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Kinetics of island formation in organic film growth

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Three dimensional islands with flat tops, steep edges, and a characteristic height are grown by organic molecular beam deposition. The mesalike shape of the organic islands results from an efficient ascending interlayer transport process, which originates from different effective step-edge binding energies of strained layers and unstrained layers. The molecules preferentially attach onto the upper step edges, which possess higher effective binding energy with the molecules. Numerical simulations based on the model agree well with the experimental results.

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An important feature of functional organic materials[1,2] is that their physical and chemical properties are readily tunable by molecular design. The performances of organic devices, however, depend not only on the molecule itself, but also on the arrangement of molecules in the films. Due to the large lattice mismatch between the organic layer and the substrate, the growth of organic films on reactive substrates preferentially follows the Stranski-Kranstanov (SK) mode:[3] Beyond the initial wetting layer with a thickness of one or a few monolayers (MLs), three dimensional (3D) islands are formed.[4–8] To investigate the film growth, the kinetic processes should be considered on the molecular scale, among which the interlayer mass transport determines the film morphology.[3,9,10] To date, the role of the step-down process on film growth has been well understood. During a step-down process, the molecules encounter an additional step-edge barrier, or Ehrlich-Schwoebel (ES) barrier appending on the surface diffusion barrier when molecules cross a step edge. In the case of an efficient step-down interlayer transport, nucleation of a second layer takes place after the full coalescence of the layer underneath, resulting in layer-by-layer (LBL) growth. In contrast, inefficient interlayer transport results in a 3D mound formation and increases the roughness of the film. Given the inhibited interlayer mass transport, molecules remain on the layer on which they are deposited and mounds with a terraced wedding-cake-like shape are formed.[3]

Here, we study the formation of mesalike islands upon the wetting layer during the growth of organic thin films. It is found that organic islands with steep edge, flat top, and characteristic height are formed on a metallic substrate at certain range of temperatures. To understand the organic island formation, a model is proposed in which not only the descending interlayer transport process but also the ascending process is taken into account.

As a model system, oligoethylene-bridged diferrocene (diFc), $\mathrm{Fc(CH_2)_{14}Fc}$ (Fc=ferrocenyl), was deposited on a Ag(110) surface by organic molecular beam deposition with an average rate about 0.2 nm/min.[11,12] The nominal thickness of the organic films is about 5 nm. The film growth follows the SK mode with 3D islands formed on a wetting layer. As investigated by scanning tunneling microscopy, the wetting layer surrounding the 3D islands exhibits the same superstructures as the ML films grown on Ag(110) reported elsewhere.[12] Figure 1(a) shows the atomic force microscopy (AFM) image of a typical diFc island grown at 300 K. The islands exhibit straight edges with characteristic orientations, indicating the crystalline structure. Three straight edges of the island in Fig. 1(a) are marked by E1, E2, and E3, which coincide with the (0, 1), (1, 1), and (1, 0) directions in the (−2 1 1) plane of the diFc molecular crystal [Fig. 1(b)], respectively. The measured angles enclosed between E1 and E2 and between E1 and E3 are about 50° and 81°, agreeing with the values in the crystal, 49.6° and 79.5°, respectively.

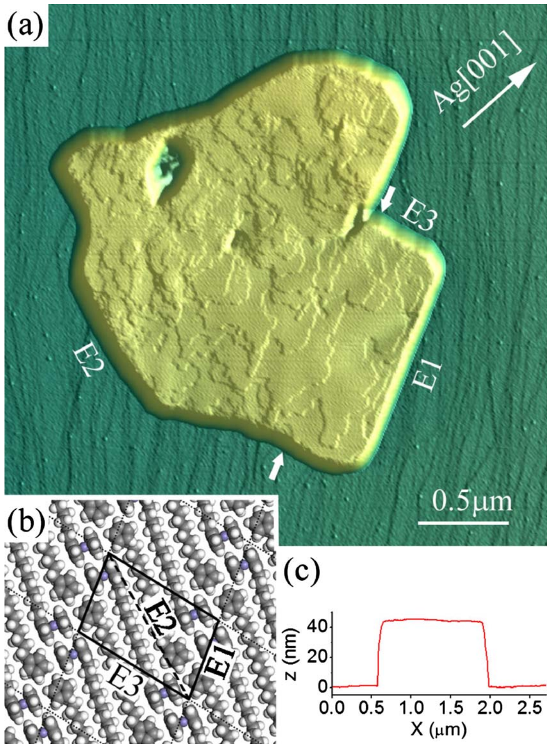

FIG. 1. (Color online) Mesalike organic island grown on a Ag(110) surface (covered with a wetting layer). (a) AFM image. (b) The (−2 1 1) plane in the molecular crystal. The edges of the island in (a) marked by E1, E2, and E3 correspond to the (0, 1), (1, 1), and (1, 0) directions in the (−2 1 1) plane, respectively. (c) Height profile crossing the island along the arrowed direction in (a).

