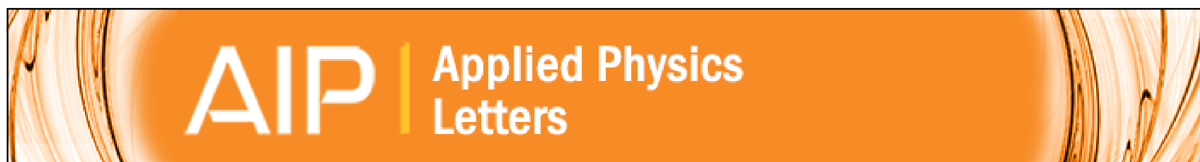

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Citation: Applied Physics Letters **90**, 191901 (2007); doi: 10.1063/1.2737364
View online: http://dx.doi.org/10.1063/1.2737364
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Soft-mold-induced self-construction of polymer patterns under microwave irradiation

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(Received 17 January 2007; accepted 12 April 2007; published online 7 May 2007)

In this study, the authors used a soft-mold-induced self-construction method to fabricate three-dimensional patterns under microwave irradiation for 1 min. The authors estimated the actual pattern growth temperature using a fluorescence probe technique. The temperature at which pattern growth originated was, by necessity, higher than the glass transition temperature of the novolak resist. Electrostatic forces and surface tension effects under the electromagnetic field contributed significantly to the pattern growth, and the use of an antisticking agent allowed easy demolding.
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The use of nontraditional lithography techniques, i.e., those using molds, for pattern generation has several advantages over the relatively more costly conventional photon and electron lithography methods. When the mold is a hard material, usually fabricated from silicon or fused silica substrates, the approach is known as "hard imprint lithography."[1,2] Imprint lithography requires tools that can offer either the high pressure[3] required for pattern definition or UV light[4] for curing of the monomer. When the mold is soft, e.g., when the mold material is an elastomer, the lithographic method is referred to as "soft lithography."[5] If the pattern on the soft mold is pressed forcefully into the polymeric material coated onto the substrate, the pattern dimensions achieved [Fig. 1(a)] are narrower than those of mold itself because of the compression effect of the elastomer upon the applied force.[6] Indeed, with soft mold imprint methods it is not easy to control the pattern dimensions because of the effects of elastic deformation. In comparison, soft-mold-induced self-construction (SMISC) [Fig. 1(b)] has several advantages: patterns having dimensions identical to those of the mold pattern, a reduced number of fabrication steps, the avoidance of using highly expensive exposure tools, and low cutting costs.[7–9]

The method used to form the self-construction pattern is complex; it relies upon the effects of the electric field gradient, surface tension, and/or dispersive interactions.[9–12] The prerequisite for the SMISC is to melt the polymer by raising the film's temperature above the glass transition temperature (T_g). The melting polymer is attracted upward, against the gravitational force and surface tension, to the mold surface. Several experimental and theoretical reports suggest[9,10] that the rigid mold-induced pattern first grows at the site of a local strong electric field. The most challenging aspect of the present self-construction method is the long processing time (from 10 min to several hours), in addition to the voltage applied at both electrodes. A decrease in the pattern growth time is desirable.

We present a rapid microwave-assisted SMISC patterning technique using a polymeric soft mold. A CEM MARS-5 microwave system[13] was used in this study, with the turntable inside the instrument rotated to randomize the direction of electromagnetic absorption. Prior to soft mold fabrication, we used a Canon I-line stepper and a LAM etcher to fabricate the silicon master with the following dimensions: 3 μm lines, 1.5 μm spaces, and 500 nm thickness. The master was then immersed into the antisticking agent solution according

