Reversal imprinting by transferring polymer from mold to substrate

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A reversal imprinting technique was developed in this study. A polymer layer was first spin coated on a patterned hard mold, and then transferred to a substrate under an elevated temperature and pressure. The reversal imprinting method offers an advantage over conventional nanoimprinting by allowing imprinting onto substrates that cannot be easily spin coated, such as flexible polymer substrates. Another unique feature of reversal imprinting is that three different pattern-transfer modes can be achieved by controlling the degree of surface planarization of the mold after spin coating the polymer resist as well as the imprinting temperature. ''Embossing'' occurs at temperatures well above the glass transition temperature (T_g) of a polymer; ''inking'' occurs at temperatures around T_g with nonplanarized polymer coating surface on the mold; and ''whole-layer transfer'' occurs at temperatures around T_g but with a somewhat planarized surface. These three imprinting modes have been quantitatively correlated with the surface planarization of the mold after polymer coating and the imprinting temperature.
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I. INTRODUCTION

The demand to rapidly and economically fabricate nanoscale structures is a major driving force in the development of nanoscience and nanotechnology. Nanoimprint lithography (NIL), also known as hot embossing lithography, in which a thickness relief is created by deforming a polymer resist through embossing with a patterned hard mold, offers several decisive technical potentials, in particular as a low-cost method to define nanoscale patterns.[1] It has already been demonstrated that NIL is capable of patterning features in large areas and with a lateral resolution down to <6 nm.[2–5] In conventional NIL, a substrate needs to be spin coated with a polymer layer before it can be embossed with the hard mold. Borzenko *et al.* reported a bonding technique for nanolithography in which both substrate and mold were spin coated with polymers.[6] In the current study, we developed a reversal imprinting technique that avoids spin coating a polymer layer on the substrate. Instead, a polymer layer was spin coated onto the mold only, and transferred to a bare substrate by imprinting under suitable temperature and pressure. The reversal imprinting method offers a unique advantage over conventional NIL by allowing imprinting onto substrates that cannot be easily spin coated with a polymer film, such as flexible polymer substrates. Another interesting feature of this method is that three different pattern transfer modes can be achieved by controlling the degree of planarization of the spin-coated film on the mold and the imprinting temperatures. Furthermore, in two of these pattern transfer modes, reliable patterning can be achieved at temperatures and pressure well below those required by conventional NIL.

II. EXPERIMENT

Two kinds of patterned molds were used in our study. They were made in SiO_2 on Si wafer and patterned by optical lithography and subsequent dry etching. One mold has features varying from 2 to 50 μm in size and a nominal depth of 190 nm. The second type of mold is a uniform grating with a 700 nm period and a depth ranging from 180 to 650 nm. All molds were treated with a surfactant, 1H,1H,2H,2H-perfluorodecyl-trichlorosilane, to promote polymer release.[7] The substrates used were polished (100) Si wafers and flexible, 50 μm thick polyimide films (Kapton®). Poly(methyl methacrylate) (PMMA) with a molecular weight of 15 000 ($T_g = 105\,°C$) was used for imprinting. In a typical reversal imprinting experiment, a mold was spin coated with a toluene solution of PMMA at a spin rate of 3000 rpm for 30 s and then baked at 105 °C for 5 min to remove residual solvent. The coated mold was pressed against a substrate in a pre-heated hydraulic press under a pressure of 5 MPa for 5 min. The pressure was sustained until the temperature fell below 50 °C. Finally the mold and the substrate were demounted and separated. For compari-

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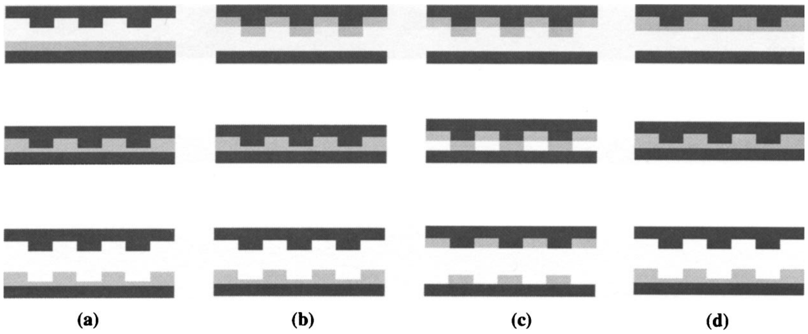


FIG. 1. Schematic illustrations of the pattern transfer processes in (a) conventional nanoimprinting, (b) reversal imprinting at temperatures well above T_g, (c) ''inking'' at temperatures around T_g with nonplanarized mold, and (d) ''whole-layer transfer'' around T_g with planarized mold.

son, conventional NIL, in which the polymer layer was coated on the Si substrate, was also performed under similar imprinting conditions.

