Effects of molecular diffusion length on area-selective growth of organic patterns

Yue Jiang1, Yichen Cai1, Jianping Li1, Naibo Chen1, Laigui Hu2, Wenchong Wang2, Qing-Miao Nie1 and Bo Yan3
1 Department of Applied Physics, Zhejiang University of Technology, 288, Liuhe Road, Hangzhou, 310023, People’s Republic of China
2 School of Information Science and Technology, Fudan University, Shanghai 200433, People’s Republic of China
3 Physikalisches Institut and Center for Nanotechnology, Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany

E-mail: nieqingmiao@zjut.edu.cn and boyan@zjut.edu.cn

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Abstract

Organic devices have gained much progress in the past decades, as a promising candidate for flexible/wearable electronics. However, the realization of organic microelectronic systems for wide applications is still difficult, due to the incompatibility of organic semiconductors (OSCs) with the conventional top-down lithography techniques for inorganics. To solve this challenge, bottom-up lithography-compatible methods have been developed for organic device arrays, i.e., template-directed growth or area-selective growth (ASG). Unfortunately, the physics on the dynamic process of the ASG method for molecular semiconductors is still not well understood. In order to explore this issue, the growth of particles on prepatterned surfaces under different diffusion lengths (Ld) was simulated in a microscopic point of view by using kinetic Monte Carlo method. Simulation results show that ASG of the particles is strongly related to the Ld of the particles, periodicity and size of prepatterned surfaces. It is notable that such simulated results were found to fit well with those of our experiments, which can be favorable for improving the ASG method for patterning functional molecules.

1. Introduction

With the emergence of flexible, wearable or even implantable electronic devices, organic micro/nano devices, with the capabilities of flexibility, ease of fabrication, low cost and compatibility with organisms [1], have received more and more attention. Different from their inorganic counterparts, organic materials constructed with van der Waals forces are incompatible with current matured silicon-based processing techniques (such as photolithography and dry/wet etching) [2]. Organic materials are usually very susceptible to ultraviolet light, solvents, high temperature, and, thus traditional top-down lithography and etching techniques cannot be directly applied to the preparation of micro/nano patterns of organic materials. Though some patterning techniques can also be employed for OSCs, such as vacuum deposition with shadow masks [3], soft imprinting [4], and ink-jet printing [5, 6], they still have some technical defects, such as low resolution, poor scalability and complex operations.

Recently, a bottom-up patterning strategy compatible with photolithography for OSCs was proposed [7–12], i.e., using a template with microstructures for directed growth of molecular films during physical vapor deposition (PVD). This approach shows the capability that micro-sized OSC devices and arrays can be self-assembled on pre-patterned substrates. Due to the difference in binding energy or surface energy between organic molecules and substrates or modification layers of substrates, organic molecules arriving at the substrates from evaporation sources randomly move along the surface and tend to nucleate where the binding energy is stronger. In this way, the positioning and controllable growth of organic molecules can be achieved on various micro-structures with different materials including octadecysilane (OTS)-patterned surface [13].
patterned metal electrodes [14] and other organic functional patterns [15]. For instances, self-assembled monolayers (SAMs) with well-ordered structures as templates have been successfully applied to control the selective nucleation of OSC crystalline films [16–19]. With this strategy, organic films can be designedly grown on the top of or in the gaps of micro Au electrodes [14]. OSC nanowires can also be realized using selective patterned growth on metal electrodes [20, 21]. Up to date, various OSCs, such as NPB [21], pentacene [22], rubrene [17], and Ag-TCNQ [20] have been investigated by using the ASG method. Furthermore, the ASG method is capable to pattern OSCs for organic devices, typically for the organic light-emitting diodes (OLEDs) [15, 23, 24]. In addition, the ASG of OSCs in the gaps of electrodes (source/drain electrodes) can lead to semiconducting channels for film transistors, even organic single crystal field effect transistor arrays can be obtained [13, 25].

