Effects of mold geometry and taper angles on the filling mechanism of a nanoimprinted polymer using molecular dynamics

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A B S T R A C T
Molecular dynamics simulations are used to investigate how the nanoimprint lithography mechanism influences the filling interaction and mechanical deformation on polymethylmethacrylate (PMMA) surfaces. The effects of two mold geometries and various taper angles were investigated using stress, slip vector, molecular trajectories, and applied force analysis. For the PMMA formation mechanism on a concave-like mold imprint, the molecules were extruded upward into the mold space after the molecules on two sides were downward compressed by the mold. The formation mechanism is opposite to that for the tip-like mold imprint because the molecules are firstly compressed downward by the tip. The results show that the slowest filled areas of the pattern were at the two corners of the tip where stress value was low. The filling speed in both the tip-like mold and the concave-like mold imprint increased with the taper angle increased due to filling space and smaller capillary flow. Due to the effect of capillary flow, the concave-like mold needs much more loading force to transfer the pattern than the tip-like mold. The loading force and curve oscillation increased with the taper angle in the tip-like mold imprint, but they significantly increased with decreasing taper angle in the concave-like mold. The high stress was mainly concentrated on the molecules near the tip and underneath the mold for the tip-like mold and the concave-like mold imprint, respectively. The relationship of the magnitude of taper angle to the loading force is similar to stress and slip vector.

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1. Introduction
Nanoimprint lithography (NIL) is a simple technique to fabricate nanoscale patterns on large substrates. NIL has been considered as a popular method with high resolution (sub-10 nm feature size), cost effectiveness, and high throughput [1,2]. Although some processing methods, such as electron beam lithography and focused ion beam writing, can be used to produce patterns with features down to sub-10 nm, they are not practical enough due to low throughput and high cost. NIL fabricates nanoscale patterns by pressing a hard mold with nanoscale features into a thin film (polymer or metal) and then deforming the film mechanically.

Most studies on NIL have focused on experiments. Chou [3] employed NIL to fabricate uniform patterns over a 15 mm by 18 mm area on polymethylmethacrylate (PMMA) films. Austin et al. [4] demonstrated 5 nm linewidth and 14 nm line pitch in resist at room temperature. Hsu et al. [5] created a PMMA film with photonic crystal structures in the organic light-emitting diode (OLED) components to increase lightening efficiency of the OLED components. Few studies on NIL have used numerical methods. Molecular dynamics (MD) simulation is a powerful scientific tool for studying material behavior at the nanometer scale. Many nanosystems have been analyzed using MD, including the deformation [6] and hydrogen storage capacity of graphenes [7,8], nanoforming [9,10], metal nanowires under torsion [11,12], and dip-pen nanolithography [13,14]. The pattern formation and mechanics of NIL were investigated by varying the imprint temperature [15,16] and velocity [15] and taper angle of mold [17,18]. Kang et al. [19] studied pattern transfer on an amorphous PMMA film by using molds with the various aspect ratio patterns. They found that amount of springback of residual film increases with increasing aspect ratio of pattern. The friction force between a mold and a film becomes larger than the adhesion force when the pattern aspect ratio increases.

In the present study, a short-range order of PMMA molecule layer in the horizontal direction is considered as the imprinted film. The effects of the mold geometries (tip-like and concave-like) and the taper angle on the NIL process are investigated using MD...
simulations. The objectives of this study are to determine the physical behavior of deformation, filling characteristics, imprint force, stress, and slip vector distribution during the imprint process.

2. Methodology

Fig. 1(a) and (b) shows schematic models with geometries of tip-like and concave-like NIL molds, respectively. The angle $\theta$ on the mold is changed to study the effect of the taper angle on nanoimprint filling. The model consists of a nickel (Ni) mold and PMMA film with a horizontal arrangement, as shown in Fig. 1(c). The Ni mold consists of a perfect face-centered cubic (FCC) single crystal with a lattice constant of 0.352 nm. To simplify the imprint problem, the mold was assumed to be a rigid body with a unit displacement of 0.003 nm to imprint per time step (imprint velocity is 30 m/s). The time step unit of $10^{-15}$ s was employed for the whole simulation. The characteristic height of the mold was fixed at 5 nm. The width and height of the PMMA film, which was composed of 100 PMMA molecules, were 15 and 20 nm, respectively. The molecular weight of each molecule was 10,016 (degree of polymerization = 100). A two-dimensional system was simulated with the surface normal parallel to the Z-axis, X-, Y-, and Z-axes were in the (1 1 0), (1 0 0), and (1 0 1) directions, respectively. A periodic boundary condition was applied to the X- and Y-axes. Four fixed layers of Ni atoms were imposed beneath the PMMA film to constrain the whole system in the vertical direction. The PMMA molecules obey Newton’s second law and their velocities are adjusted to maintain the molecules in an isothermal state of 300 K.

