

Control of initial growth processes of epitaxial films using pulsed molecular beams

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Kinetics of epitaxial thin film growth was analyzed from the experiments using pulsed organic molecular beams. It was found that a minimum appears in the nucleation density as a function of on-off cycle time when the substrate temperature is near the threshold between growth and reevaporation. This feature can be explained by assuming desorption of molecules induced by mutual collision on the surface, for which orientation-sensitive intermolecular forces are responsible.

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When the substrate temperature during vacuum deposition is elevated, the sticking coefficient decreases and no growth will be observed at temperatures high enough. Although this phenomenon has been explained using steady state thermodynamics,¹ precise processes dominant near the threshold between growth and reevaporation have not been understood well. The growth/reevaporation transition is important because it leads to the difference in the sticking coefficient among substrate materials, which is now extensively used in semiconductor and organic nanostructuring as selective growth phenomena.²⁻⁶ We here report an unexpected kinetic factor determining the threshold that is found during the epitaxy of organic molecules using pulsed molecular beam technique. In the growth of organic thin films, the kinetic process becomes particularly important because the time scale for settling to the energy minima is longer than other systems due to weak van der Waals interaction mediating the growth.

We have chosen quinacridone ($C_{20}H_{12}N_2O_2$; QA) on (001) surfaces of alkali halides (NaCl and KCl) and C_{60} on α - $MoTe_2$ (0001) as the grown organic materials and the substrates, respectively. The materials combination has been selected because the effect of atomic height steps was found to be negligible among them. The alkali halide substrates were cleaved in air and annealed at 130 °C for 4 h in the ultrahigh vacuum (UHV) growth chamber to remove large steps. α - $MoTe_2$ was cleaved in air and heated 150 °C for 4 h in UHV. The substrate was kept at certain growth temperatures during the molecular beam irradiation. QA was purified by vacuum sublimation and C_{60} (purity 99.5 %) was used as purchased. The pulse source consists of a disk with four round holes which are evenly spaced. By rotating the disk with a constant speed, the molecular beam has intensity profile as shown in Fig. 1(a). The ratio of open time to one cycle time was about 0.13 ($=d$) in the present experiment. The instrumental detail of the pulsed beam source is described elsewhere.⁷ The total growth time (“on”+“off” time) was constant for all of the experiments for one materials system, resulting in the same total number of the molecules impinging onto the substrate surface. After the growth, the sample was cooled down and taken out to ambient atmosphere. An atomic force microscope (AFM; SEIKO SPI-3800) was used to study the growth feature, in particular, the shape and density of the organic crystallets formed on the surfaces.

Figure 1 shows AFM images of QA film grown on KCl with various “cycle time” (τ), namely the period between the beginning of “open” and the end of “close” of the rotating slit. The temperatures of the substrates (T_{sub}) and evaporation sources (T_{source}) were 100 °C and 320 °C, respectively. As seen in the images, QA forms rod-shaped islands whose orientation is almost aligned with (100) and (010) axes of the substrates. It should be noted that the shape and the density of the islands are not affected by steps on the substrates. The difference in the nucleation density for various τ is easily noticed.

Figure 2 shows the density of the islands as a function of the cycle time (τ). The error bars are estimated from the