In order to investigate the molecular dynamic process for the ASG, kinetic Monte Carlo (KMC) method has been employed to simulate the growth of particles on prepatterned surfaces [17, 26]. By representing organic molecules as spherical particles and choosing the interaction energies among organic molecules, substrates and electrodes accordingly, KMC method can simulate the adsorption/desorption, diffusion/aggregation processes of the molecules to achieve the positional and controllable growth of the molecules. Although the anisotropic properties existing for most organics are not considered, especially for planar molecules for which molecular shape and anisotropy strongly influence the ASG process [14, 27, 28], it is very encouraging that the simplified particle model is capable to reproduce the experimental observations for many typical OSCs [12, 26, 29–35]. This can be ascribed to the fact that the length scales of the system (dot distance and radius) are much larger than the size of the molecule [33]. In an ideal case that all the deposited molecules nucleate on the top of predefined patterns, nucleation control efficiency of one hundred percent is usually expected. However, it is hard to be achieved in reality. By tuning the strength of interactions among organic molecules, different morphology such as localized growth, bulge formation, and cluster formation are found in KMC simulations [27, 33–39]. Besides the interactions among particles (i.e., molecules), or between particles and substrates/electrodes, the final morphology of deposited particles is related with electrode sizes and incident flux. In addition, another important factor is the substrate-temperature dependent diffusivity of particles. For a given molecule and substrate system, a large $L_d$ resulting from high substrate temperatures is favorable to achieve a full control of nucleation. Until now, much works have been performed to investigate the effects of the former factors on the ASG method [40–48]. However, little attention has been paid to the latter one. Herein, the influence of substrate temperature in terms of $L_d$ of particles on the quality of ASG was investigated systematically by using KMC method. The detailed aggregation behavior of incident particles on various templates with different $L_d$ were successfully simulated, which fits well with experimental results. The goal of this work is to analyze the relationship between the $L_d$ and the quality of ASG method, giving a deeper insight for the ASG approach.

2. Simulation method

As reported in the literatures, Au patterned SiO$_2$ template was typically employed for the ASG method [8–10]. In the simulation, we used a three-dimensional periodic grid $100a \times 100a \times 2a$ ($a$ is the lattice constant and set to 1) to simulate SiO$_2$ substrates. In addition, a rectangular parallelepiped with a length of 30a, a width of 30a and a height of 4a was arranged on the substrate with a period of 50a to simulate a gold electrode in experiments. A coarse-grained model was used in the simulation, that is, spherical particles with different physical parameters were used to represent substrate particles ($s$), gold electrode particles ($g$) and deposited organic particles ($p$). The setup of our system is depicted in figure 1. In the simulation, a periodic boundary condition was applied in $x$ and $y$ directions. We set the range of movement of incident particles in $z$ direction to 20a. When the $z$-position of incident particle was larger than 20a, the particle was considered to overflow from the system, and thus the impact of the particle on the system was not considered any more.

Since the representing particles of substrate and gold electrode were fixed, we just considered three kinds of interactions: deposited particle-deposited particle interaction $\varepsilon_{pp}$, deposited particle–gold electrode interaction $\varepsilon_{pg}$ and deposited particle–substrate interaction $\varepsilon_{ps}$. The interaction between any two particles can be expressed by:

$$ E_{ij} = -\varepsilon_{ij} \sigma_i \sigma_j f(r_{ij}), $$  \hspace{1cm} (1)$$

where $\sigma$ denotes material category (i.e., $p$, $g$ or $s$). $r_{ij}$ is the distance between particle $i$ and $j$, $f(r_{ij})$ represents a coefficient related to particle distance. Interactions are considered only for adjacent particles with a distance of $a$, $\sqrt{2}a$, or $\sqrt{3}a$. We stipulated that when $r_{ij} \leq \sqrt{2}a$, $f(r_{ij}) = 1$; when $r_{ij} = \sqrt{3}a$, $f(r_{ij}) = 0.5$, and when $r_{ij} \geq \sqrt{3}a$, $f(r_{ij}) = 0$. Here, we set a truncation radius of $\sqrt{3}a$, which is the distance between diagonal particles in the cubic lattice. In this way, we can only consider the interactions between a central particle and its surrounding 26 particles in the simulation, ignoring large number of remote particles. In this way, one can greatly reduce the amount of calculation and shorten the simulation time. Then total potential energy $E_s$ of all the particles in the
In one Monte Carlo step, we stipulated that the particles can only diffuse along one of the six neighboring directions by one lattice length $a$. Moreover, new possible position should be not occupied by other particles. Larsson energy barrier which has to be overcome by the deposited particles during the diffusion process is expressed as

$$\Delta E_b = \beta (E_n + E_o) - E_o.$$  \hfill (3)

Here $E_n$ is total energy of the particles after diffusion, and $\beta$ is the weighting coefficient, which is set to 0.25886 [33]. Ehrlich-Schwoebel (ES) energy barrier should be overcome by the particles in continuous systems when the particles move across top corners of the electrode. The ES energy barrier closely depends on the lattice structure [49]. In order to be consistent with the ES energy barrier in a continuous system, in our simulation we increase the interaction between deposited particles and the electrode at the corner from $2\varepsilon_{pg}$ to $3\varepsilon_{pg}$ [27, 34], when particles diffuse from the electrode side wall to its top surface.