III. RESULTS AND DISCUSSION

Since conventional NIL relies on viscous polymer flow to deform the polymer film and create the thickness contrast, high temperature and pressure are required.[8–10] To achieve reliable pattern transfer, imprinting is typically performed at temperatures between 70 and 90 °C above T_g and under pressures as high as 10 MPa.[8,9,11] Certain modifications to the conventional NIL technique such as the polymer bonding method developed by Borzenko *et al.*[6] reduce the temperature and pressure requirements considerably. However, the polymer bonding method suffers the additional disadvantage of leaving a thick residue layer after imprinting, which complicates the subsequent pattern transfer process.

In contrast, the reversal imprinting technique developed here can be used at significantly lower temperatures and pressures. Furthermore, depending on the degree of planarization of the polymer coated mold and the imprinting temperature, three distinct pattern transfer modes are observed. Successful and reliable pattern transfer can be achieved at temperatures as low as 30 °C below T_g and pressures as low as 1 MPa.

Figure 1 schematically illustrates the three reversal imprinting modes in comparison with the conventional NIL. In conventional NIL [Fig. 1(a)], the mold is pressed against a flat polymer film at a temperature well above T_g. During imprinting, considerable polymer flow occurs as the material deforms in accordance to the shape of the mold. At temperatures well above T_g, similar polymer flow can also occur in reversal imprinting. Even if the mold is not planarized as shown in Fig. 1(b), the material on the protruded areas on the mold can be squeezed into surrounding cavities during imprinting. Under such conditions, the behavior of reversal imprinting is very similar to that of conventional NIL. Since the underlining mechanism for imprinting in this situation is the viscous flow of the polymer, we term this imprinting mode ''embossing''.

A distinct advantage of reversal imprinting over conventional imprinting is that patterns can also be transferred to the substrate at temperatures around or even slightly below T_g. Within this temperature range, the imprinting result is strongly dependent on the degree of planarization of the mold after spin coating the polymer film. For molds with nonplanarized coating, only the film on the protruded areas of the mold will be transferred to the substrate as illustrated in Fig. 1(c). Since this process is similar to the stamping process with liquid ink, we term this imprinting mode ''inking''. Different from the embossing mode, in which a negative replica of the mold is produced on the substrate, inking results in a positive pattern instead.

On the other hand, if the coated mold is close to being planar after spin coating, the entire coated polymer layer can be transferred to the substrate without large scale lateral polymer flow during imprinting around T_g [Fig. 1(d)]. We call this imprinting mode ''whole-layer transfer''. Similar to the embossing mode, the entire layer transfer mode also results in a negative replica of the mold.

From the discussion above, it is clear that the degree of surface planarization and imprinting temperature are the two most important factors in determining the final imprinting result. In the sections below, we will discuss the quantitative correlation between imprinting conditions and final results.

A. Surface planarization after spin coating

In conventional NIL, a generally adopted method for promoting polymer release in separation is to treat molds with an antiadhesion agent. It is also necessary to modify the surface energy of the molds in reversal imprinting in order to promote transference of the polymer layer to the substrate. 1H,1H,2H,2H-perfluorodecyltrichlorosilane, a superb release coating in conventional imprinting,[12] was used as the release agent in our study. However, spin coating PMMA onto an antiadhesive treated mold was not straightforward. Because of the low surface energy of the treated mold, PMMA solution in polar solvents, such as chlorobenzene, will not form continuous films after spin coating. In contrast, PMMA solution in toluene can be successfully spin coated onto the surfactant treated molds. This might be ascribed to the low polarity and high volatility of toluene. Spin coating of toluene solution of PMMA onto a surfactant-treated surface yields film quality and thickness similar to those on an untreated surface.

