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A kinetic Monte Carlo simulation of surface microfluidic patterning organic molecules based on anisotropic wetting

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ABSTRACT

In this Letter, the kinetic Monte Carlo simulations are employed to study the microscopic mechanisms of patterning molten organic particles based on liquid behavior on templated surfaces. The simulated results show that the binding energy difference between the organic particle and templated surface plays a key role in the anisotropic wetting of organic particles. And the square root of time law between the spreading distance and simulated time on different temperatures is well consistent with experimental observation. We also note that the geometry effect of channel edge has very significant effect on the dependence of spreading velocity on template dimensions.

1. Introduction

Small molecule organic semiconductors have attracted much attention owing to their intensive applications in electronics and optoelectronics [1]. Besides materials, film patterning also plays a crucial role in organic semiconductors [2–5]. In these experiments, driven by developing a photolithography compatible patterning technique, template-direct-growth was proposed to deposit organic molecules on pre-defined areas [6–10]. Initially the experimental techniques were performed on Au patterned SiO_2 surfaces under vacuum conditions, with versatilities in film patterning, molecule separation and physical property tuning [6–8].

Recently, being taken advantage of liquid behavior of some functional molecules, the technique was also utilized to create organic addressable structures and hetero-patterns [9,10]. Very recently, it was further extended to pattern molecules directly in air [11]. For example, Figure 1 shows our current research about temporal evolution of candle wax on Au line in width of 50 μm. The Au line is patterned by shadow mask on SiO_2, which is connected with two pads in size of 2 mml. The candle wax powder is firstly placed on one of the Au pads. When heated to 80 °C, the wax melts into liquid and spreads out gradually. In the experiment, the liquid can be confined completely on the Au pad with propagating along the channel, shown in Figure 1a. When the liquid reach the second pad, it spreads out and fills the second pads, shown in Figure 1b. A closed look at the liquid/air interface shows that a thin diffusion layer is the key point dominating the process. The experiments showed that the molecules can dismantle from the liquid drop and diffuse over the Au surface to form a precursor layer which consequently directs the meniscus.

The previous studies in liquid behaviors were mainly concentrated on 'lab on a chip' which dealt with the mixtures, separations, mass transports, and reactions which occurred on much smaller time and length scales [12–14]. The theoretical efforts in the spreading mechanism of microfluidics usually focused on wetting dynamics of a single droplet [15–17]. And the theoretical treatments on the application of microfluidics in direct patterning on templated surfaces were rarely reported. To gain deeper insight on the atomistic mechanisms, the kinetic Monte Carlo (KMC) algorithm based on the coarse-grained model is conducted to analyze the spreading behaviors of organic molecules on the prepatterned template in this Letter. The relationship between the area-selective spreading and molecular interaction energy, the relationship between spreading morphology and molecular interaction energy, the effect of temperature and template dimensions on the spreading velocity of precursor are systematically explored in the present work.

2. Simulation details

The Monte Carlo simulations have been demonstrated as promising method for investigating the mechanism of the multilayers growth and template-directed nucleation [18–21]. Due

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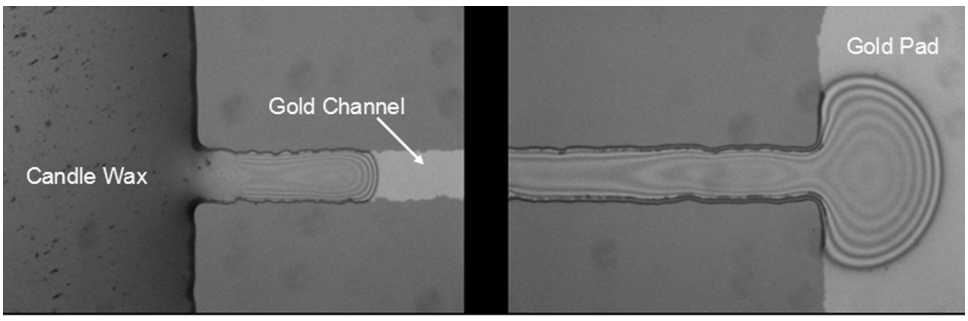

Figure 1. Optical microscope images of candle wax on Au patterned SiO_2 with different time. (a) 18 s, and (b) 210 s. The time 0 s is set when the liquid starts to fill the channel.

to the same molecules diffusion mechanism, the methods have been widely used in the theoretically studies for spreading of liquid droplets and precursor formation [22–24]. Based on the close relationship between nucleation modes and wetting regimes, the Lattice Monte Carlo method used in the template-directed nucleation even has been directly employed in the bulge formation of the liquid by Heuer [25]. In this present work, the KMC simulation previously used in step-induced nucleation [26] was modified to explore the spreading behaviors of liquid in the directly patterning system. The main point is to analyze the micro-scale mechanisms of molten particles spreading and patterning. Therefore, the rectangular lattice model [6,25,26] based on the coarse-grained model and employed in modeling the amorphous silica dioxide, gold channel and organic molecules with an ordered crystalline is appropriate in the present KMC simulation. In the coarse-grained model, one particle could be considered as one or more molecules at the molecular level. Although the different scale effects between the experiment and simulation exist, the KMC model can represent the nano-scale or micro-scale experimental phenomenon and give us a quantitative explanation for the experimental observation.

