Classical nucleation theory applied to molecular orientations in vapor-deposited organic thin films

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Molecular orientational mechanism during physical vapor deposition of various linear long-chain compounds has been interpreted on the basis of a classical nucleation theory modified for the anisotropic nucleus formation. In this model, the anisotropy of the surface energy is considered, and initial small nuclei with two fundamental orientations (normal and lateral) are assumed to be formed and dissociated repeatedly by the thermal energy. The critical energy of nucleus formation for each orientation is calculated as a function of the chemical-potential change of the system. The calculated results are similar to those observed for actual orientational phenomena of long-chain molecules at various chemical-potential changes; i.e., a higher substrate temperature and/or a lower deposition rate result/s in a higher degree of normal orientation. © 2005 American Institute of Physics.

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I. INTRODUCTION

Since the publication of a work titled *Molecular Electronic Devices*,¹ many researchers have believed that organic materials will serve as the elementary units of electronic systems with extremely high component density and configuration flexibility. From an industrial point of view, simpler and easier techniques are required to produce organic devices, such as organic electroluminescence (EL) devices and organic transistors, utilizing the properties peculiar to organic molecules. In such high-performance organic devices, it is essential to control the structures having highly ordered packing, stacking, and orientation of molecules in the crystals.²

The physical vapor deposition (PVD) method, sometimes termed vacuum evaporation or thermal deposition, can meet the requirements and has been considered as one of the most promising techniques for the preparation of high-functional organic devices in electronics and optics.³ For linear long-chain compounds, such as paraffin,^{4–6} fatty acid,^{7–9} alkyl diamine,¹⁰ poly(vinylidene fluoride) (PVDF),^{11,12} poly(*p*-phenylene) (PPP),¹³ molecular orientations of vapor-deposited films are strongly dependent on the deposition conditions, especially on the substrate temperature and the annealing temperature. In general, a high substrate temperature or a low deposition rate results in an orientation normal to the substrate surface, whereas a low substrate temperature or a high deposition rate gives rise to a lateral orientation or an amorphous structure. Here it should be emphasized that Matsuzaki *et al.* summarized the dependence of molecular orientation on the deposition conditions by using only one parameter, *supersaturation*, associated with both of the substrate temperature and the deposition rate.⁷

Although it can actually produce organic thin films exhibiting such high molecular order, only a few organic devices are commercially produced by this method mainly because the film formation mechanisms of organic thin films are still uncertain or unknown and it is somewhat difficult to control the precise structure in comparison with the Langmuir-Blodgett (LB) technique. It is therefore necessary to understand the elementary processes and the mechanism of film formation for the precise control of the film structure.

For metal and inorganic thin films, numbers of researches have actually been made on the film growth and the structure formation by using electron microscopy and mass spectroscopy.^{14,15} In contrast, a few reports on the film formation mechanism have been made for organic materials,^{16–18} since it is rather difficult to observe the microscopic structures of organic thin films that are mechanically weak and are easily damaged by the irradiation of electrons.

The physics behind the orientational behavior in organic thin films must be simple because these tendencies have been observed for various long-chain compounds.^{3–13} In the above point of view, we have discussed, in our previous paper, the effects of substrate temperature and have demonstrated a framework of the orientational mechanism based on a simple physical model involving some elementary processes that can be expressed by a set of rate equations.¹⁹ The essential of this model is the balance of two competing factors affecting the anisotropic crystal growth: (1) anisotropy in the reevaporation of adsorbed molecules and (2) anisotropy in the adsorption energy on a substrate. At a high substrate temperature, reevaporation from the surface will be the dominant factor that controls the growth rate, whereas at a low substrate temperature the number of initial nuclei will primarily govern the growth rate. Although this kinetic model successfully reveals the substrate temperature effects on the orientation, it cannot unfortunately elucidate all the orientational phenomena because the orientation is also dependent on the

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FIG. 1. Schematic illustrations of (a) laterally and (b) normally oriented clusters.

molecular flux incident to the substrate in actual experimental data. This fact prompted us to take supersaturation into account, as Matsuzaki pointed out.⁷ It is clear that the description of nucleation and growth in organic thin films can also be treated by modification of the classical nucleation theory for anisotropic materials²⁰ instead of the kinetic model.¹⁹ Moreover, the classical nucleation theory has an advantage in the use of a prediction tool because the physical meaning is clearer and the exact forms of solution can be obtained.

