONS

Growth of tetracene films on SiO_2 was initially carried out with a deposition rate of 1 nm/min, which is an optimal flux rate leading to quasi-layer-by-layer growth of tetracene on H/Si(001).[15,16] Figure 1 shows a typical image with film nominal thickness of ~4 nm (~3 ML). There are bright three-dimensional (3D) faceted dendrites with narrow branches (~15–20 nm in height), flatter (~4 nm in height) islands often contoured with thick edges, and large substrate gaps in between these islands. Clearly, the optimal deposition rate is substrate dependent and what was found appropriate for H/Si(001) substrate does not produce a desirable film on SiO_2 substrate.

However, tetracene on SiO_2 shows abundant similarities with reported behaviors of tetracene on H/Si(001).[15] When the deposition rate is increased to ~3 nm/min [Fig. 2(a)],

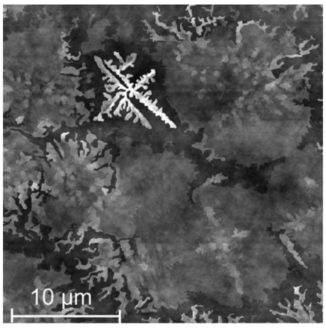

FIG. 1. AFM images (30×30 μm^2) of ~3 ML tetracene films grown on SiO_2 at room temperature with deposition rate of 1 nm/min.

the absence of bright 3D dendrites and the appearance of terraced islands manifest a relatively uniform film of layered morphology. The 3 nm/min flux rate appears to be the onset rate for realizing an optimal tetracene film. Similar film morphologies have also been obtained under flux rates up to ~6 nm/min. For instance, with a flux rate of 4.5 nm/min, a similar film to that in Fig. 2(a) has been obtained as shown in Fig. 2(b). There are darker lines or "canyons" in these films. The image areas with a square frame in Fig. 2(a) and a rectangular one in Fig. 2(b) are enlarged to show some canyons in detail. The AB and CD line profiles show that at the bottom, a canyon may be the exposed substrate (darkest locations in the images) and in most cases a number of molecular layers above the substrate as indicated by the dashed lines in AB and CD line profiles. The AB line profile also shows that a terraced island (near point A) away from the nearby canyon has monolayer steps, while the steep edges of canyons appear as in multiples of the molecular length in height, indicating a film structure of standing molecules. Figure 3 presents closed-up views of the films away from the canyons, which are similar to that of a tetracene film on hydrogen-passivated Si(001) under a flux rate of 1 nm/min (Ref. 15) except that the island densities are higher, which is most likely due to the higher-flux rates applied. Apparently, the edge contours of terraced islands appear more isotropic for Fig. 3(d) (4.5 nm/min) than that for Fig. 3(b) (3 nm/min), suggesting that the higher-flux growth deviates more from forming equilibrium island shapes, consistent with that obtained for tetracene films on H/Si(001).[15] Compared with the previous reports that tetracene films on SiO_2 were largely dominated by granular growth structures, the current results shown in Fig. 2 represent significant improvements in the film quality, demonstrating that the layered morphology and good film connectivity can be achieved for tetracene on SiO_2.

The flux-dependent morphological change and the appearance of terraced islands on SiO_2 closely resemble those of tetracene films on H/Si(001),[15] indicating some common film growth kinetics in these two cases: low-deposition rates favor near-equilibrium growth processes leading to bright bulklike crystals [Fig. 1(a)] and high-deposition rates impede admolecule diffusions and kinetically leave them less time to relax to their equilibrium configurations, resulting in forming a layered morphology.[15] The onset optimal flux rate appears higher on SiO_2 (3 nm/min) than on H/Si(001) (1 nm/min), suggesting a weaker molecule-substrate interaction for tetracene on SiO_2. Because weaker molecule-substrate interactions lead to a lower energy barrier for the molecules to diffuse on the substrate surface and result in relatively stronger intermolecular interactions, so that the film growth is more inclined in forming equilibrium crystalline structures, a higher-deposition rate in growth is thus required to suppress such equilibrium structure formation in order to achieve a layered morphology. Although both SiO_2 and H/Si(001) substrates are inert, different chemical termination and different ordering of substrate surface [i.e., amorphous SiO_2 vs

