Kinetics Study on Initial Growth Stage in Vapor Deposition of Organic Thin Film Using Quartz Crystal Microbalance

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The deposition behavior of stearic acid evaporated in vacuum was observed using a quartz crystal microbalance technique and the time evolution curves of the amount of admolecules in the initial growth were compared with a theoretical curve calculated using a rate equation proposed on the basis of physisorption. From the results, it was demonstrated that the proposed rate equation for the early stage of the film formation well reflected the experimental results and the growth kinetics for organic thin films was dependent on the substrate temperature. Basic parameters for thin film growth, such as the mean stay time on the substrate of deposited molecules, can be estimated from the fitting of the theoretical equation to the experimental results at each substrate temperature. It should be noted that the basic parameters were sensitive to a small change in substrate temperature.

Detailed studies of organic thin film formation during physical vapor deposition (PVD) are of considerable practical significance since PVD is used for preparing organic thin films. Several investigations have been conducted on organic thin film growth from vapor phase[1-5]. It was found that the molecular orientation and the morphology of organic thin film prepared by PVD are strongly dependent on the substrate temperature and the molecular flux to the substrate. However, the mechanism of formation for organic thin films is not still well understood and it seems to be difficult to control the precise structure of the produced film. It is therefore necessary to understand the elementary processes in vapor deposition in order to precisely control the organic film structure for high-performance organic devices.

In the present study, we focused attention on the initial stage of organic thin film growth because the early processes of organic film formation have great influences on the growth manner, and more important for organic ultrathin film of recent years. Since organic molecules are generally weak and are easily damaged by irradiation of high energy such as accelerated electrons and ions, a quartz crystal microbalance can be used for a precise measurement of the adsorption characteristics of weak organic compounds, and for an in-situ observation of organic film formation during PVD[6,7]. Additionally, the growth behaviors at various substrate temperatures were kinetically studied using growth rate equations based on the model proposed by Zinsmeister et al. [8-13].

The experimental setup is schematically illustrated in Fig. 1. Stearic acid ($C_{17}H_{35}COOH$), which is a higher fatty acid, was purchased from Tokyo Kasei Kougyo Co. Ltd. and used without further purification. Stearic acid was evaporated by heating in vacuum and was supplied into the vacuum chamber through a heated copper tube with an on-off valve. The vacuum chamber with a capacity of 1.1×10^{-2} m^3 had been evacuated to a system pressure below 1×10^{-3} Pa in advance of the deposition. The distance from the feeding tube to the substrate was fixed to 0.1 m. The molecular supply to the substrate was controlled with an on-off shutter in front of the substrate. The time change in the amount of admolecules was monitored using a quartz crystal microbalance technique (QCM), which is based on a resonant frequency shift of quartz oscillator accompanied by the mass change[14]. A quartz crystal covered with Au electrodes was used as the substrate. The substrate purchased from ULVAC, Inc., is AT-cut and prepared with the resonant frequency of 5 MHz. Immediately after an ultrasonic cleaning and an ozone cleaning, the quartz crystal substrate was fastened on a holder equipped with a port for inserting a thermocouple and maintained at a given temperature with circulated water. The holder was electrically connected to an oscillator circuit for QCM measurements and the frequency was measured with a frequency counter (CRTM-5000, ULVAC, Inc.). Both of the source temperature and the tube

temperature were maintained at 120℃ in all of the experiments.

Figure 2 shows time evolution curves of the amount of admolecules on the QCM substrates covered with Au maintained at 20℃, 25℃ and 30℃. The results indicate that the average deposition rate decreases with an increase in the substrate temperature. This tendency can be explained by an increase in re-evaporation rate from the substrate. Additionally, time change in the amount of admolecules at 30℃ shows a non-linear increase while that at 20℃ and 25℃ show mostly linear increases. It may suggest a difference of the growth regime.

For the results, we attempted the fitting of a rate equation based on a growth mode and kinetically analyzed the deposition behavior of stearic acid.

The growth model is based on the following assumptions.

ⅰ. Two physisorbed states of deposited molecules are involved. One is a free state, in which molecules easily re-evaporate from the substrate and transition to the other state. The other is a metastable state where molecules trapped in stable nucleus or adsorbed sites can hardly re-evaporate from the substrate.

ⅱ. The amount of admolecules in the metastable state is proportional to that in a free state.

ⅲ. The re-evaporation rate of deposited molecules in a free state is proportional to the amount in the free state, and same applies to that in the metastable state.

ⅳ. The state of the incident molecules cannot directly undergo the metastable state, that is, deposited molecules attain to the metastable state through a free state.

The model is schematically illustrated in Fig. 3.
The deposition rates in each state are expressed as the following equations:

$$\frac{dn_1}{dt} = J - R_1 - R_t, \quad \cdot \cdot \cdot (1)$$

$$\frac{dn_m}{dt} = R_t - R_d, \quad \cdot \cdot \cdot (2)$$

where n_1 is the amount of admolecules in a free state, J is molecular flux to substrate, R_1 the re-evaporation rate of deposited molecules in a free state, R_t the transition rate from a free state to a metastable state, n_m the amount of admolecules in a metastable state, R_d the re-evaporation rate of deposited molecules in a metastable state.

Here, R_1, R_t and R_d can be expressed as

$$R_1 = \frac{n_1}{\tau_1}, \quad \cdot \cdot \cdot (3)$$

$$R_t = \frac{n_1}{\tau_t}, \quad \cdot \cdot \cdot (4)$$

$$R_d = \frac{n_m}{\tau_d}, \quad \cdot \ \cdot \ \cdot \ (5)$$

where τ_1 the mean stay time of deposited molecules in a free state, τ_t the mean transition time from a free state to a metastable state, and τ_d the mean stay time of deposited molecules in a metastable state.