In this paper, we propose a classical nucleation theory applied to the initial stage of crystal growth in the vapor deposition of organic long-chain molecules, in an attempt to elucidate the orientational mechanism.

II. THEORETICAL MODEL

A. Normally and laterally oriented nuclei

The formation of organic thin films involves two fundamental processes, namely, nucleus formation (nucleation) and crystal growth. The latter has been precisely discussed in our previous paper; here we must consider nucleus formation as the first process of thin-film formation.

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 rodlike molecules can be aggregated to form two types of fundamental clusters; clusters oriented normally and laterally to the substrate surface generally exhibit their respective specific shapes, as shown in Fig. 1.^{3,19,21} Due to the cylindrical symmetry of the rodlike 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, “thick segment,” which is part of a disklike cluster with the molecular axis lying parallel to the thickness direction along the substrate surface. This arched shape of lateral clusters can be considered as a two-dimensional droplet. It is important to note that the growth rate along the $\langle 00l \rangle$ direction R_{00l} , which is generally parallel to the molecular axis, is negligibly small in comparison with those along $\langle hk0 \rangle$ directions R_{hk0} , which is generally perpendicular to the molecular

axis ($R_{hk0} \gg R_{00l} \approx 0$).³ Therefore both the height of the normally oriented cluster and the depth of the laterally oriented one correspond to the molecular length.

B. Free energy of nucleus formation

In general the free energy of nucleus formation, ΔG , can be expressed as follows:²⁰

$$\Delta G = -n\Delta\mu + \oint_S \sigma dS, \quad (1)$$

where n is the number of molecules in the nucleus, $\Delta\mu$ is the chemical-potential change for nucleation, σ is the surface free energy per unit area, and dS is a small area on the surface. The nuclei shown in Fig. 1 must exhibit a variation of σ depending on the direction, as opposed to an isotropic nucleus having a constant surface free energy σ . Here, let us use subscripts L and N for the laterally and normally oriented nuclei, respectively. The free energy for each orientation, ΔG_L and ΔG_N , can be expressed as follows:

$$\Delta G_L = -n\Delta\mu + \sigma_{lv}S_{Ltop} + \sigma_{bv}S_{Lside} + (\sigma_{ls} - \sigma_{sv})S_{Lbottom}, \quad (2a)$$

$$\Delta G_N = -n\Delta\mu + \sigma_{bv}S_{Ntop} + \sigma_{lv}S_{Nside} + (\sigma_{bs} - \sigma_{sv})S_{Nbottom}, \quad (2b)$$

where σ is the free energy density of the cluster surfaces exposed to the substrate or the gas phase; the subscripts l and b refer to the lateral area and the base of the cluster, respectively, s to the substrate surface, and v to the vapor phase. The subscripts “top,” “side,” and “bottom” are used for the top, side, and bottom surfaces, respectively, of each nucleus shown in Fig. 1.

Note that the surface energies are associated with the contact angle θ as follows:

$$\cos \theta = (\sigma_{sv} - \sigma_{ls})/\sigma_{lv}. \quad (3)$$

Using the above Young’s equation, we can rewrite Eqs. (2a) and (2b) into the following simpler forms:

$$\Delta G_L = -(\Delta\mu - \Delta\mu_{L0})n + 2d\sqrt{a_0\beta_L}\sigma_{lv}\sqrt{n}, \quad (4a)$$

$$\Delta G_N = -(\Delta\mu - \Delta\mu_{N0})n + 2d\sqrt{a_0\beta_N}\sigma_{lv}\sqrt{n}, \quad (4b)$$

where a_0 is the cross-sectional area occupied by the molecule, d is the length of the molecule, β_L and β_N are shape factors for respective orientations,

$$\beta_N = \pi, \quad (5a)$$

$$\beta_L = \frac{2\theta - \sin 2\theta}{2}, \quad (5b)$$

and $\Delta\mu_{L0}$ and $\Delta\mu_{N0}$ are the critical values of $\Delta\mu$ for the lateral and normal orientations, respectively,

$$\Delta\mu_{L0} = 2a_0\sigma_{bv}, \quad (6a)$$

$$\Delta\mu_{N0} = a_0(\sigma_{bv} + \sigma_{bs} - \sigma_{sv}), \quad (6b)$$

which determine the lowest value of $\Delta\mu$ for the formation of nuclei to take place.