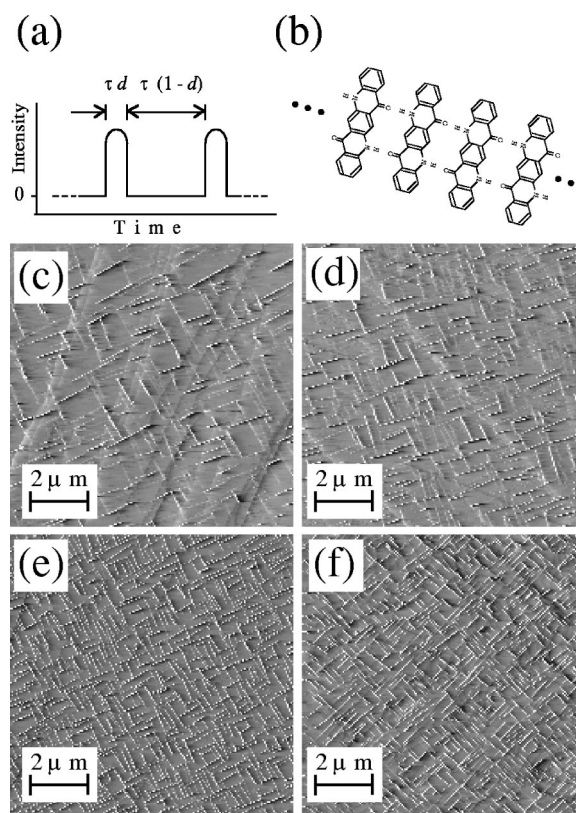


FIG. 1. (a) Shape of the impinging molecular pulses. (b) Molecular arrangement in QA crystals. (c)–(f) AFM images of QA grown on KCl(001) at 100 °C with ON/OFF duty $d=0.13$. (c) $\tau=38$ ms, (d) $\tau=150$ ms, (e) $\tau=560$ ms, (f) $\tau=2.7$ s.

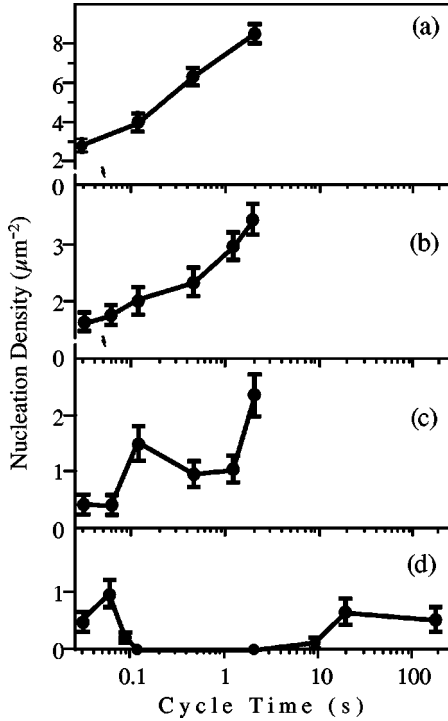


FIG. 2. Nucleation density of QA on alkali halides as a function of cycle time (t). The substrate materials and temperatures are as follows. (a) KCl, 90 °C; (b) KCl, 110 °C; (c) NaCl, 90 °C; (d) NaCl, 110 °C.

square root of the counted numbers of the islands, which were larger than the standard deviation derived from several experiments. The nucleation on KCl substrate in Figs. 2(a) and 2(b) show monotonous increase in the log scale of τ . On the other hand, the growth on NaCl substrates was different [Figs. 2(c) and 2(d)]. Both Fig. 2(c) ($T_{\text{sub}}=110$ °C) and 2(d) ($T_{\text{sub}}=90$ °C) show an increase, take a peak, then decrease, and finally increase. The cycle time, which gives the peak density, is (c) ~ 210 ms and (d) ~ 427 ms. Note that no growth of the islands is observed in (d) for the cycle time between ~ 427 ms and ~ 1400 ms, while nucleation is observed on KCl at the same condition. Measurement of the nucleation density on lower temperatures was impossible because too many islands are formed on the substrate surface. The density of flower-like C_{60} monolayer islands on $\alpha\text{-MoTe}_2(0001)$ only showed the increasing nucleation density as a function of τ for various sets of substrate temperature and molecular flux (Fig. 3).

We have attempted to reproduce the experimental results by using rate equations as shown in the following equations:

$$\begin{aligned} \dot{n}_1 = & I(t) - k_0 n_1 - k_1 + n_1^2 - \sum_{j=2}^{c-1} k_j + n_1 n_j + 2k_1 - n_2 \\ & + \sum_{j=3}^{c-1} k_{(j-1)} - n_j, \end{aligned} \quad (1)$$

$$\dot{n}_i = k_{(i-1)} + n_1 n_{i-1} - k_i + n_1 n_i + k_i - n_{i+1} - k_{(i-1)} - n_i, \quad (2)$$