The potential energy model proposed by Okada et al. [20] is adopted to describe interactions for the PMMA molecules, as shown in Eq. (1). In this model, the united atom (UA) model is used, in which hydrogen atoms are included in the connecting carbon atoms; thus a methyl or ethyl group is treated and showed as one interacting carbon atom, as shown in Fig. 2. The figure shows the molecular structure of PMMA, UA model, and the schematic period for a chain.

$$U = \sum_{\text{bonds}} k_r (r - r_0)^2 + \sum_{\text{angles}} k_{\theta} (\theta - \theta_0)^2 + \sum_{\text{torsions}} \sum_{i=1}^{n} (V_{\theta} \cos n\phi)$$

$$+ \sum_{\text{improper torsions}} (K_1 (\varphi - \varphi_0) + K_2 (\varphi - \varphi_0)^2)$$

$$+ \sum_{1,2,3,4\text{nonbonds}} \frac{A}{r^{12}} - \frac{C}{r^6}$$

(1)

where the first and second terms represent the bond stretching potential ($r = $ bond length and $r_0 = $ bond length in equilibrium) and the angular bending potential ($\theta = $ bending angle and $\theta_0 = $ bending angle in equilibrium), respectively. The third and fourth terms represent the torsion potential ($\phi = $ torsion angle) and the improper torsion potential ($\varphi = $ sum of three neighboring bending angles, $\varphi_0 = $ sum of three neighboring bending angles in equilibrium), respectively. The fifth term is the Lennard-Jones (LJ) potential between two atoms/molecules in the distance of four bond distances.
Fig. 2. (a) Molecular structure of PMMA, (b) unit atom model, and (c) schematic period for a chain.

Fig. 3. Snapshots of MD simulation of NIL for the tip-like mold with taper angles of 30°, 40°, and 50° for different imprint depths (D).
contact area and deformation amount. The effect is clearly shown in Fig. 9(b) and (c). Seeing the taper angle of 30° in Fig. 9(a), there are three major areas of high slip vector distribution; in order of magnitude are the area closest to the tip, the area near the tip, and the area underneath the mold, respectively. The magnitude of the first two slip areas is proportional to the taper angle and the imprint depth, but the magnitude of the area underneath the mold is inversely proportional to the taper angle. For the concave-like mold imprint shown in Fig. 9(d) and (e), the area with the highest slip vector is underneath the mold, the second area are molecules at the concave mold. In the concave-like mold imprint, the slip vector decreases with increasing taper angle at the same imprint depth because more extruded molecules are generated. For a taper angle of 15°, as shown in Fig. 9(e), the slip vector was extremely high and the distribution was uniform from surface to deeper layers. Even molecules packed inside the mold had a very high value because all molecules were compressed strongly by the mold.

4. Conclusion

The stress and slip behavior of imprinted PMMA surfaces were investigated using molecular dynamics. For the PMMA formation mechanism on the concave-like mold imprint, the molecules were extruded upward into the mold space after the molecules on two sides were downward compressed by the mold. The formation mechanism is opposite to that for the tip-like mold imprint because the molecules were firstly compressed downward by the tip, and then the molecules on two sides were extruded upward. A larger taper angle increases the filling speed in the tip-like mold and the concave-like mold imprints, due to increase filling space and a smaller capillary effect between the mold walls and PMMA molecules. The concave-like mold needs much more loading force than does the tip-like mold to transfer the pattern. The loading force and curve oscillation increased with increasing taper angle in the tip-like mold imprint, but they increased with decreasing taper angle in the concave-like mold. The high stress was mainly concentrated on the molecules near the tip and underneath the mold for the tip-like mold and the concave-like mold imprints, respectively.

The relationship of the magnitude of taper angle to the loading force is similar to the stress and the slip vector. The slip vector analysis shows the characteristics of the flow field for the two mold types and at the various taper angles.

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