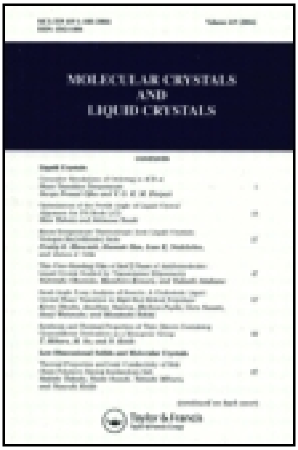

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Orientational Mechanism for Long-Chain Organic Molecules During Physical Vapor Deposition

Atsushi Kubono [a] & Ryuichi Akiyama [a]
[a] Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto, Japan

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Orientational Mechanism for Long-Chain Organic Molecules During Physical Vapor Deposition

ATSUSHI KUBONO and RYUICHI AKIYAMA

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto, Japan

Molecular orientations during physical vapor deposition of various linear long-chain compounds are interpreted on the basis of a simple model for the initial stage of anisotropic crystal growth. In this model, the initial stage involves adsorption from vapor, surface migration, re-evaporation from the substrate, capture into a cluster, re-evaporation from a cluster, and re-orientation, where the anisotropy of the molecules are considered. In addition, two fundamental orientations of initial small nuclei are assumed to be under thermal equilibrium. The set of differential equations for the individual elementary processes can be solved numerically. The calculated results agree well with actual orientational phenomena of long-chain molecules at various substrate temperatures, i.e., a higher substrate temperature results in a higher degree of normal orientation.

Keywords: vapor deposition, orientation, organic molecules, mechanism, film growth, substrate temperature

INTRODUCTION

During physical vapor deposition molecular orientations of linear long-chain compounds are strongly dependent on the deposition conditions, especially on the substrate temperature and the annealing temperature [1–9]. In general, high substrate temperatures result in an orientation normal to the substrate surface, whereas low substrate temperatures give rise to lateral orientation or an amorphous structure. These tendencies have been observed for various long-chain compounds [1] having a flexible moiety, such as paraffin [2–4], fatty acid [5], diamine [6], and vinylidene fluoride (VDF)

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Address correspondence to Atsushi Kubono, Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan. E-mail: akubono@ipc.kit.ac.jp

oligomer [7–9], as well as rigid rodlike molecules such as oligophenylene [10]. Typical experimental results are shown in Figure 1.

The mechanism of orientation, however, has not been elucidated adequately. Although there has been an attempt made for the interpretation of the orientational mechanism involving a precession mode of molecules [3], the mechanism accounts for no more than the tendency for higher substrate temperature to afford the wider distribution of the tilting angle. Hence, it is still unclear why the normal orientation should be dominant for high substrate temperatures.

Concerning metals and inorganic materials, thin film devices have been commercially produced, and the mechanisms of the film formation have been precisely investigated [11–15]. On the other hand, it is difficult to investigate the film formation process of organic compounds because of

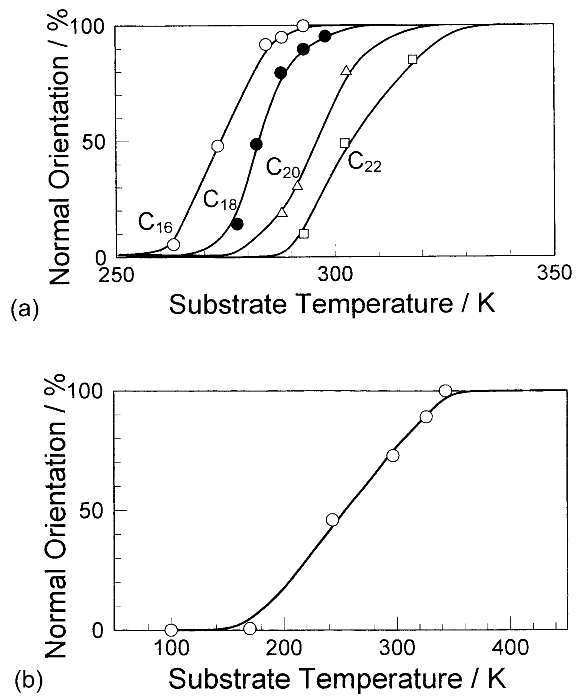

FIGURE 1 Concentration of normal-oriented molecules for (a) fatty acids on KCl and (b) paraffin (C_{40} : $C_{40}H_{82}$) on glass as a function of substrate temperature. For fatty acids, open circles, closed circles, open triangles, and open squares refer to the data of palmitic acid (C_{16} : $C_{15}H_{31}COOH$), stearic acid (C_{18} : $C_{17}H_{35}COOH$), arachidic acid (C_{20} : $C_{19}H_{39}COOH$), and behenic acid (C_{22} : $C_{21}H_{43}COOH$), respectively. Original experimental data were first reported by (a) Inoue et al. [5] and (b) Tanaka et al. [3].