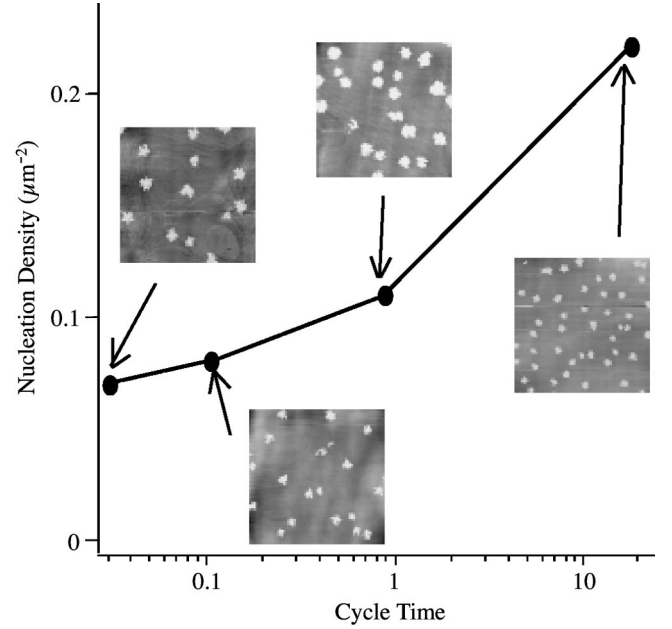


FIG. 3. Typical example of nucleation density in the pulsed molecular beam growth of C_{60} on $\alpha\text{-MoTe}_2(0001)$. The temperatures of the substrate and the source were 100 °C and 400 °C, respectively. Insets are AFM images with $50 \mu\text{m} \times 50 \mu\text{m}$.

$$\dot{n}_c = k_{(c-1)} + n_1 n_{c-1}, \quad (3)$$

where n_i is the concentration of cluster with size i , c is the size of critical nuclei which is the smallest for being thermodynamically stable. k_{i+} and k_{i-} are rate constants corresponding to the creation of clusters with size $i+1$ and decomposition of clusters with size $i+1$, respectively. k_0 is the desorption rate constant of monomers. Here it is assumed that enlarging or shrinking of the clusters must involve merging or releasing of monomers. Impinging molecules are expressed using a integer m as

$$I(t) = \begin{cases} I_0 & (m\tau \leq t < (m+d)\tau), \\ 0 & ((m+d)\tau \leq t < (m+1)\tau). \end{cases} \quad (4)$$

We have performed extended numerical examination with various parameters, but it was impossible to reproduce the minima of the nucleation rate as a function of cycle time. The reason can be explained as follows. Shown in Fig. 4 are the typical numerical results of concentrations of monomers (n_1) and largest unstable clusters (n_{c-1}) as functions of time ($c=4$ for the figure). It is noticed that there are three regions of τ that are distinctly different from each other. For small τ , both of n_1 and n_{c-1} are almost constant [case (i): Figs. 4(a) and 4(b)]. For intermediate τ , n_1 has a similar feature with impinging pulse and n_{c-1} is slightly oscillating around a finite value [case (ii): Figs. 4(c) and 4(d)]. For large τ , both of n_1 and n_{c-1} have pulsed shapes that are nearly proportional to the impinging flux [case (iii): Figs. 4(e) and 4(f)]. Asymptotic values of the growth speed \dot{n}_c can be calculated for each case by assuming $n_1 \gg n_2 \gg \dots \gg n_{c-1}$ which leads to the approximation of Eq. (2) as

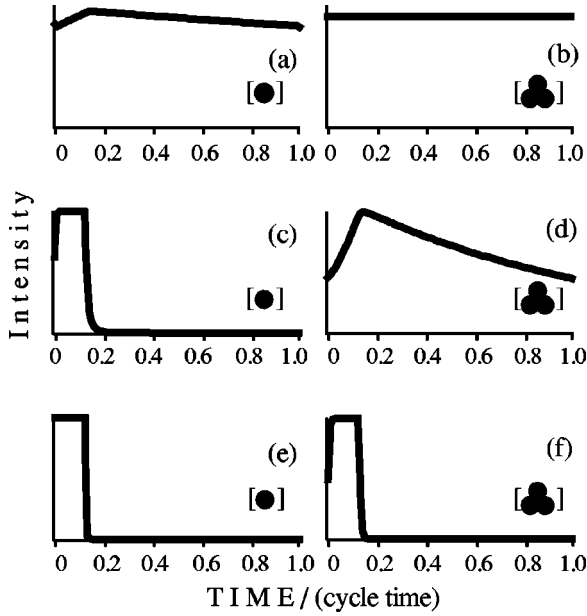


FIG. 4. Typical numerical results for the cluster concentration for various regions of τ by using the rate equations (1)–(4). Parameters are as follows: $c=4$, $I_0=10$, $k_0=10$, $k_{1+}=1$, $k_{1-}=0.2$, $k_{2+}=1$, $k_{2-}=0.2$, and $k_{3+}=1$. (a), (b) $\tau=0.01$; (c), (d) $\tau=5$; and (e), (f) $\tau=1000$.