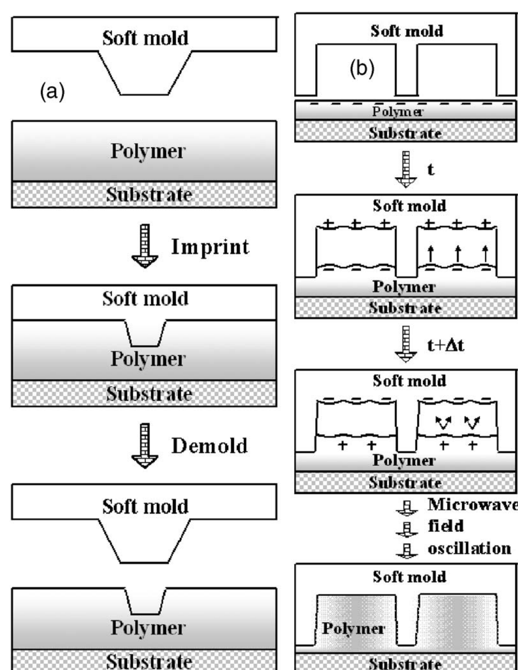

FIG. 1. Schematic illustration (not to scale) of (a) soft mold imprinting under a force field and (b) soft-mold-induced self-construction under a microwave field.

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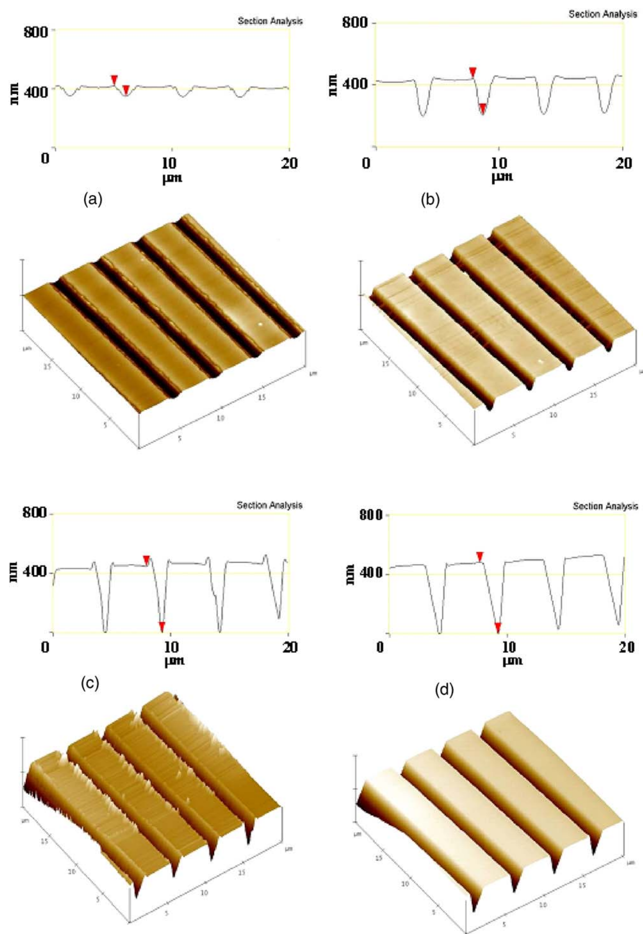

FIG. 2. Growth of polymer patterns through SMISC after microwave irradiation for (a) 20, (b) 40, (c) 60, and (d) 180 s.

to a procedure described previously.[2] The flexible soft mold was fabricated from the silicon master. The Sylgard 184 agent (Dow Corning) was mixed at a ratio of 10:1 (rubber base:cure) to form the polydimethylsiloxane (PDMS) solution. The solution was degassed within a vacuum chamber and then poured onto the silicon master and cured at 70 °C for 1 h to provide the PDMS mold. The polymeric photoresist (FH-6400L, Fujifilm Arch), which contained ~20% novolak polymer (average molecular weight: 5321 g/mol), ~60% ethyl lactate, ~15% ethyl-3-ethoxy propionate, and ~5% diazonaphthoquinone, was spin coated to a thickness of 500 nm onto the silicon substrate. Fluorescent rhodamine B was spiked at a concentration of $8\times10^{-4}M$ into the polymer solution prior to film formation. A previously described optical system[14] was used for fluorescence intensity measurements.