the limitation in the observations of their formation behavior and the measurements of their properties. The difficulties are mainly due to the sensitivity of organic molecules, which can easily be damaged by radiation of X rays and electron beams. Also to be considered are the anisotropy of the shape and physical properties. Although molecular dynamics simulations successfully revealed the molecular aggregation of long-chain organic compounds from the melt [16] and from the vapor [17], the results of the simulations have unfortunately indicated no information about the effects of substrate temperature. Hence, the mechanism of orientation during thin film formation in vaccum is still unclear for organic materials, even when using computer simulations.

It should be noted that the orientational behavior is found for a number of long-chain organic compounds, while the critical substrate temperatures for the orientation vary. This fact indicates that the individuality of molecules, such as the type of the functional groups, is not so essential for the orientational behavior of our present interest. It is important for the molecules to have overall anisotropy. Actually, for liquid-crystalline molecules calculations on the assumption of a simple rigid rod successfully reveal the liquid-crystalline properties, such as phase transitions and director orientations [18,19]. These facts have led us to think of a simple model for molecular orientation during vapor deposition including some elementary steps where the long-chain molecules can be regarded as anisotropic rods.

In this paper, we propose a fairly simple model for the initial stage of crystal growth in vapor deposition of organic long-chain molecules and try to elucidate the orientational mechanism.

THEORETICAL MODEL OF CLUSTER GROWTH ACCOMPANIED BY MOLECULAR ORIENTATION

Elementary Steps and States

It is important to make a simple approximation in order to avoid complexities and to construct the framework of the mechanism. Here, we assume that the molecules under consideration exhibit cylindrical symmetry in the same manner as the simulation for liquid crystals. The long-chain molecules are regarded as anisotropic rigid rods in the clusters, whereas in the vapor phase and the initial adsorbed phase they no longer exhibit a rigid rodlike shape, showing free-moving chains with random conformation instead. In addition, the molecules have two spherical heads which represent the end groups, suggesting that the end groups may play a role in film formation. It is found that the orientational behavior of a long-chain compound depends on the type of the end group, as shown in Figure 1. The effects of such end groups can be considered in the calculation as activation energies in this model.

Moreover, we assume that the mechanism of film growth accompanied by an orientation includes a few elementary steps and a few adsorption states. The correspondence between calculation and experiment would be better if we would assume other types of additional steps. The model, however, would fall into an arbitrary multiparameter fitting to be deficient in reliability, unless the validity of the associated parameter values could be confirmed by other experimental methods.

Concerning these points of view, we propose a simple model for the initial stage of film formation that includes a few elementary steps and states, as illustrated in Figure 2. The process involves the following steps: (1) adsorption from vapor, (2) surface migration, (3) re-evaporation from the substrate, (4) capture into a cluster, (5) re-evaporation from a cluster, and (6) reorientation. These steps take place after nucleation, as described in the next section. In addition, the molecules are assumed to exist on the substrate in three individual states: (1) adsorbed single molecular state where molecules can migrate, (2) lateral captured state where molecules lie parallel to the substrate, and (3) normal captured state where molecules stand normal to the substrate. In this model, only normal and lateral orientations are

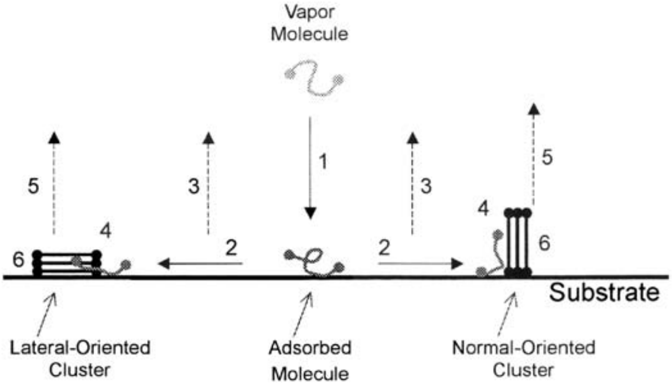

FIGURE 2 Schematic illustration of initial thin film growth: (1) adsorption from vapor, (2) surface migration, (3) re-evaporation from the substrate, (4) capture into a cluster, (5) re-evaporation from a cluster, and (6) reorientation.

