Computational Study of Pattern Formation in UV Nanoimprint Lithography

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We have investigated the pattern formation process in ultraviolet (UV) nanoimprint lithography by stochastic and molecular dynamics (MD) simulations. The UV-curing process was investigated by stochastic simulations. The simulations show the polymerization process of UV-cured molecules. The effect of the photoinitiator concentration of the UV-cured resist was also investigated by stochastic simulations. The sizes and shapes of the reacted monomers in UV-cured resists with various molecular weights were also shown. The de-molding process was investigated by MD simulations. For a resist with a relatively low molecular weight, fracture and stretching of the pattern are observed during the de-molding process.

Keywords: Ultraviolet nanoimprint lithography, Ultraviolet curing, De-molding process, Stochastic simulation, Molecular dynamics

1. Introduction

Ultraviolet nanoimprint lithography (UV-NIL) is an effective method for nanometer-scale fabrication [1,2]. Sub-10-nm resolution has been experimentally demonstrated in UV-NIL [3,4]. To realize well-controlled patterning in UV-NIL, understanding the physical and chemical phenomena during the resist filling, UV curing, and de-molding processes is important. As the pattern size becomes smaller than several tens of nanometers, understanding the phenomena at the atomic level becomes increasingly important. Computational methods, such as stochastic and molecular dynamics (MD) simulations, become powerful tools for such a purpose.

We recently proposed the stochastic simulation technique for UV curing in UV-NIL and investigated the basic UV-curing characteristics of a resist [5]. The molecular weight distribution of the polymers and the effect of the photoinitiator concentration of the UV-cured resist were investigated. The basic UV-curing characteristics can be well described by stochastic simulations. We have also discussed the effects of the pattern size and shape on the UV-curing characteristics in UV-NIL [6]. By including the deactivation effect at the resist surface, the decrease in the conversion ratio with decreasing feature size observed in experiments can be reproduced by stochastic simulations.

The motion of the polymers in the UV-cured resist cannot be studied by stochastic simulations, so the de-molding process in UV-NIL was not discussed in our previous studies. In the present work, we investigated the UV-curing process by a stochastic approach, and investigation of the de-molding process was separately performed by MD simulations.

2. Simulation model

The stochastic simulation model of UV curing used in this work is the same as that reported in our previous studies [5,6]. A schematic illustration of the stochastic model is shown in Fig. 1. Each monomer is expressed as a unit cluster molecule. The monomers and photoinitiators are randomly placed in space. In the present simulations, each monomer is a virtual monofunctional molecule with a molecular weight of 100. The density of the resist is 1.18 g/cm³.
The UV-curing model used in the simulations is as following. The chain reaction starts when the initiator is activated by UV exposure. The activated monomer reacts with a randomly selected monomer within a critical reaction radius and a chemical bond forms between them. The bonded monomer is then activated and the next chain reaction occurs. When there is no virgin monomer within the reaction radius, the reaction radius is increased step by step up to the maximum allowable radius and the chain reaction occurs within the expanded reaction radius. If there is no virgin monomer within the reaction radius or the activated monomers react with each other, the chain reaction stops.

![Schematic illustration of the UV-curing model](image)

In the stochastic simulations of the UV-curing process, the motion of the UV-cured polymers cannot be traced. Therefore, we performed MD simulations developed for thermal nanoimprint lithography (T-NIL) to analyze the de-molding process [7–9]. Because the force field for the UV-cured resist is not known, we investigated the de-molding process of the poly(methyl methacrylate) (PMMA) resist. To reduce the calculation load, the methyl and methylene groups are assumed to be unit giant atoms in the simulations.

The force field for the PMMA resist consists of bond stretching, bond bending, and torsion potentials, and nonbonding interactions, including Lennard–Jones and Coulomb potentials [10]. In the MD simulations, the material of the mold and substrate is Si. Lennard–Jones potentials are used between the resist polymer and Si atoms. The potentials between the Si mold and PMMA resist are increased by 1.3 times to investigate deformation of the resist during the de-molding process. The potentials between the Si substrate and PMMA resist are increased by one order of magnitude to avoid delamination of the resist from the substrate. The mold and substrate are assumed to be rigid bodies to reduce the calculation time. The resist filling and relaxation processes are performed in the same manner to those in the T-NIL simulation [7,8].

3. Results and discussion

3.1. UV-curing process

Figure 2 shows snapshots of the polymerization process of UV-cured molecules in the present simulation. Three molecules are selected as examples. The lengths of the molecules increase as the chain reaction progresses from Figs. 2(a) to (d). The shapes of the molecules are stochastically determined during the chain reactions.

![Snapshots of the polymerization process](image)

Figure 3 shows the conversion ratio as a function of the number of reaction events for three initiator concentrations. The shape of the resist is cubic and the edge sizes are 50 nm. In one reaction event, one chain reaction proceeds for each reacted polymer. With increasing initiator concentration, the conversion ratio increases and saturates earlier. The saturated conversion ratio increases with increasing initiator concentration.

Figure 4 shows the molecular weight distributions of the polymers for the three initiator concentrations calculated by stochastic simulations. With increasing initiator concentration, the peak molecular weight of the distribution decreases. This trend is appropriate considering the experimental results as reported in our previous study [5]. The number-average molecular weight...
Fig. 3. Conversion ratio as a function of number of reaction events for three initiator concentrations.

Fig. 4. Molecular weight distributions of the reacted monomers for three initiator concentrations.

Fig. 5. (a) Shape and size of the resist pattern. (b)–(d) Snapshots of the reacted monomers in the patterned resists with initiator concentrations of 10.1%, 3.40%, and 1.12%, respectively. Twenty molecules are selected as examples. The $M_n$ values of the resists are (b) 1500, (c) 4000, and (d) 10000.