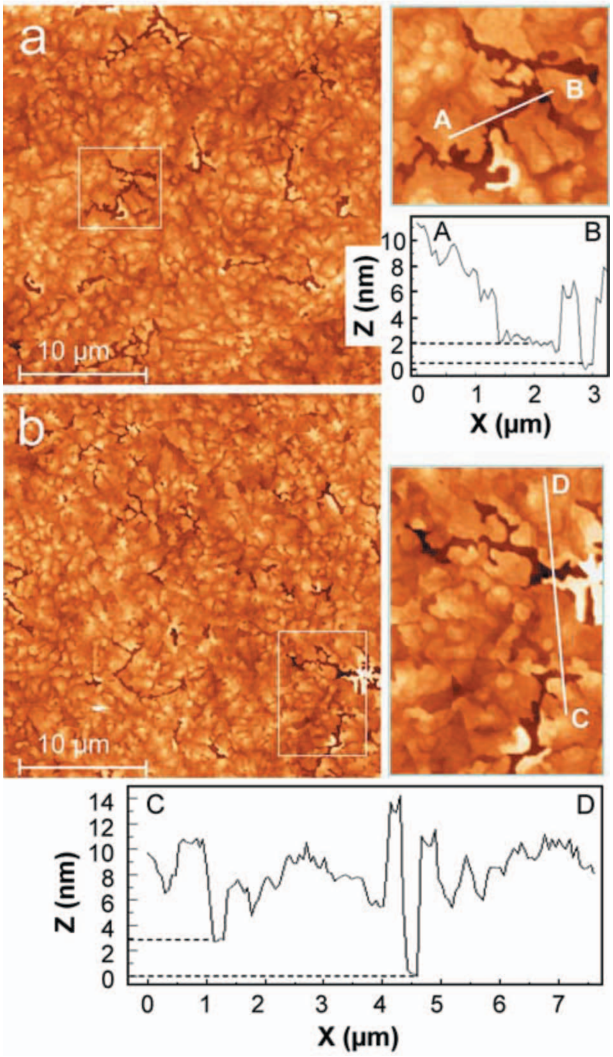

FIG. 2. (Color) Topographic images (30×30 μm^2) of ~3 ML tetracene films grown on SiO_2 with deposition rate of (a) 3 and (b) 4.5 nm/min. The square frame in (a) is enlarged with AB line profile showing the details of a canyon; the darkest location is the exposed substrate and the most part of this canyon is ~1.5 nm (about one molecular length 1.35 nm within the noise level) above the substrate as marked by the dashed lines in the AB profile. The rectangular frame in (b) is enlarged with a line CD passing through two canyons; the upper canyon is nearby a pinning-center induced 3D (bright) structure and the lower one is ~3 nm (i.e., about two molecular layers in height) above the substrate as shown by the dashed lines in the CD profile.