considered as the stable orientations because no more orientational freedom has been observed in the vapor-deposited thin films of simple long-chain compounds with crystallinity like paraffin and fatty acid. This may be due to the crystalline structures of long-chain molecules. Although, of course, tilted orientation can be found for the molecules exhibiting a monoclinic or triclinic crystal lattice, the tilting angle is fixed by the packing. In these cases, a tilted orientation can be observed instead of normal orientation and can be regarded as a kind of normal orientation because c* axis is normal to the substrate.

We will limit ourselves to the discussion of the elementary molecular steps for the clusters located so far away from the neighboring clusters that each cluster can grow individually. Moreover, we will assume that all of the molecules arriving at the surface are thermally accommodated during migration on the surface for the period of the average lifetime denoted by τ, i.e., the accommodation coefficient is unity.

Initial Nuclei

The nucleation takes place when two molecules meet to coalesce or other molecules are captured into the aggregate to form a relatively stable cluster. In this paper we will not deal with the detailed initial nucleation mechanism because a number of complicated steps involved in the nucleation would make the analysis difficult. Therefore we will begin by considering the equilibrium of the orientations after the formation of initial small nuclei. Here we assume the orientation of the initial small nucleus formed from n_0 molecules changes rapidly and repeatedly between normal and lateral ones, as shown in Figure 3a, because the dependence of the potential on the tilt angle can be assumed, as shown in Figure 3b, suggesting two stable states, normal ($\alpha = \pi/2$) and lateral ($\alpha = 0$), where the molecular tilt from the substrate surface is denoted by α [24]. Moreover we assume that each initial nucleus includes three molecules ($n_0 = 3$) because at least three molecules would be necessary to form a 2-dimensional lattice, and it has been reported that the orientational change of paraffin during annealing process occurs for a bundle consisting of about four molecules [4]. At this stage we neglect the effects of entropy because the number of equienergic states for normal and lateral-oriented initial nuclei would not differ from each other. Although each cluster actually has a degree of freedom for rotation around the axis normal to the substrate surface, the degree should be limited if the substrate surface shows n-folded axis normal to the surface. Hence the degrees for normal and lateral orientations

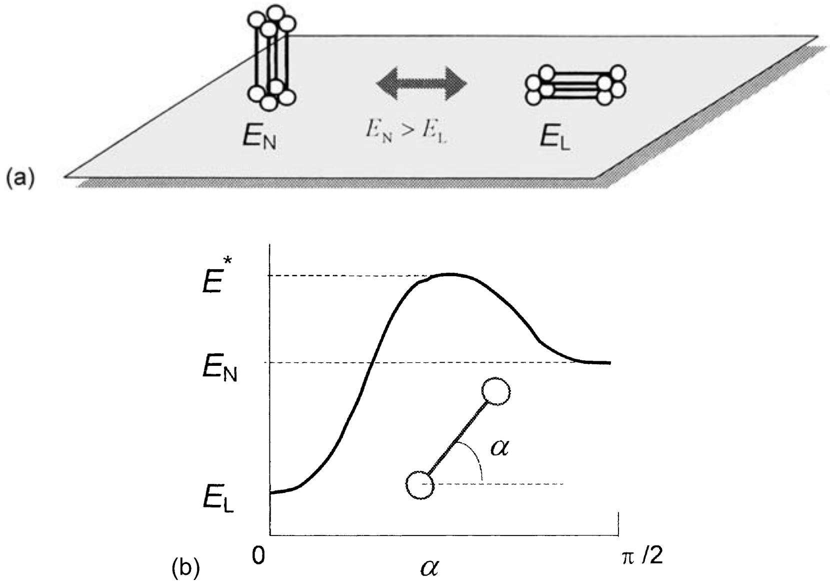

FIGURE 3 Equilibrium between normal and lateral orientations of initial nuclei: (a) schematic illustration of orientational equilibrium and (b) potential energy as a function of molecular tilt angle α. This potential curve may result in two stable states, lateral ($\alpha = 0$) and normal ($\alpha = \pi/2$).

should be identical. Therefore we may assume that the entropy is independent of the orientation.