$$\dot{n}_i \approx k_{(i-1)+} n_1 n_{i-1} - k_{(i-1)-} n_i. \quad (2a)$$

In case (i), the impinging pulses are smeared out by the migration of the monomers that results in $I(t) \approx I_0 d$ and $n_1(t) \approx \bar{n}_1 \equiv I_0 d / k_0$. n_i are obtained from stationary condition $\dot{n}_i \approx 0$ as $\bar{n}_i = (k_{(i-1)+} / k_{(i-1)-}) \bar{n}_1 \bar{n}_{i-1}$ for $i < c-1$. The growth rate R is

$$R = \frac{1}{\tau} \int_{\tau} \dot{n}_c dt = k_{(c-1)+} \left(\prod_{j=1}^{c-2} \frac{k_{j+}}{k_{j-}} \right) \bar{n}_1^c = A \left(\frac{I_0}{k_0} \right)^c d^c,$$

where

$$A = k_{(c-1)+} \left(\prod_{j=1}^{c-2} \frac{k_{j+}}{k_{j-}} \right).$$

In case (ii), the smearing of the pulsed feature becomes significant at some marginal m -mer ($1 < m < c$) and the concentration of clusters larger than m becomes nearly constant as the function of time. The maximum value of pulsed $n_1(t)$ is the saturation value $\hat{n}_1 \equiv I_0 / k_0$ for a continuous beam of strength I_0 . As for the plateau value of $n_i(t)$,

$$\hat{n}_i \approx \left(\prod_{j=1}^{i-1} \frac{k_{j+}}{k_{j-}} \right) \hat{n}_1^{i-1}$$

for $i < m$ is derived using Eq. (2a) and $\dot{n}_i = 0$. Since the integration of $\dot{n}_i = k_{(i-1)+} n_1(t) \bar{n}_{i-1} - k_{(i-1)-} \bar{n}_i$ over one cycle is zero for $m < i < c$, it follows $\bar{n}_i = (k_{(i-1)+} / k_{(i-1)-}) \bar{n}_{i-1} \hat{n}_1 d$ ($i > m$). At the transition from constant to

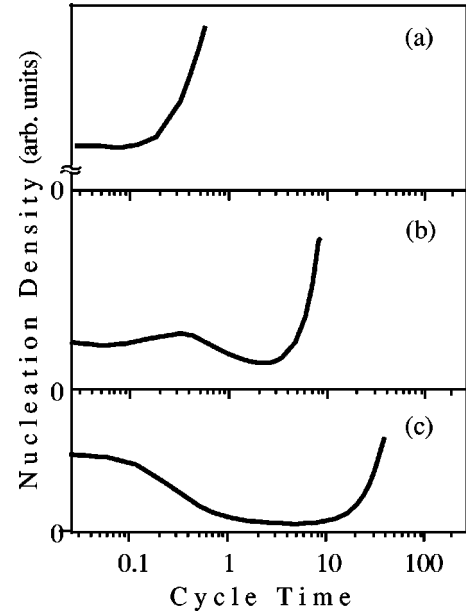


FIG. 5. Numerical simulation of nucleation density to reproduce the experimental results by using the rate equation including collision induced desorption [Eq. (1a)]. Parameters are as follows and only α was changed through (a)–(c): $c=4$, $I_0=10$, $k_0=10$, $k_{1+}=1$, $k_{1-}=0.2$, $k_{2+}=1$, $k_{2-}=0.2$, and $k_{3+}=1$. (a) $\alpha=10$, (b) $\alpha=100$, (c) $\alpha=1000$.