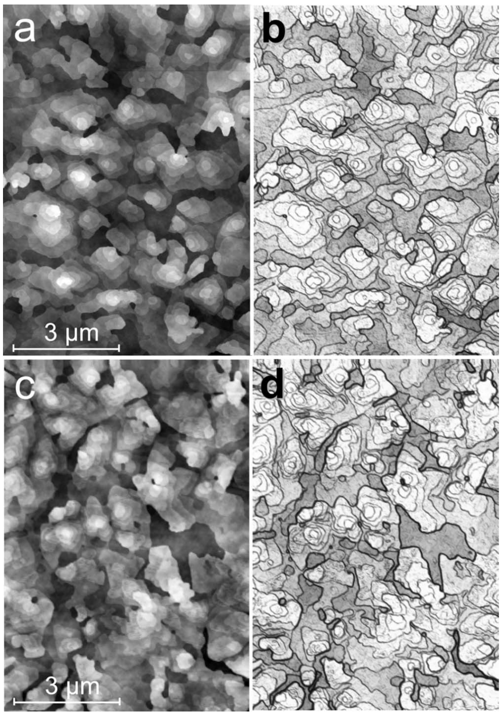

FIG. 3. Closed-up views of the films in Fig. 2 with deposition rates of (a) 3 and (c) 4.5 nm/min. (b) and (d) are the contour views of (a) and (c), respectively. Image sizes: $7\times10\ \mu\text{m}^2$.

crys5talline lattice of $\text{H/Si(001)}-2\times1$] could be the origin for the relatively weaker interaction on SiO_2.

To investigate whether tetracene nucleation of the layered films is related to the diffusion-mediated growth behavior, as observed in pentacene film growth on silicon oxide,[17,19] we have carried out submonolayer island-size distribution (ISD) analysis. We follow a method reported for pentacene film growth (Ref. 17). To achieve a reasonable density of nucleation within a typical AFM image for statistical analysis, we use submonolayer films grown under a flux rate of 4.5 nm/min. Figure 4(a) shows such a film with tetracene first-layer islands at coverage $\theta=0.35$ ML. According to the ISD analysis,[17,20] if the film growth is diffusion mediated, the distribution of islands of size a per unit area, $N(a)$, should scale with the average island size $A=[\Sigma aN(a)]/\Sigma N(a)$ in the form of $N(a)=\theta A^{-2}f(u)$, where $u=a/A$ and $f(u)$ is a dimensionless theoretical scaling function. The $f(u)$ depends on the critical island size i in the approximate form of $f(u)=C_iu^i\exp(-b_iiu^{1/b_i})$, where C_i and b_i are functions of i that can be obtained numerically.[20] From the AFM image [Fig. 4(a)], $N(a)$ and a can be measured and, thus, through the scaling relationship above, $f(u)$ can be experimentally obtained as $N(a)A^2/\theta$. The experimental data (bar graph) in Fig. 4(b) are best fitted by the theoretical scaling function $f(u)$ with $i=3$ [solid curve in Fig. 4(b)]. The quantitative agreement between the scaling function and the measured data confirms that the initial tetracene growth mimics the inorganic two-dimensional (2D) diffusion-mediated growth with the smallest stable cluster consisting of $i+1=4$ molecules as in the case of pentacene nucleation on SiO_2 at room temperature.[17] In addition, power-density spectrum of the data in Fig. 4(a) (i.e., the Fourier transformation of the AFM image) is found to have a ringlike structure [inset of Fig. 4(b)] with a well-defined radial maxima located at $k_m\approx3.2\ \mu\text{m}^{-1}$. The ringlike structure, as was also the case of pentacene fractals on silicon oxide,[17] demonstrates a strong spatial correlation between the 2D islands with a unique characteristic island separation $(2\pi/k_m)$, consistent with the diffusion-mediated growth picture.[17]

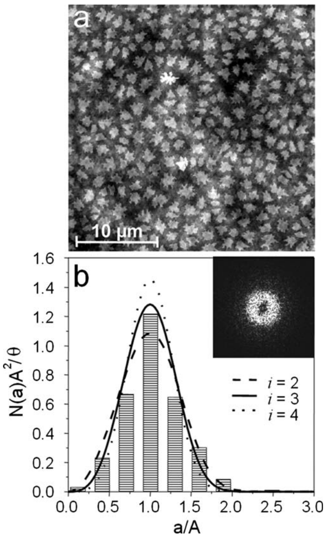

FIG. 4. (a) AFM image $(30\times30\ \mu\text{m}^2)$ of a ~0.35 ML film with tetracene first-layer islands grown at a flux rate of ~4.5 nm/min. (b) Normalized island-size distribution (ISD) of the film is best fitted by the scaling function for $i=3$ (solid line). Inset: power-density spectrum of (a).

