Rapid thermal imprinting of high-aspect-ratio nanostructures with dynamic heating of mold surface

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High-aspect-ratio nanostructures are thermally imprinted with dynamic heating of the mold surface. A thin-film current heater located at the back of the mold realized rapid heating, and an upper punch and a heater substrate as coolants make the cooling time short. This heater is applied to stamping-type imprinting and injection molding. The authors demonstrated imprinting nanostructures with aspect ratios of 2–3 in the cycle time of 15 s. This equipment concept is practical for high-throughput and low-energy thermal nanoimprinting. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3517608]

I. INTRODUCTION

Since nanoimprint lithography was proposed,[1–5] technologies for replicating nanostructures onto a polymer surface have been increasingly developed. Thin resist of high-aspect-ratio nanostructures (HARNs) is important for deeply etching a substrate or films on substrates for advanced applications such as microelectromechanical or nanoelectromechanical devices. Nanostructured surfaces on bulk polymer have various potential applications including optical devices, optical memories, and bioanalysis templates.[6] Above all, bulk polymers with HARN surface have attracted much attention owing to their applications as antireflection structures.[7]

Thermal nanoimprinting is a simple replication method in which a nanostructured mold is pressed onto a thermoplastic film or substrate and then heated and cooled. Conventional thermal nanoimprinting has the following four main steps: (1) a mold and a polymer substrate are pressed together using upper and lower punches; (2) they are heated over the glass transition temperature (T_g) and a polymer is filled into the nanostructures of the mold; (3) they are cooled under T_g; and (4) the imprinted substrate is demolded from the mold. In this process, the cycle time is limited by the heat capacities of the upper and lower punches. However, all that is required for imprinting is that the surfaces of the mold and polymer substrate are heated and then cooled together. To date, the concept of local heating of the mold surface has been applied to nanomolding and nanoimprint lithography for high-throughput replication. Local heating by light[8] or Joule heating[9,10] requires low energy and has a high cooling rate.

In this study, we developed thermal imprinting processes involving the dynamic heating of the mold surface for the rapid replication of HARNs. The mold surface is locally heated to above T_g using a thin-film heater, then the polymer replica and mold surface are cooled by the upper and lower punches, which are kept below T_g. We demonstrated two main processes, namely, stamping-type imprinting [Fig. 1(a)] and injection-molding-type imprinting [Fig. 1(b)]. Note that the injection molding of HARNs requires heating the mold surface over T_g during injection because the skin layer is formed.[10]

II. EXPERIMENT

A. Experiment on stamping-type imprinting

The designed dynamic heating system and experimental details are described as follows. We fabricated the thin-film heater by sputtering Cr as a conducting layer (thickness of 500 nm) and SiO_2 as an insulating layer (thickness of 1 μm) on a polished AlN substrate (thickness of 2 mm and thermal conductivity of 160 W/m K). This heater was additionally covered with a polyimide sheet tape (thickness of 75 μm) for better insulation. A Ni-electroplated mold (thickness of 300 μm) or Si mold (thickness of 500 μm) is placed on this thin-film heater, and a polymethyl-methacrylate (PMMA) film of 100 μm thickness is placed on the face of the nanostructures. A thermocouple (ϕ50 μm) is inserted between the mold and the PMMA film to measure the temperature of the mold surface. A 1-mm-thick silicone sheet is placed on the backside of the PMMA film to prevent partial contact. These parts (thin-film heater/mold/thermocouple/PMMA film/silicone sheet) are pressed together by upper and lower punches (aluminum alloy A2017, JIS, thermal conductivity of 130 W/m K). The average pressure was 0.1 MPa. A current in the thin-film heater heated the mold and the PMMA film. Figure 2 shows simulation results of the temperature of the mold surface during rapid heating/cooling (heater power of 50 and 100 W/cm^2). The temperatures at which the heater is turned on and off were 20 and 120 °C, respectively. For rapid heating within several seconds, a high-power heater is needed. At the same time, heating at a higher power will result in reaching the imprinting temperature with a lower total energy and a shorter cooling time.

B. Experiment on injection-molding-type imprinting

We also demonstrated injection-molding-type imprinting of HARNs. The thin-film heater was fabricated by the same

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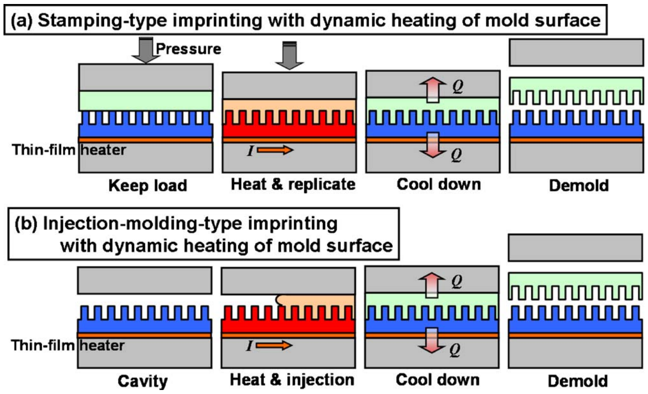