Solving eq. (1) for n_1 under the initial condition of $t = 0$, $n_1 = 0$, $n_m = 0$, we obtain

$$n_1 = J\tau\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}, \quad \cdot \ \cdot \ \cdot \ (6)$$

where

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_t}. \quad \cdot \ \cdot \ \cdot \ (7)$$

Then, substitution of eq. (4), (5) and (6) in eq. (2) leads to

$$\frac{dn_m}{dt} = J\frac{\tau}{\tau_t}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\} - \frac{n_m}{\tau_d}. \quad \cdot \ \cdot \ \cdot \ (8)$$

Solving eq. (8) by a numerical approach based on Runge-Kutta method, we finally obtain the total amount of admolecules, $n = n_1 + n_m$, as a function of deposition time.

Fitting the solutions of the theoretical equation to the results obtained from QCM measurement, we can estimate each mean time defined above as fitting parameters. Furthermore, the validity of the theoretical model can be discussed from the accuracy of the fitting to experimental results.

Measuring the deposition rate of stearic acid at low substrate temperature, we determined the molecular flux to substrate, J, to be 5.84×10^{16} m^{-2} s^{-1} in advance of the fitting, that is, only the three fitting parameters, τ_1, τ_t and τ_d, should be considered in this fitting analysis. Figure 4 shows the results of the fitting at the substrate temperatures of 29℃, 30℃, 31℃ and 32℃.

The theoretical curves shown in Fig. 4 fit well with experimental data. These results suggest that the basic processes proposed in Fig. 3 are essential in the initial growth of stearic acid thin film. More specifically, stearic acid deposited on QCM substrate can exist in two states, a free state and a metastable state.

It should be noted that theoretical curve excluding the re-evaporation process of the metastable state does not fit with experimental results in the initial part as shown in Fig. 5. This demonstrates that the re-evaporation of deposited molecules in a metastable state cannot essentially be negligible as a key process in the initial growth stage of stearic acid thin film.

Below the substrate temperature of 28℃, the amount of deposited stearic acid increased linearly with deposition time. This is because the mean stay time, τ_1, is sufficiently long at a low temperature and the metastable state can be negligible in the

growth process.

Table 1 shows, τ_1, τ_t and τ_d, as fitting parameters at each substrate temperature. From the results in table 1, both mean stay times, τ_1 and τ_d, decrease with increasing substrate temperature. This suggests that a high substrate temperature can facilitate the re-evaporation of deposited molecules. Actually, the deposition of stearic acid can no longer be observed at the substrate temperature of 34℃.

The mean transition time, τ_t, from a free state to a metastable state decreased with increasing the substrate temperature, as well as other time constants. This result arises from an increase in the probability of the trap of the deposition molecule on a stable adsorption site and/or a coalescence of deposited molecules. It should be considered an increase in the diffusion length of deposited molecules.

Moreover, a relatively large difference in the parameters was found between 29℃ and 30℃. This difference can afford a change in the growth mode within a small range in the substrate temperature.

The deposition behavior of stearic acid was observed using a quartz crystal microbalance technique. The deposition behavior at early growth stage varied depending on the substrate temperature. This result is ascribed to the increase in the re-evaporation rate of deposited molecules from the substrate. Furthermore, the proposed theoretical rate equations can be applied to the deposition behavior. Basic parameters in the growth process of stearic acid thin film, such as mean stay time, were estimated from the fitting with the proposed rate equations. Additionally, it was found that molecules deposited at relatively high substrate temperature can possess a free state or a metastable state. The results indicate that even slight change in the substrate temperature affects the growth mode of organic thin films and associated basic parameters. A strict control of the preparation condition therefore should be required for highly-functional organic thin films.

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Fig. 1. Experimental setup.

Fig. 2. Time evolution curves of the amount of admolecules on QCM substrate covered with Au electrode maintained at 20℃ (a), 25℃ (b) and 30℃ (c). The scale on the right-hand side of the graph represents the average film thickness.

Fig. 3. Schematic illustration of the physisorption model.

Fig. 4. Time evolution curves of the amount of admolecules on QCM substrate covered with Au electrode maintained at 29℃ (◇), 30℃ (○), 31℃ (□) and 32℃ (△). The plots and the solid lines refer to experimental data and the curves calculated using a rate equation, respectively.

Fig. 5. Time evolution curve for the initial stage of film formation on QCM substrate covered with Au electrode maintained at 30℃. The open circles refer to experimental data, the solid line and the dashed line show the curves calculated using the rate equations described above and without the consideration of re-evaporation from metastable state, respectively.

Table 1. Variation in the fitting parameters with substrate temp.

Substrate temp.	τ_1	τ_t	τ_d
29℃	1 7 s	4 0 s	8 0 0 s
30℃	2.6 s	5.0 s	5 2 s
31℃	1.5 s	3.8 s	5 0 s
32℃	0.9 s	3.3 s	4 9 s

Fig.1.

Vacuum gauge

Shutter   QCM holder   IN

Cu tube   Circulator

Source   OUT

Temp.
Controller   Freq.
                    counter
                                   PC   Vacuum
                                                system

Fig.2.

Fig.3.

R_1

R_d

J

re-evaporation

diffusion

R_t

free state
n_1

metastable state
n_m

Fig. 4.

Fig.5.