If the populations of normal- and lateral-oriented nuclei obey a Boltzmann distribution based on an activation process and all nuclei have the same size, the ratio between the populations of these orientations is given as follows:

$$\frac{N_N}{N_L} = \exp\left(-\frac{E_N - E_L}{kT}\right), \tag{1}$$

where N_N and N_L are the number of nuclei in which molecules align normal and lateral to the substrate, respectively, E_N and E_L are the potential energies for the respective orientations of nuclei, k is the Boltzmann's constant, and T is the substrate temperature. It should be noted that N_N is always smaller than N_L because of lower E_L associated with strong interaction between the molecules and the substrate; i.e., lateral-oriented initial nuclei will be preferentially formed on the substrate at any temperature. Considering the fact that normal orientation is obtained preferentially for a high substrate temperature, we may conclude that, besides the equilibrium of initial nuclei, the kinetics of the growth process is essential to account for the orientational behavior.

Cluster Growth

The normal- or lateral-oriented initial nucleus will capture the molecules adsorbed on the substrate. As the nuclei grow larger, the orientation can no longer be changed. The grown nucleus having a stable orientation will grow further by capturing molecules migrating on the substrate if the re-evaporation and dissociation of molecules are adequately small; i.e., the substrate temperature is not too high.

It should be noted that the direct impingement of the molecular vapor onto the surface of the clusters can be negligible [20]. Therefore the molecular supply to the clusters is governed by the surface migration of the adsorbed molecules. It is reasonable that single adsorbed molecules are migrating individually with so random a conformation and/or so random an orientation that we can ignore the anisotropy and the orientation of the molecules until the molecules are captured into a cluster. In other words, the single molecules are adsorbed only in one state, where each parameter, such as the diffusion constant and the adsorption energy, is unique. In addition, we assume that the substrate surface exhibits no anisotropy, i.e., the diffusion constant is independent of the direction along the surface. Consequently, anisotropy is essential only for the molecules in clusters.

Next, we assume two typical shapes of the normal- and lateral-oriented clusters as shown in Figures 4a and 4b. Considering the cylindrical symmetry of the molecules, the normal orientation results in a disklike cluster where the molecular axis is parallel to the disk thickness direction and normal to the substrate surface, whereas the lateral orientation gives rise to an arched shape, in other words, a "thick segment," which is part of a disklike cluster with the molecular axis lying parallel to the thickness direction along the substrate surface. It is natural to assume these shapes, since these shapes of crystals have actually been reported for vapor-deposited thin films of a long-chain paraffin [21]. This arched shape of lateral clusters can be considered as a 2-dimensional droplet. It is important to note that the growth rate along the $00l$ direction, R_{00l}, which is generally parallel to the molecular axis, is negligibly small in comparison with those along $hk0$ directions, R_{hk0}, which is generally perpendicular to the molecular axis ($R_{hk0} \gg R_{00l} \approx 0$) [1]. Therefore the height of the normal-oriented cluster and the depth of the lateral-oriented one correspond to the molecular length. If we were able to observe the cluster with a microscope, the top-view