FIG. 1. (Color online) Schematics of rapid thermal imprinting by dynamic heating of mold surface: (a) stamping method and (b) injection molding method.

procedure as that used in the stamping-type imprinting. We used a Ni-electroplated stamper with an antireflection structure. The pitch and depth of the holes were 200 and 200–400 nm, respectively. The Ni stamper is fixed on a mold base (A7075, JIS, thermal conductivity of 130 W/m K). The cavity size, i.e., replica size, was $33 \times 38 \times 2\ \mathrm{mm}^3$. Polystyrene (PS) melted at 240 °C is injected from the nozzle immediately after the thin-film heater reaches its target temperature, and then the heater is turned off. The injected replica is cooled by both mold bases. We verified the replication degree when the peak temperature of the stamper reached 50, 85, and 125 °C. The profiles of the imprinted surface were determined by atomic force microscopy (AFM). We also measured the reflectivity of the imprinted surface using a spectrophotometer (CM-2600d, Konica Minolta Sensing, Inc.).

III. RESULTS AND DISCUSSION

A. Results of stamping-type imprinting

Figure 3 shows the result of the cyclic test of rapid heating/cooling of the thin-film heater. The PMMA film was not unloaded/loaded and was kept pressed during the test. The temperatures at which the thin-film heater was turned on and off were 75 and 130 °C, respectively. The heating time

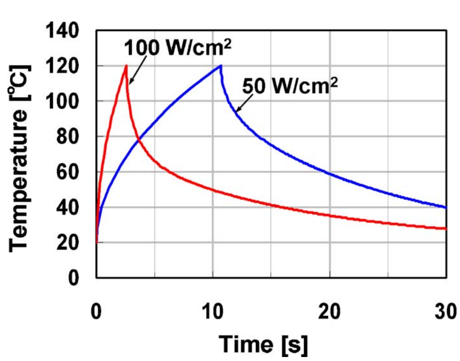

FIG. 2. (Color online) Finite element method simulation results of rapid heating and cooling.

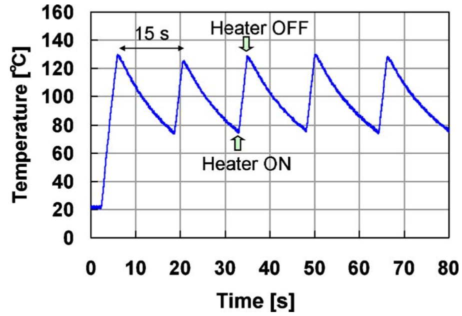

FIG. 3. (Color online) Result of cyclic test of heating/cooling. The heater is turned off when the mold surface temperature reaches 130 °C, and turned on when it reaches 75 °C.

from 75 to 130 °C was approximately 2–3 s and cooling time was 12–13 s. The profile showed high repeatability. Except for the load/unload (and demold) time of the PMMA film, the cycle time was 15 s. Figure 4 shows the cross-sectional scanning electron microscope (SEM) images of the molds and imprinted PMMA films. The Ni mold has trenches with width, pitch, and depth of 200–300, 1000, and 700 nm, respectively [Fig. 4(a)], and the Si mold has trenches with width, pitch, and depth of about 100, 300, and 600 nm, respectively [Fig. 4(c)]. The nanostructures obtained were well replicated [Fig. 4(b)]. These results indicate that the HARNs can be replicated with a heating time of 2–3 s and a cooling time of 12–13 s.

B. Results of injection-molding-type imprinting

Antireflection structures were imprinted by injection molding with dynamical heating of the mold surface. Figure 5 shows the AFM profiles of the (a) Ni mold used and imprinted at the peak temperatures of (b) 50, (c) 85, and (d) 125 °C. The moldability of the surface was best at 125 °C. Those obtained at 50 and 85 °C had poor moldability. The reflectivities of these films are shown in Fig. 6. For all wavelengths of 400–700 nm, the film imprinted at higher temperature had lower reflectivity. Although a flat surface had about 5% reflectivity, the surfaces imprinted at 50, 85, and 125 °C

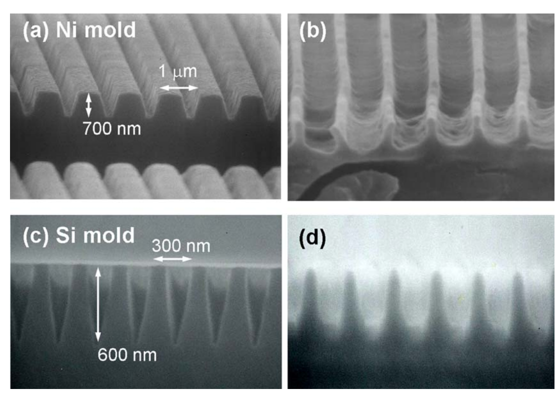

FIG. 4. (Color online) Cross-sectional SEM images of nanostructured mold and imprinted PMMA in stamping-type imprinting: (a) Ni mold, (b) imprinted PMMA using (a), (c) Si mold, and (d) imprinted PMMA using (c).