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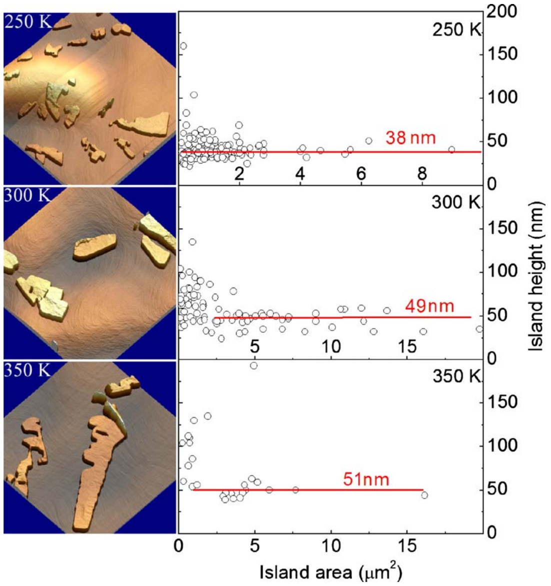

FIG. 2. (Color online) AFM images (left, $10\times 10\ \mu\text{m}^2$) and the height-area relations (right) of organic islands grown at 250, 300, and 350 K. The lines and the values on the right column show the central location of a Lorentz fitting of the height distribution.

The molecular steps observed on the top of an island have a height about 0.6 nm, consistent with the interlayer distance of the bulk (−2 1 1) plane. The result above indicates that the 3D islands are grown with the (−2 1 1) plane parallel to the substrate surface. The island is mesalike with steep edges and flat tops [see the height profile in Fig. 1(c)], different from the hutlike islands of metals or inorganic semiconductors.[13–15]

Figure 2 shows the AFM images and the height-area relation of the islands grown at 250, 300, and 350 K. Although the size of the islands is various in a wide range, the height of the islands grown at a certain temperature shows a narrow distribution, especially for the larger islands. The characteristic heights for samples grown at 250, 300, and 350 K are 38 ± 6, 49 ± 13, and 51 ± 10 nm, respectively. The characteristic heights presented here implies that the formation of organic islands may obey different mechanisms in comparison to the hutlike islands,[13–15] the height of which is proportional to the lateral size.

Similar island growth with uniform height has been reported for some inorganic epitaxial systems, for instance, Bi and Ag on Si(111) (Refs. 16 and 17) and Pb on Cu(111),[18] due to the quantum size effect or structure phase transition. The quantum size effect related to the above systems appears at length scales in the order of magnitude of several nanometers, which is much smaller than the characteristic height of the organic islands and, thus, cannot account for our experiments. Campione *et al.*[5] attributed the mesalike shape of organic islands to the transient mobility of the deposited molecules. However, no experimental evidence has been exhibited to date, indicating that the deposited molecules or atoms retain their kinetic energy without dissipation during the diffusion on the substrate until immobilization on an island. Another factor that affects the film morphology is the strain in the epitaxial film. Recently, the formation of flat-top islands has been explained by the interplay of strain and edge energies.[19]

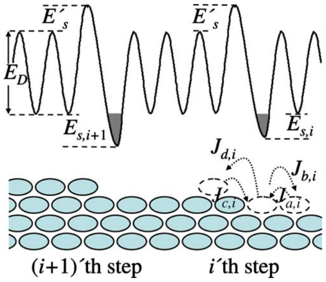

FIG. 3. (Color online) Kinetic processes of interlayer mass transport and the related energy barriers. Due to the mismatch between the substrate and the epitaxial organic layer, the additional step-edge binding energy ($E_{s,i}$) is dependent on the location of the step edge. The step edge of the relaxed layer far beyond the wetting layer possesses higher binding energy with the molecules than the step edge of the strained layer close to the wetting layer.

For understanding the formation of the flat-top organic islands as well as the hutlike inorganic quantum dots, not only the step-down interlayer mass transport, but also the step-up transport should be considered. By introducing a step-up process, the formation of hutlike facetted metallic nanocrystals has been successfully explained based on the density functional theory and kinetic Monte Carlo simulation.[13,14] According to the work, the upward diffusion of the adatoms at a step edge along the cross-channel direction on the fcc metal (110) surface is achieved via a reversible place exchange mechanism.