Using the same method, we have also carried out the ISD analysis for the similar submonolayer films grown under a flux rate of ~6 nm/min and obtained the same diffusion-mediated growth behavior with $i=3$ as that shown in Fig. 4(b), consistent with the similar morphologies obtained in our experiments under these flux rates.

With increasing deposition of tetracene, the growing islands appear to be metastable at local coverage less than three molecular layers. First, for the submonolayer films, we observe postgrowth film structural evolution taking place on the time scale of minutes in the form of mass transport from the first layer to the second layer. AFM measurements clearly indicate that the postgrowth evolution is correlated with the existence of admolecules on top of the first layer, suggesting that the appearance of second-layer molecules could destabilize the monolayer islands. As shown in Fig. 5, a first-layer island protrusion [as pointed by the lower arrow in Fig. 5(a)] shrinks in minutes while the top second-layer area is enlarged [Fig. 5(b)]. On the other hand, for the first-layer islands without any second-layer molecules, the island size and morphology remain stable over 5 h in measurements.

Second, the tendency of the postgrowth evolution continues for films at monolayer level of nominal coverage. Figure 6 shows a topographic image of a 1.2 ML film grown at a flux rate ~4.5 nm/min, which is at an intermediate stage of forming a layered film. As indicated by the closed-up view line profile, most of the top surface consists of second-layer islands but some remaining first-layer islands are evidently

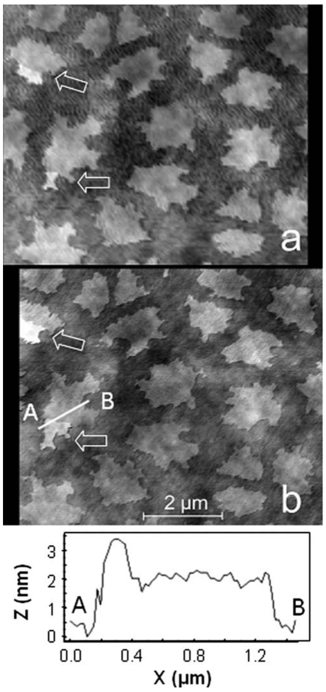

FIG. 5. AFM images (7.6×7.6 μm^2) of submonolayer islands of a $\sim$0.35 ML film grown under deposition rate of 4.5 nm/min. (a) Occasionally observed islands with admolecules on top of the first layer are marked by arrows. (b) The same islands imaged 10 min later with the second layers clearly expanded. The AB line profile shows the height of each layer. At this coverage most islands are in fact stable single-layer islands. The different gray shades in the background of these images indicate that the substrate is not atomically flat due to the substrate preparations.

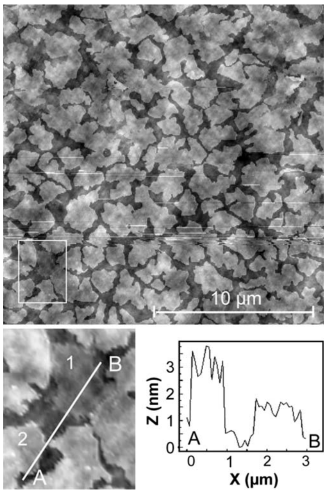

FIG. 6. AFM image (20×20 μm^2) of a 1.2 ML tetracene film grown at $\sim$4.5 nm/min about 30 min staying in air after deposition. A closed-up view of an image area (white frame) and AB line profile show the first and second layers on the surface as marked by 1 and 2, respectively.