C. Critical nuclei

When a cluster grows over a certain size n^* where the free energy of nucleus formation exhibits a maximum, it will grow spontaneously. In this sense the cluster with the size n^* is a critical nucleus of the solid phase.²⁰ Therefore the maximum value of free-energy change ΔG is considered as the energy barrier that should be overcome for critical nucleus formation to take place. Differentiation of Eqs. (4a) and (4b) with respect to n gives the critical sizes n_L^* and n_N^* and the critical nucleation energies ΔG_L^* and ΔG_N^* for the respective orientations, as follows:

$$n_L^* = \frac{a_0 d^2 \beta_L \sigma_{lv}^2}{(\Delta\mu - \Delta\mu_{L0})^2}, \quad (7a)$$

$$n_N^* = \frac{a_0 d^2 \beta_N \sigma_{lv}^2}{(\Delta\mu - \Delta\mu_{N0})^2}, \quad (7b)$$

$$\Delta G_L^* = \frac{a_0 d^2 \beta_L \sigma_{lv}^2}{\Delta\mu - \Delta\mu_{L0}}, \quad (8a)$$

$$\Delta G_N^* = \frac{a_0 d^2 \beta_N \sigma_{lv}^2}{\Delta\mu - \Delta\mu_{N0}}. \quad (8b)$$

It is easily found that they are functions of the chemical-potential change $\Delta\mu$ associated with the supersaturation.

D. Preferable orientation

Nucleation rate is proportional to the probability of overcoming the potential barrier and is thus expressed as

$$J = A \exp\left(-\frac{\Delta G^*}{kT}\right), \quad (9)$$

where A is a constant. Here, it should be noted that the nucleation rate J is less dependent on the preexponent factor A . Moreover the preexponent factor is almost independent of the orientation; it involves only orientation-independent processes such as the incident flux and the two-dimensional diffusion of molecules on the substrate. It may be somewhat less accurate that the surface diffusion is assumed to be independent of the orientation; nevertheless, molecular motions such as translation, rotation, and deformation, in fact, are so fast during the surface migration that the diffusion coefficient should be almost independent of the molecular orientation. Hence the degree of normal orientation can be defined as a simple expression $J_N/(J_N + J_L)$, namely, the number fraction of normally oriented molecules.

The chemical-potential change so that both barriers may have the same height ΔG_{th}^* can be regarded as a threshold $\Delta\mu_{th}$, at which the sign of $\Delta G_L^* - \Delta G_N^*$ changes; i.e., the preferable orientation changes from normal to lateral,

TABLE I. Surface energies used for calculations and calculated threshold free energies of critical nucleus formation.

Parameters	Larger contact angle	Smaller contact angle
σ_{lv}	30 mJ/m ²	30 mJ/m ²
σ_{ls}	26 mJ/m ²	12 mJ/m ²
σ_{bv}	22 mJ/m ²	22 mJ/m ²
σ_{bs}	22 mJ/m ²	18 mJ/m ²
σ_{sv}	24 mJ/m ²	40 mJ/m ²
θ^a	86.2°	21.0°
ΔG_{th}^*	2.19×10^{-19} J/molecule (131.8 kJ/mol)	2.54×10^{-19} J/molecule (152.4 kJ/mol)
$\Delta\mu_{th}^b$	3.78×10^{-20} J/molecule (22.8 kJ/mol)	2.22×10^{-20} J/molecule (13.3 kJ/mol)

^aCalculated from σ_{ls} , σ_{lv} , and σ_{sv} using Young's equation.