To reveal the driving force for the ascending process during the growth of organic islands, a model is proposed here in which the step-edge binding energy is dependent on the location of the steps. Figure 3 shows the energetic diagram of molecular diffusion on the surface. For a molecule descending from terrace i to terrace $(i-1)$ (step-down process), an energy barrier of E_D+E_s' is encountered, where E_s' is the ES barrier. On the other hand, for a molecule ascending from terrace $(i-1)$ to terrace i (step-up process), the energy barrier equals $E_D+E_{s,i}+E_s'$, where $E_D+E_{s,i}$ is the step-edge binding energy and $E_{s,i}$ the additional binding energy on step i. Four processes contribute to the interlayer mass transport (see Fig. 3): (a) a molecule adsorbed on terrace $(i-1)$ attaching onto step edge i, (b) a molecule on the step edge i detaching onto terrace $(i-1)$, (c) a molecule adsorbed on terrace i attaching onto step edge i, and (d) a molecule on the step edge i detaching onto terrace i. We assume that the surface of the epitaxial front is a square lattice with lattice constant a. The fluxes (number of molecules per second and per unit cell) of the four processes at the step edge along (0, 1) or (1, 0) directions of the square lattice are written as

$$J_{a,i}=\nu_0 n_{i-1}e^{-E_d/k_BT}, \tag{1a}$$

$$J_{b,i}=\nu_0 e^{-(E_{s,i}+E_d)/k_BT}, \tag{1b}$$

$$J_{c,i}=\nu_0 n_i e^{-(E'{}_s+E_d)/k_BT}, \tag{1c}$$

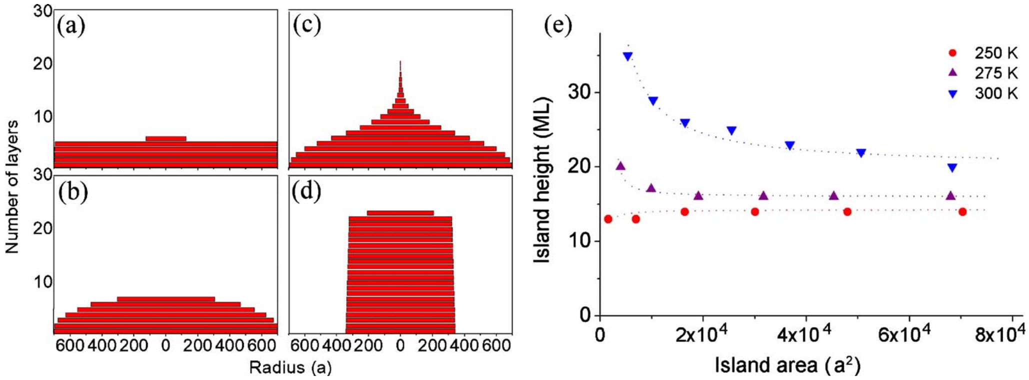

FIG. 4. (Color online) Results of numerical simulations based on Eqs. (1a)–(1d) and (2a)–(2c). (a) LBL growth with efficient descending mass transport. (b) Mound formation with inefficient descending process. (c) Statistical growth without interlayer mass process. (d) mesalike island formation with an ascending process. (e) Height-area relations of the mesalike islands at 250, 275, and 300 K (the dotted lines are a guide for the eye). See text for the simulation parameters.

$$J_{d,i}=\nu_0 e^{-(E_{s,i}+E'_s+E_d)/k_BT}, \tag{1d}$$

where k_B is the Boltzmann constant, T is the temperature, n_i is the density of molecules adsorbed on terrace i (number of molecules per unit cell), and ν_0 is the attempt frequency (s^{-1}). In Eqs. (1a) and (1c), the fluxes for molecules on a terrace attached to the step edge are proportional to the density of the molecules adsorbed on the terrace.

A key point of our model is that the effective step edge binding energies are different for different step edges. The binding energy at a step edge is determined by the configuration of the molecule on the adsorption site with its neighboring molecules. Due to the mismatch between the wetting layer and the organic layer beyond the wetting layer, the effective binding energy on the first step edge is lower than that on the step edges far away from the first layer, in which the configuration of the molecules are well relaxed. As a result, the molecules prefer to bind on the step edges far away from the first layer. The effect of strain on the diffusion of adatoms on a surface has been reported in Refs. 20 and 21. Due to the anisotropic interaction, the energy barriers related to the surface diffusion of organic molecules are rather complicated. In order to focus on the fundamental point in the diffusion process, the detailed features of individual molecules are smeared and the interaction between the molecules is considered isotropic in our model.