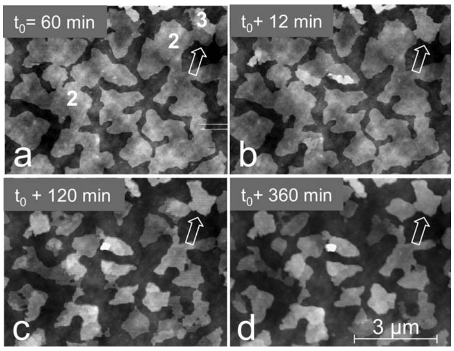

FIG. 7. AFM images (8×6 μm^2) of the same 1.2 ML tetracene film shown in Fig. 6 after staying in the air for (a) $t_0=\sim60$ min, (b) t_0+12 min, (c) t_0+120 min, and (d) t_0+360 min after deposition. The second and third layers are marked by 2 and 3 in (a). An island (marked by an arrow) becomes stable once the third layer is complete.

observable. Figure 7 shows a series of AFM tracking images of a surface area of the same film shown in Fig. 6. About one hour after deposition, predominant islands exhibit double layers with double-layer steps [Fig. 7(a)]. These double-layer steps indicate the kind of postgrowth film evolution previously mentioned; the originally exposed first-layer molecules in a terraced island may have been transported to the second layer as a result induced by the existing second-layer molecules. The morphology in Fig. 7(a) is in strong contrast to tetracene on H/Si(001) at this coverage, where terraced islands are stable for weeks with single-layer steps,[15,16] indicating a sensitive role played by the substrate here.

Lastly, we further observe that the double-layer islands in Fig. 7(a) also evolve with time. As shown in Fig. 7, the islands less than three molecular layers are all subject to change—mass transports from lower layers to higher layers. Noticeable dewetting appears in the 1.2 ML film in the form of substrate patches developing with time. However, once an evolving island [e.g., as the one marked by an arrow in Figs. 7(a) and 7(b)] is completely covered by three layers, it becomes quite stable [Figs. 7(c) and 7(d)].

Sufficiently stable films can be realized when stopping growth at coverage higher than 3 ML. As shown in Fig. 2, a 3 ML film already exhibits a rather stable morphology.[21] Figure 8 shows topographic images for 15 ML tetracene films grown at flux rates of 3 [Fig. 8(a)] and 6 nm/min [Fig. 8(b)]. Both films in Fig. 8 have a similar morphology with grains of layered structure on the surface, similar to that reported for pentacene grains on SiO_2 under 2D nucleation.[22] Also, both films are stable in air for up to one year without any visible morphological changes revealed from AFM imaging.

With a 1.2 ML tetracene film kept under the vacuum for 2 h after deposition, we observe no film left on the surface under AFM. In other words, under the vacuum conditions, tetracene desorption could be an important factor to cause evolutions for an as-grown thin film. But, under ambient conditions, the effect of desorption appears negligible because the integrated film volumes in the observed area remain approximately the same for images in Fig. 7 and the film is still observable after staying in air for months. Presumably, the adsorption of the molecules in the atmosphere may effectively suppress the tetracene desorption.

All the above results seem to imply a coverage-dependent structural transition for tetracene on SiO_2. Alongside the rapid postgrowth film evolutions observed, we recollect that

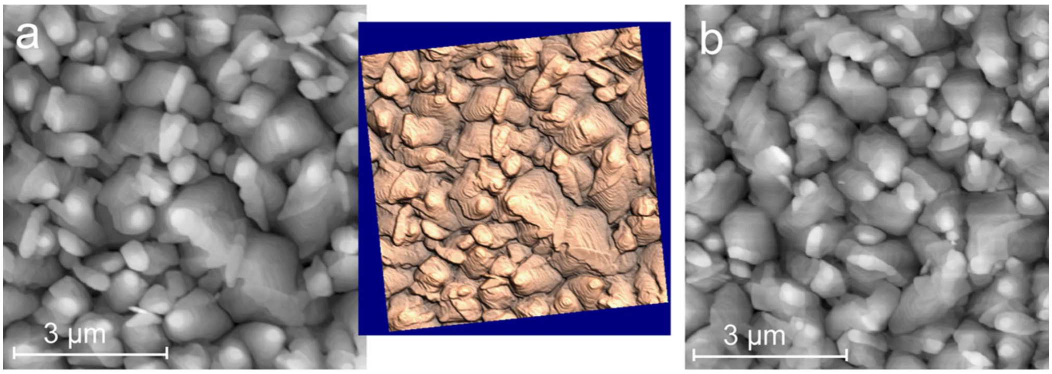

FIG. 8. (Color online) AFM images (7×7 μm^2) of tetracene 15 ML films grown under flux rate of (a) ~3 and (b) ~6 nm/min. (Middle inset) A perspective view of the layered film shown in (a).