Because of the topology on a typical mold, it is necessary to investigate the degree of planarization of the spin coated polymer layer. For molds with larger feature size, obtaining a planarized polymer coating is more difficult. Under usual conditions, spin coating the 190 nm deep mold with

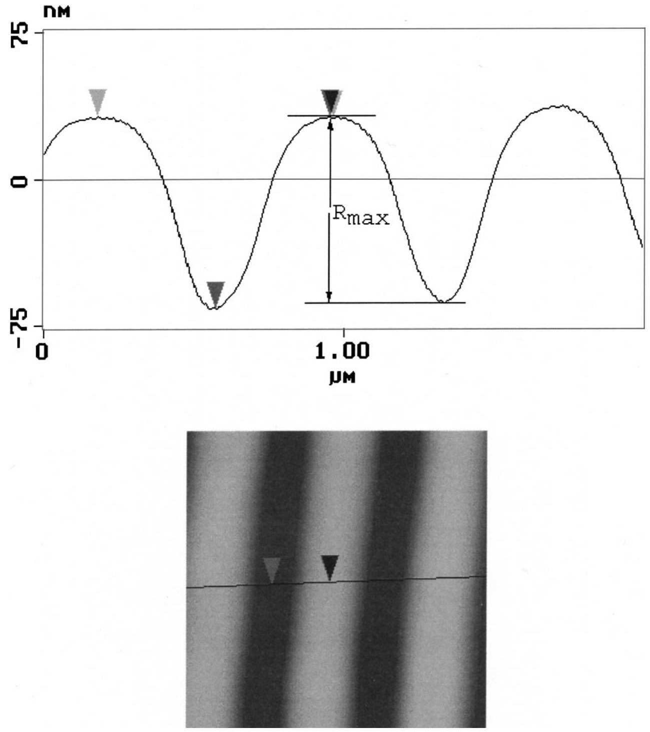


FIG. 2. AFM section analysis of a 300 nm deep grating mold coated with 6% PMMA solution at 3000 rpm.

micrometer-sized features results in the formation of a conformal coating on the mold. In the case of the submicrometer grating mold, the degree of planarization is a strong function of the concentration of the solution used for spin coating, which determines the thickness of the coated film. A typical atomic force microcopy (AFM) section analysis of the coated mold is shown in Fig. 2. After spin coating, the step height of the coated mold depends both on the mold depth and film thickness. As shown in Fig. 2, we characterize the degree of planarization by the average peak-to-valley height of the coated mold $R_{\max}$. Figure 3 summarizes the change in $R_{\max}$ as a function of solution concentration in grating molds with different depths. For a given feature depth, a higher solution concentration gives a thicker film and results in a lower $R_{\max}$ or higher degree of planarization.

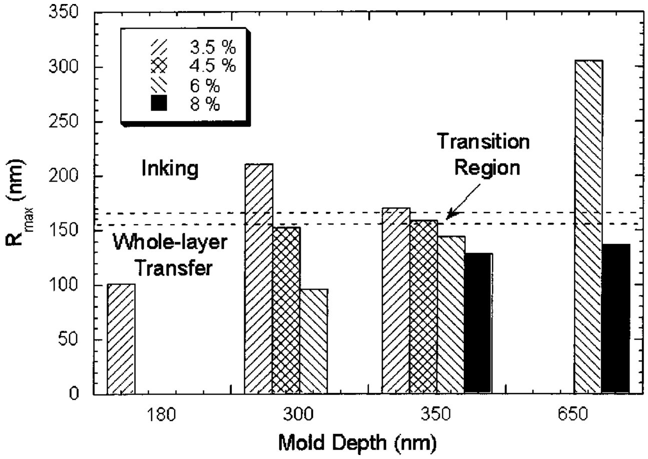


FIG. 3. Average peak-to-valley step height in grating molds with different depths after spin coating with different solutions at 3000 rpm. Regions of different pattern transfer modes at 105 °C and 5 MPa pressure are specified, with the dotted lines indicating the transition region between the two modes.