Then, we can calculate the probability of one diffusion event by

$$p_i = D e^{-\left(\frac{\Delta E_b}{k_B T}\right)},$$  \hfill (4)

where $D$ is the effective vibration frequency of the particles, which is set to be $10^{13}$ per second. During each Monte Carlo step, one diffusion direction $k$ is chosen pseudo-randomly from all of the $K$ events as given by:

$$\sum_{i=0}^{k-1} p_i < R_1 \sum_{i=0}^{K} p_i < \sum_{i=0}^{k} p_i,$$  \hfill (5)

where $R_1$ is a random number, uniformly distributed between 0 and 1. After selecting an accepted event, the time increment of computation clock is given by

$$\Delta t = \frac{\ln(1/R_2)}{\sum_i p_i}.$$  \hfill (6)

Here $R_2$ is another random number, and $p_i$ is the probability of occurrence of the $i$-th diffusion event.

The KMC simulation is then performed to mimic the continuous flux in PVD experiments. We assumed that the time interval of each incoming particle is $10^{-8}$ second. When the total diffusion time of each incoming particle is greater than this interval, one new particle was added into the system. The simulations were stopped after the deposition of all the particles. The diffusion distance of the particles is limited within $L_d$ to reflect the effects of $L_d$. In order to consider the effects of $L_d$, we set the interactions $\varepsilon_{pg}$ to 1.3 $k_BT$ and $\varepsilon_{ps}$ to 0.3 $k_BT$, where $k_B$ is Boltzmann’s constant and $T$ is the absolute temperature. All statistic results shown in our work are averaged over 10 independent realization samples.

3. Results and discussion

In order to discuss the influence of the $L_d$ on the template-directed positioning and nucleation of the deposited particles, the simulations with four sets of $L_d = 10a, 20a, 40a$ and $60a$ were conducted. 5000 particles were
simulated with a long enough time to get the final results as shown in figure 2 with \( \varepsilon_{pp} = 3.5 \, k_B T \). For each \( L_d \), the deposition morphology in the stage of initial (500 particles) and the final (5,000 particles) nucleation was simulated, respectively. When the \( L_d \) is 10a, it can be seen from figure 2(a) that nucleation occurs on the electrodes close to their edges in the initial stage. There are multiple nucleation points on each electrode. As the number of particles continue to increase, particles are continuously deposited around each nucleation point, and eventually larger islands form on the electrodes, as shown in figure 2(b).

As the \( L_d \) increases and reaches around 40a, one can see that the initial nucleation of particles tends to move towards the center of the electrodes. The nucleation points in our simulation demonstrate a certain deviation from the center of each electrode. We found that the multiple nucleation points on each electrode at the initial stage merged into nearly one per electrode, due to the increase of \( L_d \). As the number of particles continues to increase, a single island-like film is formed on each electrode. With the further increase of \( L_d \) to 60a (figures 2(g) and (h)), we note that the nucleation points are not generated on each electrode any more, but on a randomly-selected electrode. As the number of particles continues to increase, the particles will pile up at the nucleation site. This implies that an extremely long \( L_d \) or a very high temperature can lead to a failure of the ASG method.

In order to investigate the deposition of particles on each electrode more clearly, we counted the number of particles deposited on each electrode under different \( L_d \), as shown in figure 3(a). We can see that when the \( L_d \) is between 20a and 40a, the number of particles surrounding each electrode is roughly the same. It can be thought that the particles are basically evenly distributed around each electrode. We expected that the quality of ASG for incident particles is high when \( L_d \) is less than 40a. But when the \( L_d \) reaches about 60a, it can be seen that the number of particles on three of the electrodes quickly drops to nearly zero, and the particles nucleate on a certain electrode. Therefore, the effectiveness of the ASG method is disabled when the \( L_d \) of incident particles is too large, or at a too high substrate temperature at which most OSCs may be destroyed or evaporated.
We further investigated the effects of $L_d$ on the aggregation behavior of particles. The center deviation from each electrode with different $L_d$ was calculated, as shown in figure 3(b) with the box-line plot in which the height of box body is proportional to the dispersity of data. We can see that the particles show a better effectiveness for the ASG method with the $L_d$ decreasing and exhibit a smallest center shift when the $L_d$ approaches $\sim 40a$. It means that the particles tend to gather into a film toward electrode center. However, when $L_d$ is larger than 40a, center shift starts to increase with $L_d$.