^b $\Delta G_L^* > \Delta G_N^*$ at $\Delta\mu < \Delta\mu_{th}$, $\Delta G_L^* < \Delta G_N^*$ at $\Delta\mu > \Delta\mu_{th}$, and $\Delta G_L^* = \Delta G_N^* = \Delta G_{th}^*$ at $\Delta\mu = \Delta\mu_{th}$.

$$\Delta\mu_{th} = \frac{\beta_N \Delta\mu_{L0} - \beta_L \Delta\mu_{N0}}{\beta_N - \beta_L}, \quad (10)$$

$$\Delta G_{th}^* = \frac{a_0 d^2 (\beta_N - \beta_L) \sigma_{lv}^2}{\Delta\mu_{L0} - \Delta\mu_{N0}}. \quad (11)$$

Using the surface energies σ_{bv} , σ_{bs} , σ_{sv} and the contact angle θ , the threshold $\Delta\mu_{th}$ can be expressed as

$$\Delta\mu_{th} = a_0 \left[(\sigma_{bv} + \sigma_{bs} - \sigma_{sv}) + \frac{2\pi(-\sigma_{bv} + \sigma_{bs} - \sigma_{sv})}{2\theta - \sin 2\theta - 2\pi} \right]. \quad (12)$$

In general, the interaction between an adsorbed molecule and the substrate is larger than that between a molecule and its vapor phase; i.e., $\sigma_{bs} < \sigma_{bv}$. Considering that $(-\sigma_{bv} + \sigma_{bs} - \sigma_{sv})$ is negative, it appears that a lower contact angle results in a lower $\Delta\mu_{th}$. This indicates that the lateral orientation becomes more preferable with an increase in the interaction between the molecules and substrate.

III. RESULTS AND DISCUSSION

A. Free energies of nucleus formation

Basic parameters associated with the thin-film formation of long-chain-organic compounds must be estimated from those of other organic compounds,¹⁹ since most of them can hardly be obtained experimentally as mentioned in the Introduction. Thus estimated values listed in Table I were used in the calculation of the nucleation rates.

Figure 2 shows the free energy of nucleus formation as a function of the cluster size. All curves exhibit a maximum so that critical nuclei exist. At the chemical-potential change of $\Delta\mu = 3.44 \times 10^{-20}$ J/molecule, the energy of critical nucleus formation for lateral orientation ΔG_L^* is larger than that for normal orientation ΔG_N^* . In contrast, at $\Delta\mu = 4.24 \times 10^{-20}$ J/molecule, that for lateral orientation ΔG_L^* is smaller than ΔG_N^* . These results indicate that smaller $\Delta\mu$ affords a normal orientation, whereas larger $\Delta\mu$ gives rise to a lateral orientation.

FIG. 2. Free energies of nucleus formation ΔG_N (solid line) and ΔG_L (dashed line) as a function of the cluster size; the subscripts N and L denote the normal and lateral orientations, respectively. The chemical-potential change $\Delta\mu$ is (a) 3.44×10^{-20} and (b) 4.24×10^{-20} J/molecule. The energies display local maxima ΔG_N^* and ΔG_L^* at the size of n_N^* and n_L^* , respectively.

This tendency can be explained by the following simple consideration. The surface free energy density of the cluster surface exposed to the vapor is larger than that contacted with the substrate. Considering the fact that a laterally oriented cluster has a larger surface area per unit volume than a normally oriented one, the total surface energy should be larger for the lateral orientation than for the normal orientation, unless interaction between the molecules and the substrate is so large. Moreover the cluster growth will widen the gap between the total surface energy for the normal orientation and that for the lateral orientation. Therefore the lateral orientation becomes less stable than the normal orientation, with an increase in the cluster size.

The dependence of ΔG^* on $\Delta\mu$ can be calculated by using Eq. (8). The calculated free energy of critical nucleus formation ΔG^* is shown in Fig. 3 as a function of the chemical-potential change $\Delta\mu$. As shown in the plots, the normal orientation has smaller ΔG^* than the lateral orientation at smaller $\Delta\mu$, as opposed to the case of large $\Delta\mu$ at which ΔG_L^* is smaller than ΔG_N^* .

B. Dependence of growth rate on chemical potential

Figure 4 shows nucleation rate calculated using Eq. (9) at a substrate temperature of 30 °C ($kT \approx 4.2 \times 10^{-21}$ J/molecule = 2.5 kJ/mol) as a function of $\Delta\mu$. The rate exhibits an abrupt increase at $\Delta\mu = 3.6 \times 10^{-20}$ and 3.7×10^{-20} J/molecule for normal and lateral orientations, re-

FIG. 3. Free energies of critical nucleus formation ΔG_N^* (solid line) and ΔG_L^* (dashed line) of normally and laterally oriented clusters, respectively, as a function of chemical-potential change $\Delta\mu$.