pulsed function, it is reasonable to assume the intermediate value $\bar{n}_m = (k_{(m-1)+} / k_{(m-1)-}) \hat{n}_{m-1} \delta$ ($d < \delta < 1$). They result in

$$\begin{aligned} R &= k_{(c-1)+} \left(\prod_{j=m}^{c-2} \frac{k_{j+}}{k_{j-}} \right) \bar{n}_m \hat{n}_1^{c-m} d^{c-m} \\ &= k_{(c-1)+} \left(\prod_{j=1}^{c-2} \frac{k_{j+}}{k_{j-}} \right) \hat{n}_1^c d^{c-m} \delta = A \left(\frac{I_0}{k_0} \right)^c d^{c-m} \delta. \end{aligned}$$

In case (iii), since the concentrations of all species have pulse shapes,

$$R = k_{(c-1)+} \left(\prod_{j=1}^{c-2} \frac{k_{j+}}{k_{j-}} \right) \hat{n}_1^c d = A \left(\frac{I_0}{k_0} \right)^c d.$$

From the above estimation the ratio of the nucleation rate in case (i), (ii), and (iii) are d^{c-1} , $d^{c-m-1} \delta$, and 1, respectively, which means the ratio increases monotonously as a function of τ . It agrees with the numerical result of full rate equations that does not take minimum for various sets of parameters.

The discussion above suggests attaching an extra term to the rate equation to enlarge the desorption rate of the monomers. We have found that the experimental result can be reproduced by adding the desorption term proportional to the square of the monomer concentration:

$$\begin{aligned} \dot{n}_1 = & I(t) - k_0 n_1 - k_{1+} n_1^2 - \sum_{j=2}^{c-1} k_{j+} n_1 n_j + 2k_{1-} n_2 \\ & + \sum_{j=3}^{c-1} k_{(j-1)-} n_j - \alpha n_1^2. \end{aligned} \quad (1a)$$

The time dependence of cluster concentrations looks similar to Fig. 4, but the absolute values of ordinate become different because of the increased desorption. If $\alpha I_0 \gg k_0^2$ and $\alpha \gg k_{1+}$, the asymptotic values of n_1 for cases (i) and (ii) and (iii) are $\bar{n}_1 = (I_0 d / \alpha)^{1/2}$ and $\hat{n}_1 = (I_0 / \alpha)^{1/2}$, respectively. It follows that the average nucleation rates R are: (i) $A(I_0 / \alpha)^{c/2} d^{c/2}$, (ii) $A(I_0 / \alpha)^{c/2} d^{c-m} \delta$, and (iii) $A(I_0 / \alpha)^{c/2} d$. These give the ratios for (i), (ii), and (iii) as $d^{(c/2)-1}$, $d^{c-m} \delta$, and 1 respectively. The first can be larger than the second if $c > 2m - 2$, which can be satisfied for large enough value of c . It should be noted that c must be at least 4 since m is not less than 1. A numerical example for the growth rate R is shown in Fig. 5, which agrees qualitatively with the experimental results. The effect of the quadratic desorption is enhanced when the condition $\alpha \gg k_{1+}$ or $c \gg 2m - 2$ is satisfied.

The physical meaning of the quadratic desorption term is the desorption of the monomers induced by mutual collision on the surface. We consider that this term, which has not been reported so far, appeared in the present experiment because the intermolecular interaction of QA is strongly sensitive to direction, as seen from the needle shape of crystallites. It means large α compared with k_{1+} , which probably facili-

tated the observation of collision-induced-desorption in the present system. This explanation agrees with the result of C_{60}/α -MoTe₂ because directional difference is not expected for C₆₀.

Although there are ambiguities in the precise determination of the rate parameters, several things can be derived from the experimental results, according to the above model. First, critical nuclei size is larger than 4 for QA on NaCl because the nucleation rate took the minimum as a function of τ . Second, the time scale of k_0^{-1} is the order of 0.1~1 s at the temperature range in the experiment, since the saturation is nearly achieved within the above range of τ .

In conclusion, pulsed molecular beam technique was applied to the analysis and control of the growth of organic molecular films near the threshold of sticking and reevaporation. It was found that the nucleation density can be changed by varying the cycle time even with constant on/off duty. The minima observed as the function of the cycle time can be explained by assuming the desorption of the migrating monomers induced by mutual collision. It should be noted for the application side that perfect selectivity in the sticking coefficient is achieved by using the pulsed molecular beams. As a materials preparation technique, the present result will be useful for the selective growth in the materials system in which only weak selectivity is expected.

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