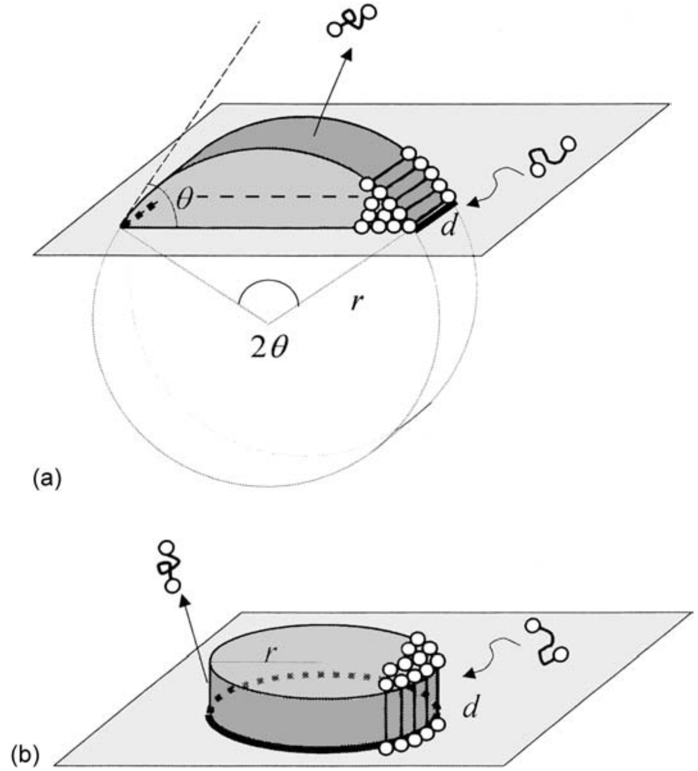

FIGURE 4 Schematic illustrations of (a) lateral-oriented and (b) normal-oriented clusters. Molecules are captured into the clusters through the capturing sites, which are located at the edges of the lateral-oriented cluster, and at the circle where the circumference of the normal-oriented one contacts with the substrate surface, as represented by the thick lines in the illustrations. Re-evaporation occurs via the (*hk*0) surfaces of the clusters: (a) the lateral area, namely, a part of the circumference of the lateral-oriented cluster, and (b) the whole circumference of the normal-oriented one.

image might reveal the existence of disklike clusters for normal orientation and rodlike clusters for lateral orientation.

Since molecules to be captured through the (*hk*0) surface can be supplied only from the substrate surface, the molecular capturing rate R_+ is proportional to the length of capturing site, l, which is indicated as thick lines in Figure 4:

$$R_+ = J_s\, l, \tag{2}$$

where J_s is the 2-dimensional molecular flux on the substrate. The length of the capturing site for a normal-oriented cluster is equal to the length of the circumference:

$$l = 2\pi r, \tag{3}$$

while that for lateral orientation is proportional to twice the molecular length, because the capturing sites are located on both edges of the cluster:

$$l = 2d, \tag{4}$$

where r is the radius of the cluster and d is the molecular length, i.e., the thickness of the cluster, as shown in Figure 4.

For re-evaporation, the molecules in a cluster can re-evaporate only from the ($hk0$) surface of the cluster. The re-evaporation rate R_-, therefore, is proportional to the area of the re-evaporation site, S:

$$R_- = J_{\text{evap}}\, S, \tag{5}$$

where J_{evap} is the flux of re-evaporating molecules. The site for a normal-oriented cluster is the circumference,

$$S = 2\pi rd, \tag{6}$$

while for a lateral orientation the site is the lateral area of the cluster,

$$S = 2rd\theta, \tag{7}$$

where θ is the 2-dimensional contact angle of the lateral-oriented cluster on the substrate.

The molecules captured into the cluster are assumed to be quickly reoriented to their favorable position, resulting in the stable shape of the cluster—namely, a disk and a thick segment for normal and lateral orientations, respectively—and therefore the rate-limiting step must be the molecular supply from the substrate surface.

Since the net growth rate is the difference of the capturing rate and the re-evaporation rate, the following differential equation is given:

$$\frac{dn_{\text{c}}}{dt} = R_+ - R_-, \tag{8}$$

where n_c is the population of molecules in a cluster and is related to the volume of the cluster, V, and the volume occupied by the molecule, v_{m}, as follows:

$$n_{\text{c}} = \frac{V}{v_{\text{m}}}. \tag{9}$$

The volume can be expressed using r, d, and θ; for a normal-oriented cluster, it is given by

$$V = \pi r^2 d, \tag{10}$$

and for a lateral-oriented cluster it is

$$V = \frac{1}{2} r^2 d(2\theta - \sin\theta). \tag{11}$$

The 2-dimensional molecular flux on the substrate, J_s, depending on the shape of the cluster, is too complicated to express in a formula. Here we may consider that adsorbed molecules within a certain distance x_s from the cluster surface will be captured [22]. This results in a 2-dimensional flux on the substrate as follows:

$$J_s = fJx_s, \tag{12}$$

where f is a factor associated with the shape of the cluster, J is the flux of arriving molecules from vapor, and x_s is termed the surface migration distance, which is given as [22]

$$x_s^2 = D\tau_s, \tag{13}$$

where D is the diffusion constant and τ_s is the average life time of the molecules on the substrate. The diffusion constant and the average life time, depending on the temperature, obey the following equations on the assumption of activation process [22]:

$$D = a^2 \nu_d \exp\left(-\frac{E_d}{kT}\right), \tag{14}$$

$$\tau_s = \frac{1}{\nu_s} \exp\left(\frac{E_s}{kT}\right), \tag{15}$$

where a is the distance between neighboring adsorption sites on the substrate, ν_d is the vibration constant for surface diffusion on the substrate, ν_s is the vibration constant for adsorption on the substrate, E_d is the activation energy for surface diffusion, and E_s is the activation energy for adsorption.