3.2. Structure of the UV-cured resist pattern

Figure 5 shows snapshots of the reacted monomers in the patterned resists for the three initiator concentrations obtained by stochastic simulations. Twenty molecules are selected as examples. The shape and size of the resist pattern are shown in Fig. 5(a). The $M_n$ values of the reacted monomers in the patterned resists in Figs. 5(b)–(d) are 1500, 4000, and 10000, respectively, which are the same as those in Fig. 4. The sizes of the resist molecules with $M_n = 1500$ are quite small, as shown in Fig. 5(b). Entanglement of molecules is rarely observed. The fluidities of the molecules are expected to be high. The sizes of the resist molecules with $M_n = 4000$ are larger than those with $M_n = 1500$ and some of the molecules are entangled, as shown in Fig. 5(c). For $M_n = 10000$, the sizes of the molecules are close to the width of the convex part of the resist pattern, as shown in Fig. 5(d). Entanglement of molecules is frequently observed. The strength of the cured resist is expected to be relatively high.

Figure 6(a) shows a snapshot of the all of the monomers in the UV-cured resist with $M_n = 4000$. The red spheres are unreacted monomers and the other colored spheres are reacted monomers. The shape and size of the resist pattern is the same as that in Fig. 5(a). The conversion ratio of this resist is 0.72. Figure 6(b) shows only the unreacted monomers in the same resist. The unreacted monomers are uniformly distributed in the whole area of the pattern. These unreacted monomers are considered to deteriorate the de-molding properties in the UV-NIL process.

Fig. 6. Snapshots of the (a) total and (b) unreacted monomers in the UV-cured resist. The red spheres are unreacted monomers and the other colored spheres are reacted monomers. The $M_n$ of the resist is 4000.
3.3. De-molding process

Finally, we investigated the de-molding process by MD simulations. PMMA resists with the same molecular weights as those in the stochastic simulations were selected as samples to evaluate the de-molding properties of resists with different molecular weights. Although the molecular weights of the UV-cured resists have the distributions shown in Fig. 4, dispersion of the molecular weights of the PMMA resists was not considered in the MD simulations. All of the molecular weights of the PMMA molecules were fixed at the $M_n$ values obtained by the stochastic simulations. To reduce the computational load, the size of the resist was smaller than that in the stochastic simulations. The sizes of the edges were reduced to one fifth of those in Fig. 5(a).

Figure 7 shows snapshots of the PMMA resists after the de-molding process. When $M_n = 1500$, the resist pattern fractures during the de-molding process, as shown in Fig. 7(a). When $M_n = 4000$, the resist pattern slightly stretches during the de-molding process, as shown in Fig. 7(b). The pattern shape of the resist with $M_n = 10000$ relatively well reproduces the mold cavity shape. Although the strength of the UV-cured resist is different from that of the PMMA resist, the de-molding properties in UV-NIL are reasonably well predicted by the MD simulations.

Fig. 7. Snapshots of the resist structures after the de-molding process obtained by MD simulations. The molecular weights of the PMMA resists are (a) 1500, (b) 4000, and (c) 10000.

4. Conclusions

We have computationally investigated the pattern formation process in UV-NIL. The UV curing process was investigated by stochastic simulations. The simulations show the polymerization process of the UV-cured molecules. With increasing initiator concentration, the conversion ratio increases and saturates earlier. The $M_n$ of the UV-cured resist decreases with increasing initiator concentration. The sizes and shapes of the reacted monomers in UV-cured resists with different $M_n$ values were shown by the stochastic simulations.

The de-molding process was investigated by MD simulations. For a resist with relatively low $M_n$, fracture and stretching of the pattern is observed during the de-molding process.

In the present work, the UV-curing and de-molding processes were separately investigated with different simulation methods. A study of the whole process using the same computational approach is required for better understanding of the UV-NIL process.

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References

1. S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Appl. Phys. Lett.*, 67 (1995) 3114.
2. M. Colburn, S. Johnson, M. Stewart, S. Damle, T. Bailey, B. Choi, M. Wedlake, T. Michaelson, S. V. Sreenivasan, J. Ekerdt, and C. G. Willson, *Proc. SPIE*, 3676 (1999) 379.
3. F. Hua, Y. Sun, A. Gaur, M. A. Meitl, L. Bilhaut, L. Rotkina, J. Wang, P. Geil, M. Shim, and J. A. Rogers, *Nano. Lett.*, 4 (2004) 2467.
4. F. Hua, A. Gaur, Y. Sun, M. A. Word, N. Jin, I. Adesida, M. Shim, A. Shim, and J. A. Rogers, *IEEE Trans. Nanotechnol.*, 5 (2006) 301.
5. M. Koyama, M. Shirai, H. Kawata, Y. Hirai, and M. Yasuda, *Jpn. J. Appl. Phys.*, 56 (2017) 06GL03.
6. M. Koyama, M. Shirai, H. Kawata, Y. Hirai, and M. Yasuda, *J. Vac. Sci. Technol. B*, 35 (2017) 06G307.
7. A. Taga, M. Yasuda, H. Kawata, and Y. Hirai, *J. Vac. Sci. Technol. B*, 28 (2010) C6M68.
8. M. Yasuda, K. Araki, A. Taga, A. Horiba, H. Kawata, and Y. Hirai, *Microelectron. Eng.*, 88 (2011) 2188.
9. R. Takai, M. Yasuda, T. Tochino, H. Kawata, and Y. Hirai, *J. Vac. Sci. Technol. B*, 32 (2014) 06FG02.
10. O. Okada, K. Oka, S. Kuwajima, S. Toyoda, and K. Tanabe, *Comput. Theor. Polym. Sci.*, 10 (2000) 371.