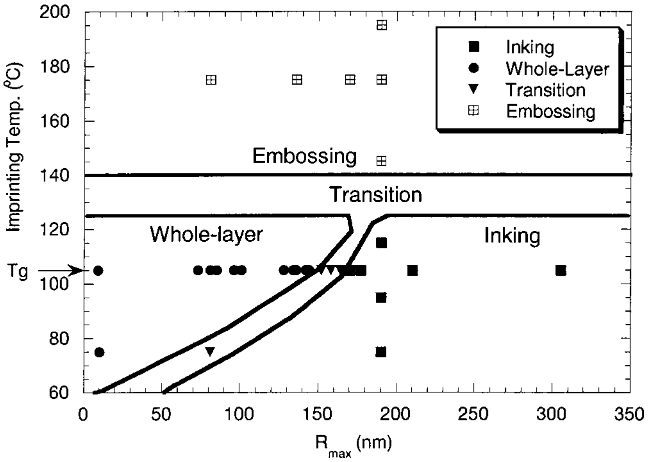


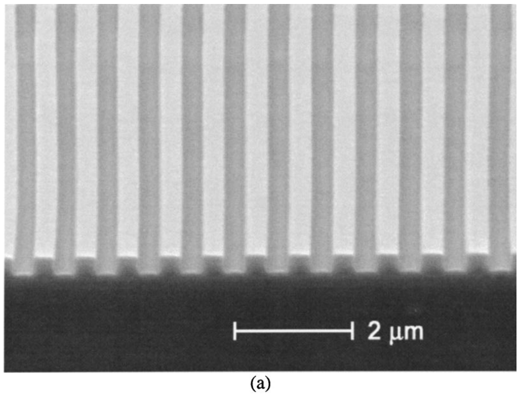
FIG. 4. Map of reversal imprinting modes as a function of imprinting temperature and $R_{\max}$ of the coated mold. The symbols are experimental data (5 MPa imprinting pressure) and the solid lines are extrapolated boundaries between different modes.

The different degrees of planarization in Fig. 3 have been correlated with the final imprinting result. At an imprinting temperature of 105 °C, when $R_{\max}$ is below ~155 nm, the whole-layer transfer mode occurs, while the inking mode occurs with $R_{\max}$ above ~168 nm. For $R_{\max}$ between 155 and 168 nm, a combination of these two modes may occur. The regions of different imprinting modes at 105 °C are indicated in Fig. 3.

B. Different modes of reversal imprinting

When the two most important imprinting parameters, i.e., degree of planarization and imprinting temperature are both considered, a map of the imprinting modes can be constructed as shown in Fig. 4. In Fig. 4, the symbols represent experimental data with different molds and different film thicknesses and the lines are estimated boundaries between imprint modes. The three main regions define the necessary conditions for the occurrence of each imprinting mode. In the transition region, combinations of two or more modes can occur. While conventional NIL requires temperatures well above T_g, reversal imprinting can be used in a wide temperature range. We have demonstrated inking and whole-layer transfer at temperatures as low as 75 °C, which is 30 °C lower than the T_g of PMMA.

Figure 4 indicates that at 105 °C, whole-layer transfer will occur when $R_{\max}$ is lower than about 155 nm. An example of such imprinted patterns is shown in Fig. 5(a). Faithful pattern transfer with few defects can be achieved. An important feature of the whole-layer transfer mode is the low residue thickness. The residue in Fig. 5(a) is less than 100 nm thick. When the solutions with the same concentrations are used, the residue thickness after reversal imprinting at a temperature around T_g is comparable to conventional NIL at a much