The molecular flux for re-evaporation obeys the following equations:

$$J_{evap} = \frac{\sigma_c}{\tau_c}, \tag{16}$$

$$\tau_c = \frac{1}{\nu_c} \exp\left(\frac{E_c}{kT}\right), \tag{17}$$

where σ_c is the number of the molecules per unit area located on the re-evaporation site of the cluster, τ_c is the average lifetime of the molecules on the re-evaporation surface, ν_c is the vibration constant for re-evaporation, and E_c is the activation energy for re-evaporation.

CALCULATIONS

The set of equations described in the previous section can apparently be solved to give an exact form by using the Lambert W function. However, we will solve them numerically because this special function is uncommon and numerical calculations are eventually needed in order to obtain the absolute values. It is necessary to rewrite the set of equations before obtaining the numerical calculations. The area of the re-evaporation surface S and the length of the capturing site, l, should be expressed in terms of the population of molecules in a cluster, n_c. First, in order to express the radius r as a function of n_c, the volume V is eliminated by using Eqs. (9), (10), and (11). Next, substitution of the radius r in Eqs. (3), (4), (5), and (6) leads to l and S in terms of n_c. We can thus express dn_c/dt as a function of n_c for each orientation.

Since only a few exact parameter values are, in fact, available, we have to estimate them in the range of the feasible values. The set of values used are presented in Table 1 unless otherwise noted. These values would be reasonable considering those of metals or other organic compounds [23–25]. Moreover, the shape factor f in Eq. (12) is assumed to be unity for simplicity.

The computation was made by the finite difference method. The time interval between every calculation steps was fixed to be 5.0×10^{-6} s. In order to obtain the total population of normal- or lateral-oriented molecules, we must consider the distribution of initial nuclei as expressed in Eq. (1). We therefore obtain the total population of molecules, n_N for normal orientation and n_L for lateral orientation, as follows:

$$n_N = n_c N_N, \tag{18}$$

$$n_L = n_c N_L. \tag{19}$$

TABLE 1 Physical parameters in calculation

Parameter	Value	Unit
θ	2.0×10	deg
J	1.0×10^{20}	molecules/m^{2}s
E_c	5.0×10	kJ/mol
E_s	5.0×10	kJ/mol
E_d	1.0×10	kJ/mol
ν_c	1.0×10^{13}	s^{-1}
ν_s	1.0×10^{13}	s^{-1}
ν_d	1.0×10^{13}	s^{-1}
a	1.0×10^{-9}	m
d	2.0×10^{-9}	m
v_m	3.2×10^{-28}	m^3
σ	8.6×10^{-19}	m^2
$E_N - E_L$	4.0×10	kJ/mol
n_0	3.0	molecules

In addition, we use the ratio $n_N/(n_N + n_L)$ for the evaluation of the degree of normal orientation.

RESULTS AND DISCUSSION

Re-evaporation

In actual deposition, we sometimes found a low deposition rate in the case of a high substrate temperature; i.e., the thickness of the film was less than expected by using a quartz thickness monitor. This result indicates that a high substrate temperature gives rise to an increase in the re-evaporation from the substrate and the clusters. More noteworthy is the fact that normal-oriented molecules remained on the substrate even at a high substrate temperature in spite of the low sticking coefficient. In order to confirm this tendency, we calculate the stability of the cluster in vacuum.

Two clusters including 2000 molecules are set in vacuum without an incident molecular flux ($J = 0$); one of the clusters is normal oriented and the other is lateral oriented. It is conceivable that these clusters must become smaller due to re-evaporation. Figure 5 shows the re-evaporation from each cluster on the substrate maintained at 260 K in vacuum. The population of molecules in each cluster, n_c, is normalized against the initial value. For both orientations, the populations decrease as a function of time due to re-evaporation. It should be noted that the lateral-oriented cluster exhibits the faster re-evaporation than the normal-oriented one. This trend is associated with the relatively large area of the re-evaporation surface, S, with respect to