Suppose molecules deposited on an area with radius of R_0 are captured by the island nucleated at the center of the area (desorption process is ignored here). The evolution of the radius of layer i ($R_i, i=1,2,3,\ldots$) (in unit of surface lattice constant a) and the number of molecules adsorbed on terrace i ($N_i, i=0,1,2,\ldots$) are described by the following equations:

$$\frac{dN_0}{dt}=\pi(R_0^2-R_1^2)F+2\pi R_1(J_{b,1}-J_{a,1}), \tag{2a}$$

$$\frac{dN_i}{dt}=\pi(R_i^2-R_{i+1}^2)F+2\pi R_{i+1}(J_{b,i+1}-J_{a,i+1})+2\pi R_i(J_{d,i}-J_{c,i}), \tag{2b}$$

$$\frac{dR_i}{dt}=J_{a,i}-J_{b,i}+J_{c,i}-J_{d,i}, \tag{2c}$$

where F is the deposition rate (molecules per second per unit cell). The density of molecules adsorbed on terrace i is written as $n_i=N_i/\pi(R_i^2-R_{i+1}^2)$. In Eq. (2b), the variation of molecule number on terrace i is determined by three parts: molecules deposited from the source (the first term), molecules detaching from and attaching onto adjacent steps (the second term), and molecules detaching from and attaching onto step i (the third term). In Eq. (2a), the variation of molecule number on terrace 0 (the wetting layer) is only contributed by the first two parts. Similarly, the variation of R_i in Eq. (2c) is a net effect of the four related attachment and detachment processes on step i.

In order to give a qualitative view of our model, numerical simulations have been carried out based on the Eqs. (1a)–(1d) and (2a)–(2c). The parameters in the simulations are obtained from our experiments and the literature and are typical of organic film growth without loss of universality. The diffusion barrier $E_D=0.32$ eV is estimated from the relation of the island density with the growth temperature from experiments.[22] The attempt frequency $\nu_0=10^{12}\ \mathrm{s}^{-1}$ is used in all simulations.[23] The nucleation of the ith layer takes place when n_{i-1} reaches a threshold value: $n_{i-1\mathrm{th}}=e^{-E_{s,i}/k_BT}$, at which $J_{a,i}=J_{b,i}$. The radii of the terraces are constrained as $R_i-R_{i-1}\geqslant a$ in order to avoid infinity of n_i.

First, different growth modes were successfully simulated when keeping the growth temperature $T=300$ K, but adjusting the ES barrier and the additional step-edge binding energy. Figures 4(a)–4(d) show the shape of the simulated islands grown on the substrate with a capture radius $R_0=700a$, deposition rate $F=1$ ML/s, and deposition amount of 5 ML. LBL growth was obtained with $E'_s=0$ and $E_{s,i}=0.15$ eV for all i, as shown in Fig. 4(a). However, mounds were formed with inefficient interlayer mass transport when a finite ES barrier was applied: $E'_s=0.05$ eV [Fig. 4(b)]. Figure 4(c) shows a wedding-cake-liked island, which was obtained without any interlayer transport ($E'_s \gg k_BT$). For the simulation of island formation with ascending process, we chose the additional step-edge binding energies as

$$E_{s,i} = E_{s,1} + \frac{i-1}{i_s - 1}(E_{s,\infty} - E_{s,1}) \quad \text{for } i < i_s,$$

$$E_{s,i} = E_{s,\infty} \quad \text{for } i \geqslant i_s,$$

where $E_{s,1}=0.05$ eV and $E_{s,\infty}=0.15$ eV are the additional binding energies at the first step edge beyond the wetting layer and the molecular layers far away from the wetting layer, respectively, and $i_s=5$ is the strain relax thickness, which is defined as the thickness of the strained layers.[24] The ES barrier is chosen as $E_s'=0.05$ eV.[25] Under this condition, the ascending process was activated, and a mesalike island was formed with a height of 23 ML and a lateral radius of 342a. The island has a flat top and steep edge, consistent with the observed experimental result.

Then, we changed the capture radius R_0 but kept other parameters the same as the simulation for Fig. 4(d), obtaining the relation of the island height to the lateral size at growth temperatures of 250, 275, and 300 K, as shown in Fig. 4(e). At a certain temperature, especially at 250 or 275 K, the island height is nearly independent of the island size, which agrees well with our experimental results. It should be noted that due to the simplicity of the model, deviations in comparison to experimental results exist in the simulation, for instance, the trend of the temperature dependence of the characteristic height. A possible reason for the deviation is that the threshold density $n_{i\text{th}}$ for the nucleation on terrace i at higher temperatures is underestimated in the simulation.

In summary, the formation of flat-top, steep-edge organic islands with a characteristic height is explained by a strain-driven ascending process. This ascending process is attributed to the difference of effective step-edge binding energy existing at strained layers near the substrate and the strain-free layers far away from the substrate. As a result, the molecules preferentially attach onto the upper step edges, which possess a higher effective binding energy with the molecules. We believe that the microscopic kinetics proposed here captures the fundamental mechanism of mesalike organic island formation on a mismatched substrate and is applicable to other systems with similar phenomena.

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