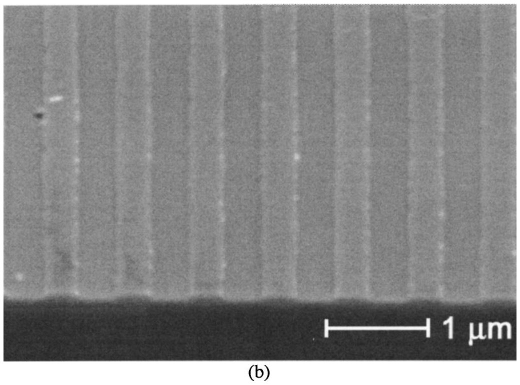


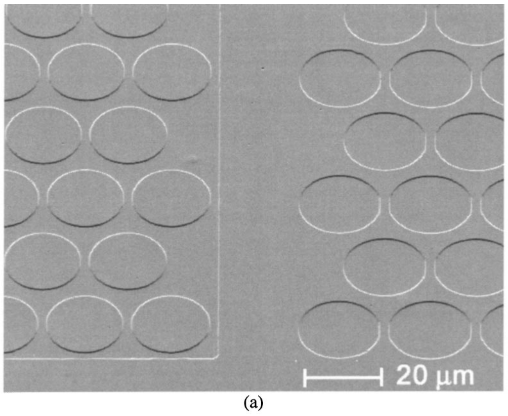
FIG. 5. Examples of PMMA imprints in different modes. (a) Imprint in the whole-layer transfer mode at 105 °C with a 350 nm deep grating mold, 7% coating, and $R_{max}=75$ nm. (b) Inking at 105 °C with a 650 nm deep grating mold, 6% coating, and $R_{max}=305$ nm.

higher temperature. Furthermore, reliable whole-layer transfer has also been achieved with a pressure as low as 1 MPa.

While the whole-layer transfer mode requires adequate surface planarization of the coated mold, larger step height after coating is advantageous to the inking mode. This is because when the step height is small, the film on the sidewalls of the features is usually relatively thick. When such a film is inked, the tearing of the polymer film near the sidewalls will result in ragged edges in the printed features. Figure 5(b) shows the inking result at 105 °C with a step height of 305 nm. Such a large step height is formed by coating a 650 nm deep grating mold with a relatively thin coating (6% solution). Under such conditions, the film on the sidewalls of the recessed features on the mold is extremely thin and will easily break during imprinting. As a result, reliable pattern transfer with relatively smooth edges can be obtained.

C. Reversal imprinting of PMMA onto a flexible substrate

In conventional NIL, a polymer film needs to be spin coated onto the substrate before it can be imprinted by a hard mold. However, spin coating is rather difficult on flexible substrates such as polymer membranes, which limits the capability of NIL in patterning such substrates. In the reversal imprinting process, since there is no need to spin coat a polymer layer onto the substrate, imprinting on a flexible substrate is quite straightforward. We have successfully employed this reversal nanoimprinting technique to transfer PMMA patterns onto a 50 μm thick polyimide film (Kapton®), which is widely used as substrates for flexible circuits. Figure 6 shows PMMA patterns created by reversal imprinting at 175 °C after spin coating the mold with micrometer-sized features and a 350 nm deep grating mold with a 7% solution. The imprints on the flexible substrate show high uniformity over the whole imprinted area (~600 mm^2) with few defects. The results shown in Fig. 6 are imprinted under the embossing mode at 175 °C. Inking and whole-layer transfer modes also occur on the flexible substrate and the imprinting results are similar to those obtained on Si substrate.



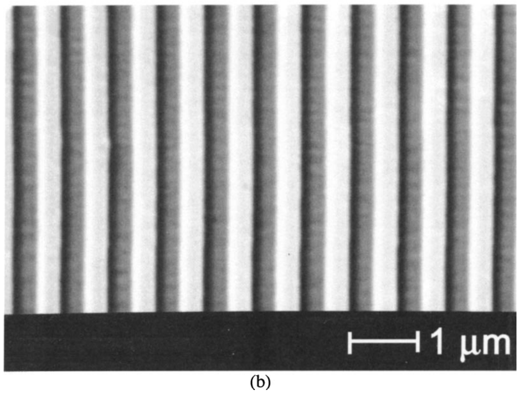


FIG. 6. Patterns in PMMA created by reversal imprinting at 175 °C on a 50 μm thick Kapton film: (a) 190 nm deep micrometer-sized mold coated with a 7% solution and (b) 350 nm deep grating mold coated with a 7% solution.

IV. SUMMARY

We have successfully demonstrated a reversal imprint process by transferring a spin-coated polymer layer from the hard mold to the substrate. Three different pattern transfer modes, i.e., embossing, inking, and whole-layer transfer, can be accomplished by controlling imprinting temperature and degree of surface planarization of the spin-coated mold. With a suitable degree of surface planarization, successful pattern transfer can be achieved at temperatures and pressures as low as 30 °C below T_g and 1 MPa, respectively, in the inking and whole-layer transfer modes. This is a significant advantage over the conventional NIL, which requires an imprinting temperature well above T_g and very high pressure. More-over, since little displacement of the polymer is required in these two pattern transfer modes, reversal imprinting is less sensitive to problems associated with polymer flow. This technique has also been successfully applied to create patterns on flexible substrates.

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