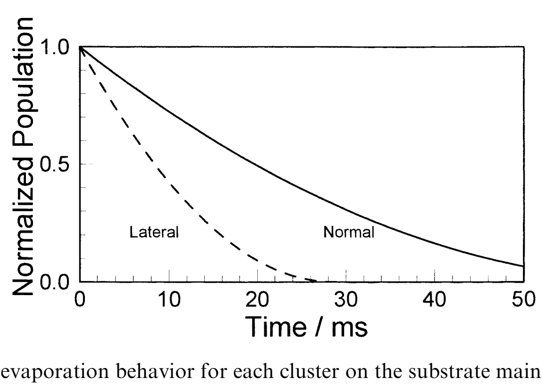

FIGURE 5 Re-evaporation behavior for each cluster on the substrate maintained at 260 K in vacuum. The molecular populations were normalized against their respective initial values. Solid and dashed lines refer to the growth of clusters with normal- and lateral-orientations, respectively.

the volume, V, of the lateral-oriented cluster in comparison with the normal-oriented one. The lateral-oriented cluster, therefore, has more re-evaporable molecules located on the re-evaporation surface than the normal-oriented one if both clusters consist of the same number of molecules. These results indicate that the re-evaporation from the cluster plays an important role in the orientational behavior.

Film Growth

Figure 6 shows the time evolution of the total population of normal-oriented molecules and that of lateral-oriented ones. At a substrate temperature of 260 K, the population of the lateral-oriented molecules increases faster than that of the normal-oriented ones, as shown in Figure 6a. This result is due to the larger number of initial nuclei having lateral orientation on the basis of thermal equilibrium. On the other hand, at a substrate

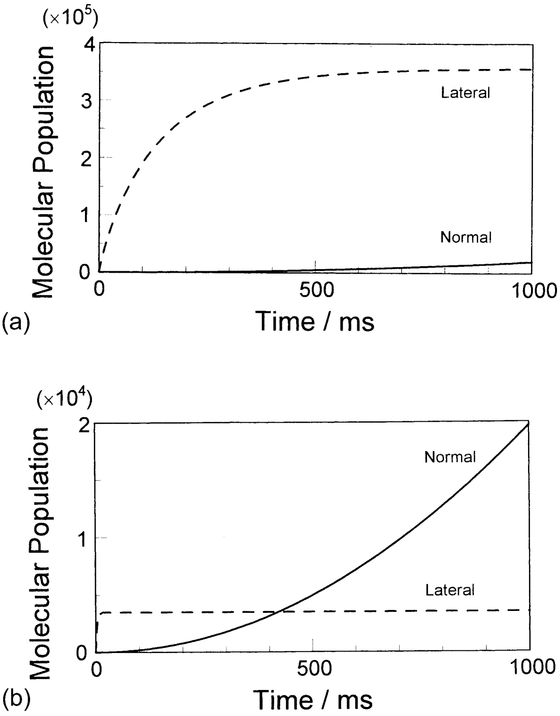

FIGURE 6 Time evolution of the molecular population during deposition on the substrate maintained at (a) 260 K and (b) 280 K. Solid and dashed lines refer to the growth of clusters with normal- and lateral-orientations, respectively.

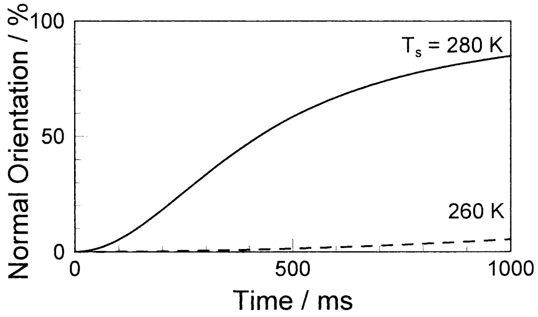

FIGURE 7 Time evolution of the concentration of normal-oriented molecules during deposition on the substrate maintained at 260 K (dashed line) and (b) 280 K (solid line).

temperature of 280 K, the population of lateral-oriented molecules becomes saturated because of their rapid re-evaporation, while marked increase is found for normal-oriented molecules, as shown in Figure 6b. Figure 7 shows the time evolution of the concentration of normal-oriented clusters formed on the substrates maintained at 260 K and 280 K. These results indicate that the preferential orientation is governed by the balance of the nucleation and the cluster growth associated with the capture and the re-evaporation of molecules depending on the orientation.