To investigate the influence of the periodicity of the gold electrodes, the interval of each electrode was increased from 20a to 40a and the interaction $\varepsilon_{pp}$ was decreased from 3.5 to 2.5, as shown in figure 4. The morphology evolution of 15000 deposited particles on the pre-patterned surfaces was simulated with the change of $L_d$ from 5a to 25a. It is found that short $L_d$ lead to many islands uniformly formed among or on the electrodes (figure 4(a)). With the increase of $L_d$ from 5a to 10a, particles tend to aggregate on the top of electrode, resulting in the appearance of blank ring domains around the electrodes (figure 4(b)). This suggests that particles outside the rings cannot move to the electrodes for aggregation due to a limited $L_d$. When compared to the larger electrode spacing of 40a, such a behavior is more distinct if one increases the $L_d$ to 15a (figure 4(c)), with some islands in the middle of the electrode gaps. The width of the blank rings becomes larger and exhibits a $L_d$ dependence. When $L_d$ exceeds half of the electrode spacing, no particles among the electrodes can be observed and all the particles nucleate on the electrodes (figure 4(d)). The coverage and uniformity of the films on the electrodes also become better. Similar trends were also observed for the same patterns with a larger electrode height of 4a (figures 4(e)–(h)).

To explore the influence of deposited particle-deposited particle interaction, ASG with a smaller $\varepsilon_{pp} = 1.5$ was also simulated, as shown in figure 5. It is noted that the effectiveness for the ASG method with a smaller $\varepsilon_{pp}$ is even better than that with the $\varepsilon_{pp} = 2.5$ (figures 4) and 3.5 (figure 2). Both the coverage and uniformity of the films on electrodes are superior to those in the former cases. It is also noted that thinner electrode thickness causes a patterned film with a higher quality. Since the area without particles on the electrodes (i.e., pin holes) decreases with the increase of $L_d$, one can expect that such pin holes can be completely removed by further increasing the $L_d$. As we can see in figures 5(d) and (h), perfect patterns without pin holes and islands in the electrode gaps can be achieved if $L_d = 25a$, exceeding half of the electrode spacing.

Our results indicate that the morphology of deposited particles strongly depends on the $L_d$ or substrate temperatures. When the $L_d$ is smaller than the size of electrodes and their spacing, the particles tend to deposit on the pre-patterned electrodes. As the $L_d$ is close to half of the electrode size, the particles can be deposited at the area close to the center of each electrode. In addition, if the $L_d$ is smaller than half of the space of adjacent electrodes, two types of patterns will form except the films on the electrodes. Since nucleation also occurs at the middle area randomly among the electrodes. However, for the $L_d$ exceeding the size of the period of the electrode array, ASG process cannot be effectively induced. Therefore, one can tune the temperature of substrates to control the $L_d$ for patterning OSCs.

To verified the theoretical simulation, PVD experiments were also performed and the well-known OSC N, N′-bis(1-naphthyl)-N, N′-diphenyl-1,1′-diphenyl-4,4′-diamine (NPB) from Shanghai Aladdin Biochemical Technology Co., Ltd. was utilized as a prototype for the ASG method (figure 6). Before deposition, silicon substrates were cleaned by using ultrasonic bath in acetone, isopropanol and deionized water each for 15 min
For the preparation of electrode patterns, photoresists were spin coated onto the substrates and photolithography was employed for dot array patterns. Subsequently, Cr/Au films were deposited by PVD method and Au dot arrays were obtained after lifting off process. Finally, NPB patterns were deposited using PVD method at a rate of 0.05 Å s\(^{-1}\) with different substrate temperatures for different \(L_d\). For the experiment in figure 6(a), the substrate with a gold electrode array was heated to 250 °C during deposition. As one can see that NPB dots randomly distributed at the top area without Au electrodes with the distance of each NPB island about 1 μm. For the area with Au electrodes, NPB nucleation occurs above or among the electrodes with a blank ring around. Both the diameters and spacing of the electrodes are 3 μm. For comparison, ASG of the NPB at a higher substrate temperature (300 °C) was also investigated, as shown in figure 6(b). The diameters and spacing of the electrodes are decreased to 2 μm. It is notable that the spacing between each NPB islands at the top area becomes larger. In addition, the size of the blank rings was also enlarged to about 1.5 μm and the NPB islands among the