As shown in Figure 2, a three dimensional cubic lattice box is conducted. During the simulation, all molecules are treated as spherical particles in the coarse-grained model. A two dimensional square lattice of size $30a \times 135a$ (a being the lattice constant) is built as the substrate representing the amorphous SiO_2. The prepatterned structures representing the Au pads and channel are built on the substrate. The pads are connected by the channel with a width of $14a$, length of $110a$, height of $4a$. At the initial simulation, the organic particles are presented on the pad as the liquid reservoir, with a distance of $5a$ to the channel. In the simulation, the organic particles are assumed to be infinite in the reservoir.

During the simulation, the positions of organic particles are restricted at the sites of the rectangular lattice. And one particle can only jump to one of its nearest empty neighbor sites for each movement. Thus the direction and length of a displacement vector are fixed. For computational efficiency, the cutoff distance is

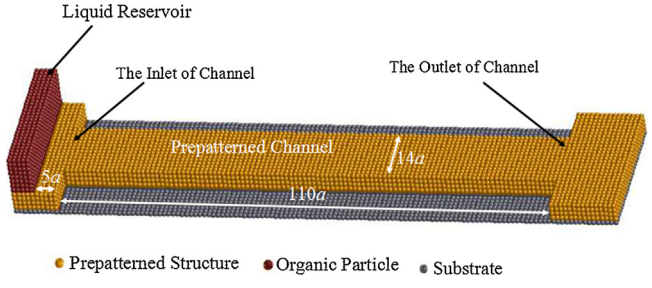

Figure 2. Setup of simulation box. The gray balls represent the substrate, the yellow balls stand for prepatterned structures, and the brown balls reflect the organic particles.

$\sqrt{3}a$ (i.e. the body diagonal distance of the cube crystal). Then only the interactions between direct neighbor particles are considered. Within the cutoff $\sqrt{3}a$, the distance scales between two particles are just a, $\sqrt{2}a$ and $\sqrt{3}a$. Since the substrate (s) and prepatterned structures (p) are fixed, there are only three energy types: organic particle–organic particle interaction ε_{oo}, organic particle–pattern interaction ε_{op} and organic particle–substrate interaction ε_{os}. For the discrete distance scales, the interaction parameters proved to be appropriate by Heuer in the template-induced patterning of organic molecules [25] are used in this Letter. The interaction between two arbitrary particles i and j of type $t(i)$ and $t(j)$ is given by:

$$E_{ij} = -\varepsilon_{t(i)t(j)} f(r_{ij}) \tag{1}$$

where r_{ij} denotes the distance between particles i and j, and $f(r_{ij})$ is defined as $f(r_{ij}) = 1$ for $r_{ij} \le \sqrt{2}a$, $f(r_{ij}) = 0.5$ for $r_{ij} = \sqrt{3}a$ and $f(r_{ij}) = 0$ for the else. The continuous interaction energy mainly used in off-lattice gas model, like Lennard–Jones pair potentials, maybe give one reasonable result. However, in our lattice model, the interactions calculated by Eq. (1) are more appropriate.

In the simulation, ε_{os} is set as 0.3 (the energies are always given in unit of k_BT). Here k_B is the Boltzmann's constant and T is the temperature. The interaction ε_{op} is fixed at 3.0, which is large enough to display significant differences to the interaction between the organic particle and the substrate. Therefore, the potential energy E_i of particle i can be calculated by the interactions with other surrounded particles:

$$E_i = \sum E_{ij} = \sum -\varepsilon_{t(i)t(j)} f(r_{ij}) \tag{2}$$

According to the Larsson's bond-counting barrier model, the diffusion barrier $E_{barrier}$ depends symmetrically on the energies of the old (E_o) and the new (E_n) site [27,28]. It can be expressed as:

$$E_{barrier} = \alpha(E_n + E_o) - E_o \tag{3}$$

where α is the weighting factor with a value of 0.25886 and derived from an analytical consideration of the relevant diffusion processes [29]. In order to discuss the impact of temperature on the spreading of the organic particle spreading, the barrier $E_{barrier}$ is assumed to be unchanged when temperature changes a little. When the substrate temperature is T_1, the absolute value of $E_{barrier}$ can be expressed as $(\alpha(E_n + E_o) - E_o)k_BT_1$. If the temperature rises up to T_2, the barrier $E_{barrier}$ is defined as $T_1/T_2(\alpha(E_n + E_o) - E_o)k_BT_2$, where T_1/T_2 is introduced to keep $E_{barrier}$ constant. Finally, the diffusion rate of particle i from old site to new site can be obtained by an Arrhenius expression:

$$V_{ij} = De^{(-E_{barrier}/k_BT)} \tag{4}$$

where D is the effective vibration frequency (taken to be 10^{13}/s for all cases in this work). For each MC step, one particle can only jump on one of its nearest empty neighbor sites. Therefore there are six