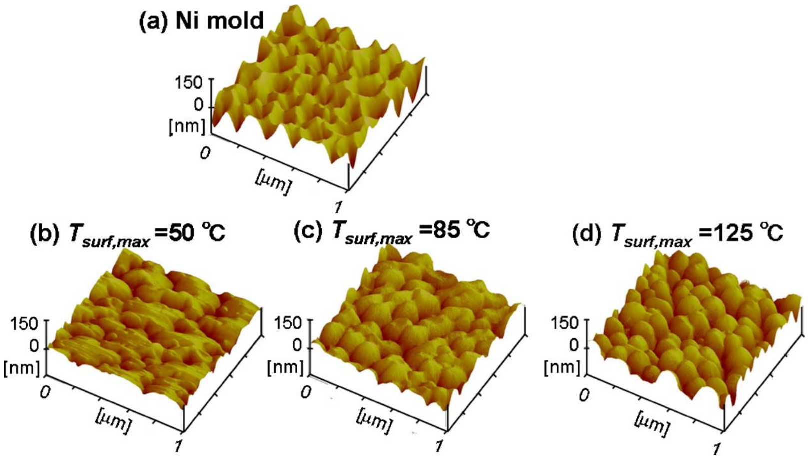

FIG. 5. (Color online) AFM profiles of (a) Ni mold and imprinted PS in injection molding, with the peak temperatures of the mold surface of (b) 50, (c) 85, and (d) 125 °C.

had about 4%, 2.5%, and 1% reflectivities, respectively. Here, the potential reflectivity was 1% (PS); this was determined with a PS sheet imprinted using a conventional thermal imprinting machine (VX-1000N-NN, SCIVAX Co., Ltd.). Therefore, the surface imprinted at 125 °C can be used to completely replicate the mold structure.

IV. CONCLUSIONS

We developed rapid thermal imprinting with a dynamic heating system. Local heating of the mold surface results in reaching the imprinting temperature in a short time; thus, the cooling time becomes short. We demonstrated stamping-type and injection-molding-type imprinting using current heating with a thin-film heater. Nanostructures with aspect ratios of 2–3 were successfully replicated in about 15 s using our setup. This concept will lead to high-throughput and low-energy thermal nanoimprint processes.

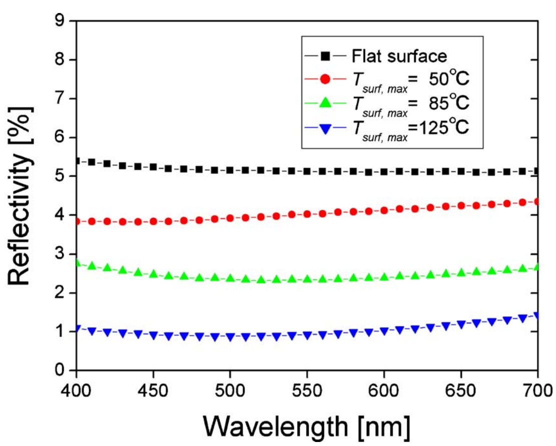

FIG. 6. (Color online) Reflectivities of flat PS surface imprinted at 50, 85, and 125 °C.

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[1] L. J. Guo, J. Phys. D **37**, R123 (2004).
[2] S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett. **67**, 3114 (1995).
[3] H. Schift, J. Vac. Sci. Technol. B **26**, 458 (2008).
[4] H. Schift, C. David, M. Gabrecht, L. J. Heyderman, W. Kaiser, S. Koppel, and L. Scandella, Microelectron. Eng. **53**, 171 (2000).
[5] Y.-C. Su, J. Shah, and L. Lin, J. Micromech. Microeng. **14**, 415 (2004).
[6] C.-J. Ting, N.-C. Huang, H.-Y. Tsai, C.-P. Chou, and C.-C. Fu, Nanotechnology **19**, 205301 (2008).
[7] K. Kuwabara, M. Ogino, T. Ando, and A. Miyauchi, Appl. Phys. Lett. **93**, 033904 (2008).
[8] S. Y. Chou, C. Keimel, and J. Gu, Nature (London) **417**, 835 (2002).
[9] M. Tormen, R. Malureanu, R. H. Pedersen, L. Lorenzen, K. H. Rasmussen, C. J. Lüscher, A. Kristensen, and O. Hansen, Microelectron. Eng. **85**, 1229 (2008).
[10] S. Hattori, K. Nagato, T. Hamaguchi, and M. Nakao, Microelectron. Eng. **87**, 1546 (2010).