**Figure 5.** Temporal snapshots of morphology evolution of 15000 deposited particles on pre-patterned surfaces with \(L_d = 5a\) (a), (c), 10a (b), (f), 15a (c), (g), 25a (d), (h). The \(L_d\) is in units of lattice constant \(a\). The snapshots on upper and lower row were taken with the height of electrode 2a and 4a, respectively. The interactions \(\epsilon_{pg}\), \(\epsilon_{pp}\) and \(\epsilon_{ps}\) are in units of \(k_B T\) and set to 1.3, 1.5 and 0.3, respectively.

**Figure 6.** (a) ASG of NPB dot patterns on a hot substrate at 250°C. The diameter and spacing of the electrodes are 3 μm. (b) ASG of NPB dot patterns on a substrate at 300 °C. The diameter and spacing of the electrodes are 2 μm. (c) ASG of NPB on PPy patterns at 180 °C and (d) 200 °C, respectively. (e) and (f) show the height profile of the NPB patterns along the top and bottom red lines in figure 6(d), respectively.
electrodes nearly merge into single lines with NPB films on the electrodes. The morphology of the obtained NPB patterns in figures 6(a) and (b) is very similar to the simulated patterns (e.g., figures 5(a) and (b), respectively).

Besides the ASG of the NPB on Au patterns, other electrodes (i.e., conductive polymer patterns) with different substrates were also investigated. Photoresist was spin coated onto indium-tin oxide (ITO) glass substrates with 10 nm Al2O3, was spin-coated and baked at 100 °C for 3 min. The photoresist was then partially exposed to UV light under a photomask for 2 s and developed for 15 s. 113.4-μL pyrrole was dispersed in deionized water by mechanical vibration, followed by adding 3-mL aqueous solution containing 30-mg FeCl3. Then, the ITO glasses with patterned photoresist were immediately put into this solution. After keeping the reaction temperature at 20 °C for 6 min, the samples were taken out with a layer of polypyrrole (PPy) on the surface. The PPy on photoresist was removed by lift-off under sonication in acetone for 5 min. The samples were ultrasonically cleaned in ethanol and water each for 3 min and then dried under nitrogen flow. After that, the ASG of NPB on the PPy patterns was carried out with the same procedures as those in figure 6(a). Atomic force microscopy (AFM) images were collected as figures 6(c) and (d) with substrate temperatures of 180 and 200 °C, respectively. Similar behavior with that in figures 6(a) and (b) was observed, i.e., the size of the blank rings was also enlarged with the increase of diffusion lengths. Figures 6(e) and (f) are the height profile along the top and bottom red lines in figure 6(d), respectively, confirming that there is no NPB particles in the rings around the electrodes. Hence, these characteristics match well with the simulation results that hotter substrates lead to a larger $L_d$ and a better effectiveness for ASG method if $L_d$ are not too large.

4. Conclusion

In order to explore the effects of $L_d$ of particles on the area selective growth method, we have systematically studied the deposition behavior of particles with different $L_d$ on various templates by using kinetic Monte Carlo method. From a microscopic point of view, the influence of $L_d$, period and height of electrodes on the patterning of deposited particles are investigated. Our simulation results fit well with experimental ones, which show that the morphology of deposited particles strongly depends on $L_d$ or substrate temperature. When $L_d$ is less than electrode spacing and electrode sizes, with the increase of the $L_d$, the incident particles tend to be deposited on the edge of the electrodes, as well as among the electrodes with a blank ring around. Further increasing the $L_d$ can induce a better effectiveness of the ASG method that most particles or even all the particles can be deposited on the electrodes. However, when the $L_d$ reaches a threshold, i.e., the period of the electrode array, the particles will randomly select an electrode for nucleation, leading to a failure of the ASG method. Hence, one can improve the quality of the ASG by arranging the layout of templates based on the $L_d$ of particles or changing substrate temperature for an optimized $L_d$ value.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Qing-Miao Nie https://orcid.org/0000-0001-7146-0555
Bo Yan https://orcid.org/0000-0002-7885-8109

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