spectively. As expected from the results of Fig. 3, the preferable orientation changes from normal to lateral at the threshold value $\Delta\mu_{th}$ estimated to be 3.78×10^{-20} J/molecule. The degree of normal orientation is shown in Fig. 5 as a function of $\Delta\mu$. The theoretical curve can qualitatively explain the experimental results reported in literature.^{3–12,17,18,21}

C. Dependence on contact angle

In this section, we will consider the effects of contact angle on the orientational behavior. Figures 6 and 7 show the nucleation behavior for a smaller contact angle. In comparison with the case of a larger contact angle shown in Figs. 3–5, the lateral nuclei are preferably growing even in lower

FIG. 4. Nucleation rates J_N (solid line) and J_L (dashed line) for normally and laterally oriented clusters, respectively, as a function of chemical-potential change $\Delta\mu$.

FIG. 5. Degree of normal orientation as a function of chemical-potential change $\Delta\mu$, for molecular clusters having a smaller contact angle.

$\Delta\mu$. As summarized in Table I, the larger contact angle ($\theta = 86.2^\circ$) gives larger $\Delta\mu_{th}$, i.e., larger supersaturation is required to form laterally oriented clusters.

It appears that the calculated results shown in Fig. 7 may have a similar tendency with the plots shown in Fig. 8, estimated from the original experimental results for stearic acid reported by Matsuzaki *et al.*⁷ The contact angles of fatty acids should be rather small because polar moieties in the molecules can strongly interact with the periodical Coulomb potential of the alkali halide surface.

D. Validity of the model

As to Figs. 7 and 8 certain qualitative deficiencies are typical in small $\Delta\mu$. This mismatch indicates that further refinement of the theory should be required. In fact, crystal growth is a nonequilibrium kinetic process, and the final macroscopic state of the system depends on the route taken through the various elementary paths. The obtained state is not necessarily the most stable, but is kinetically determined. Therefore the kinetically controlled regime may play an important role in the orientational mechanism, as well as the thermodynamically controlled regime described in this paper. The kinetic theory we previously proposed¹⁹ may be applied well to the phenomena, if the theory is further modified.

FIG. 6. Free energies of critical nucleus formation as a function of chemical-potential change $\Delta\mu$, for molecular clusters having a smaller contact angle; ΔG_N^* (solid line) and ΔG_L^* (dashed line), of normally and laterally oriented clusters, respectively.

FIG. 7. Degree of normal orientation as a function of chemical-potential change $\Delta\mu$, for molecular clusters having a smaller contact angle.

Here we must mention the merits and demerits of using kinetic or classical approaches. In general, researchers of thin films prefer kinetic analyses, whereas those who study crystal growth tend to use a classical approach. Some of the kinetic approaches can give more accurate results than the classical nucleation theory, if further elementary processes are taken into account. We can also trace the time evolution of the thin-film growth. However, a demerit is that we cannot obtain the exact forms of solution of the rate equations. All we can do is numerical calculation with less physical meaning. As opposed to such a kinetic theory, the physical meaning for the classical nucleation theory is much clearer, which can give us the exact forms of solution to easily predict the experimental results.

IV. CONCLUSIONS

Molecular orientational mechanism during physical vapor deposition of various linear long-chain compounds is interpreted on the basis of thermodynamics for the anisotropic nucleus formation. In this model, the anisotropy of the surface energy is considered. In addition, two fundamental orientations (normal and lateral) of initial small nuclei are assumed to be determined thermodynamically. The critical energy of nucleus formation for each orientation is calculated as a function of the chemical-potential change for nucleation. The calculated results are similar to the actual orientational

FIG. 8. Degree of normal orientation for stearic acid ($C_{17}H_{35}COOH$) on KCl as a function of chemical-potential change $\Delta\mu$ estimated from experimental data reported originally by Matsuzaki *et al.* (Ref. 7). The solid line is drawn on the basis of the third-order spline function.

phenomena of long-chain molecules at various chemical-potential changes associated with supersaturation; i.e., a higher substrate temperature and/or a lower deposition rate result/s in a higher degree of normal orientation.

The classical nucleation theory proposed in this article may unfortunately be less accurate than the kinetic analysis in our previous paper; nevertheless, we can easily predict the experimental results by the present theory that can give us the exact forms of solution.

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