there are situations that the films are significantly stable: (1) the first-layer islands (Fig. 5) without any second-layer molecules on top; (2) the local three-layer islands (see arrows in Fig. 7); and (3) the thick films (>3 ML). In other words, under the same ambient conditions, the stability of a thin film sensitively depends on the coverage. These stability differences could reflect the differences in the film properties. We suggest that there are defective structures or high density of domain boundaries in the low-coverage films (Figs. 5 and 7) as they may be generated by the substrate influences (e.g., local roughness caused by substrate preparations, amorphous structure of SiO_2) and by the high-flux deposition applied in growth. In such case, the rapid postgrowth evolution observed could be a self-correction process to eliminate the defective structures, leading to a more thermodynamically stable film under ambient conditions. The correction process could be enhanced by interlayer molecular interactions as the second-layer molecules appear to trigger the first-layer island evolution (Fig. 5).

Our previous study[16] of tetracene growth on H/Si(001) indicates that there is a structural transition associated with the third layer formation and that significant amount of highly crystallized islands emerges at nominal coverage of 3 ML. Analogously, we conjecture that the growth of tetracene islands on SiO_2 may likewise have a similar structural transition, considering the similar growth behaviors of tetracene on both SiO_2 and H/Si(001). Presumably, during the growth, with the excess vapor of tetracene molecules on the surface, the defective structures formed in the early growth could be adjusted continuously while the film density increases. The densification of the layers in growth would enhance the intralayer molecular interactions, favoring the film to reach a much stable configuration to form stable thick films. The detailed kinetics and the driving force of the structure transition require further investigation.

We notice from a recent report[23] on 1.3 ML pentacene films grown at a flux rate of 0.2 nm/min (i.e., well-crystallized pentacene films[24]) that there are no postgrowth morphological changes on clean SiO_2 in vacuum. Also, without pentacene desorptions in vacuum, a 1.3 ML pentacene film on a modified SiO_2 shows film evolutions and the exposure to the air changes the evolution speed significantly.[23] Considering that the standard vapor pressure of tetracene is higher than the vapor pressure for pentacene (or weaker intralayer molecular interactions for tetracene[22,25]), it is reasonable that tetracene is easier to re-evaporate from the film surface in vacuum at room temperature. On the other hand, under ambient conditions, the SiO_2 substrate we used could be modified, e.g., there could be a thin layer of water introduced on SiO_2, as was reported in a similar case on pentacene.[26] Further investigation is required to identify interface effects and their roles in the tetracene film evolutions.

IV. CONCLUSIONS

We have realized tetracene films of layered morphology on SiO_2 at room temperature under proper evaporation conditions. The initial nucleation has been confirmed to be diffusion mediated with the smallest stable cluster consisting of four molecules, similar to that in pentacene film growth on SiO_2. It is observed that a higher optimal flux rate is required in growing the layered morphology for tetracene on SiO_2 than in the case of tetracene on $H/Si(001)-2\times1$, indicating a weaker molecule-substrate interaction in the former case. Under an optimal flux rate, the stability of a tetracene film on SiO_2 strongly depends on the coverage. For a film at coverage less than three monolayers, pronounced postgrowth morphological changes occur on the time scale of minutes, leading to a noticeable dewetting of the film from the SiO_2 substrate. The postgrowth film evolution ceases at film locations where the local coverage reaches three monolayers and stable films can be realized at nominal coverage higher than three monolayers. These coverage-dependent film-stability results have been speculated such that there could be a structural transition associated with the film thickness.

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