Substrate Temperature Dependence

Figure 8 depicts the substrate temperature dependence of the concentration of normal-oriented molecules after 1000 ms deposition for various energy

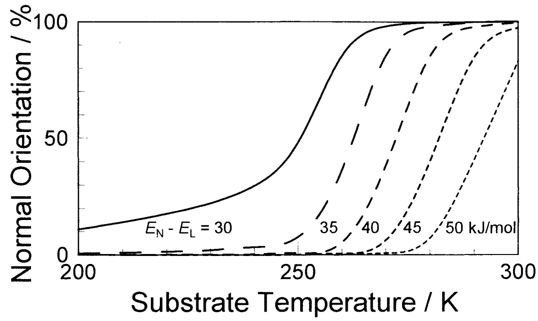

FIGURE 8 Calculated concentration of normal-oriented molecules after a 1000 ms deposition as a function of substrate temperature for various energy differences, $E_N - E_L$.

differences, $E_N - E_L$. The calculated result for $E_N - E_L = 40\,\mathrm{kJ/mol}$ is in good agreement with the experimental data for palmitic acid (C_{16}) shown in Figure 1a. There is a steep rise around 270 K, i.e., there is a threshold substrate temperature for the orientational change at about 270 K. Above 290 K only normal-oriented clusters are formed, while below 250 K all the molecules are aligned with lateral orientation. Moreover, it is clearly shown that a variation of energy differences affords shifts in the threshold temperature. As the energy difference increases, the threshold temperature shifts to a higher temperature. These calculated results are consistent with the experimental fact that a longer fatty acid gives higher threshold temperature, as shown in Figure 1a.

Validity of the Model

The results described in the previous section indicate that we can capture some of the physics of the orientation problem. It should be noted that the parameter values used in this calculation are in the range of those of metals or other organic compounds [23–25]. We may say that our model can account for the dependence of the orientation upon the substrate temperature qualitatively, while the model is rather simple.

Furthermore, the shapes of the cluster in our model seem to be reasonable, because disklike clusters with normal orientation and arch-shaped clusters with lateral orientation were observed in vapor-deposited films of linear long-chain compounds [1,3,5,21] with a transmission electron microscope (TEM), a scanning electron microscope (SEM), or an atomic force microscope (AFM). Although the actual film formation process includes a number of other steps that are not included in our model, the steps in our model seem to be essential and the others less important. It may therefore be concluded that our model consists of the most important rate-limiting steps.

In actual experimental data, we found the orientation dependent on the evaporation rate, while the present model cannot elucidate such a tendency well. This would be due to high supersaturation associated with the high deposition rate. Some assumptions made for the present model may become inadequate with an increase in the deposition rate. For high supersaturation, a quasi-liquid layer can be formed on the substrate surface, and consequently the thin film formation must be governed by the crystal growth not from the vapor but from the melt. Therefore molecules can be supplied directly from the melt onto ($hk0$) surface to form lateral-oriented clusters preferentially. A modification of the model that considers additional elementary steps is currently under way. The results will be reported in the next paper.

If we were able to measure the parameters unavailable at present, such as the surface migration distance and various activation energies associated with migration and adsorption, we could make further confirmation of the validity about the present model and the assumption. Moreover, we could also obtain an appropriate condition where the results of calculation agree well with the experimental ones. Further discussion of the validity would prompt us a more precise model concerning a somewhat complicated mechanism involving various other processes.

In order to apply the model to an actual thin film formation, besides keeping in mind the above points of view it is necessary to take into account multilayer growth. Here it should be noted that the multilayer would be formed on the initial nuclei as affected by the initial orientation; i.e., further crystal growth would occur homo-epitaxially over the initial clusters. Therefore the results considering multilayer growth would not be so different from that calculated on the basis of our present model for the initial stage of the vapor deposition.

CONCLUSIONS

The mechanism of thin film growth can be interpreted by a simple model proposed on the basis of the anisotropy in the crystal growth. The results from the calculations indicate the following tendencies. The lateral-oriented cluster exhibits the faster re-evaporation than normal-oriented one. At a substrate temperature of 260 K, the population of lateral-oriented molecules increases faster than normal-oriented ones. On the other hand, at a substrate temperature of 280 K, the population of lateral-oriented molecules becomes saturated, while marked increase is found for normal-oriented molecules. These results indicate that the molecular orientation is governed by the balance of the nucleation and the cluster growth associated with the capture and the re-evaporation of molecules, depending on the orientation. Moreover, there is a threshold substrate temperature for the orientational change around 270 K. Above the threshold temperature normal-oriented clusters are preferentially formed, while below it most of the molecules are aligned with lateral orientation. These calculated results qualitatively agree with the actual orientational phenomena of long-chain molecules at various substrate temperatures.

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