The morphologies of the SMISC patterns after various irradiation times are depicted in Fig. 2; they were recorded in the tapping mode (300 kHz) using a Veeco DI5000 atomic force microscope. The marked step heights were 67, 242, 471, and 489 nm for microwave irradiation times of 20, 40, 60, and 180 s, respectively; i.e., the dimensions of the polymer patterns increased gradually with respect to the irradiation times. None of the samples in Fig. 2 exhibited undulations in the surface morphology of its novolak polymer patterns. This result for patterning under microwave irradiation is quite different from the patterns obtained when using either a strong electric force or a temperature cycle induced by surface tension and electrostatic force. Schaffer *et al.*[10] observed surface undulations that were due to a film destabilization effect caused by the strong electric field. They claimed that the pattern could not be achieved in the absence of an applied electric field. Wu and Chou were able to grow a polymer pattern without applying an external electric field by taking advantage of the competition between the instability arising from the electrostatic force and the stabilization effect provided by the surface tension force.[9] In our case, dipole rotation from the residual solvent and diazonaphthoquinone in the photoresist film played an important role in providing rapid dielectric heating. At 2.45 GHz, the field oscillates 4.9×10^9 times/s. The electromagnetic wave quickly induces a temperature increase in the photoresist film, whereas the PDMS remains at a relatively lower temperature because of its low dissipation factor ($\tan\delta \ll 0.001$).[15] In addition, the electromagnetic field in the microwave oven oscillated in a random direction. This result implies that the external electric field on the SMISC sample may oscillate with time. Therefore, the dipole moment from charge separation on both the surfaces also varied with the field oscillation. The field oscillation [e.g., from t to $t+\Delta t$ in Fig. 1(b)] may allow the polymer molecule to relax during pattern growth, i.e., the polymer molecules become disentangled. If the electric field is unidirectional, as in the case of Schaffer *et al.*,[10] the annealing time for pattern growth must be very long (>10 h) because the force disentangles only those molecules that are aligned with the electric field. The advantage of the microwave-assisted SMISC approach is that it allows the polymer pattern to grow efficiently under a randomly distributed electric field.

The total surface energy[7,9] is another decisive parameter that affects pattern formation. Together with the Lifshitz-van der Waals (LW) and Lewis acid-base (AB) theories,[16] the detailed energy contributions from the polymeric polar and apolar terms can be extracted individually. Surface tension (γ_i) of a phase i can be expressed as $\gamma_i=\gamma_i^{\mathrm{LW}}+\gamma_i^{\mathrm{AB}}=\gamma_i^{\mathrm{LW}}+2\sqrt{\gamma_i^{+}\gamma_i^{-}}$, where γ_i^{LW} and γ_i^{AB} represent the dispersion (apolar) and polar terms of the surface tension, respectively, and γ_i^{+} and γ_i^{-} are the electron acceptor and electron donor parameters, respectively, in the polar part. The following contact angle equilibrium, based on the Young-Dupre equation, was formulated[16] by van Oss *et al.* to describe the interfacial tension between the liquid (L) and the polymer surface (S),

$$(1+\cos\theta)\gamma_L = 2\left(\sqrt{\gamma_S^{\mathrm{LW}}\gamma_L^{\mathrm{LW}}}+\sqrt{\gamma_S^{+}\gamma_L^{-}}+\sqrt{\gamma_S^{-}\gamma_L^{+}}\right),$$

where θ is the contact angle determined using three different liquids with known values of γ_L^{LW}, γ_L^{+}, and γ_L^{-}, e.g., water (21.8, 25.5, and 25.5 mJ/m^2, respectively), ethylene glycol (29, 1.92, and 47 mJ/m^2, respectively), and diiodomethane (50.8, 0, and 0 mJ/m^2, respectively).

For the novolak polymer film, the contact angles of water, ethylene glycol, and diiodomethane were 72.9°, 74.1°, and 31.9°, respectively, whereas they were 111.2°, 114.8°, and 96.7°, respectively, for the PDMS surface coated with the antisticking agent. Hence, the calculated values of the surface tensions γ_S^{LW}, γ_S^{+}, and γ_S^{-} for the novolak polymer film were 56.3, 43.4, 1.93, and 21.4 mJ/m^2, respectively. Similarly, the corresponding surface tensions for the PDMS surface coated with the antisticking agent were 14.1, 9.91, 0.69, and 6.36 mJ/m^2, respectively. The novolak polymer film has very much larger values for the Lifshitz-van der Waals (43.4 mJ/m^2) and Lewis electron donor (21.4 mJ/m^2)

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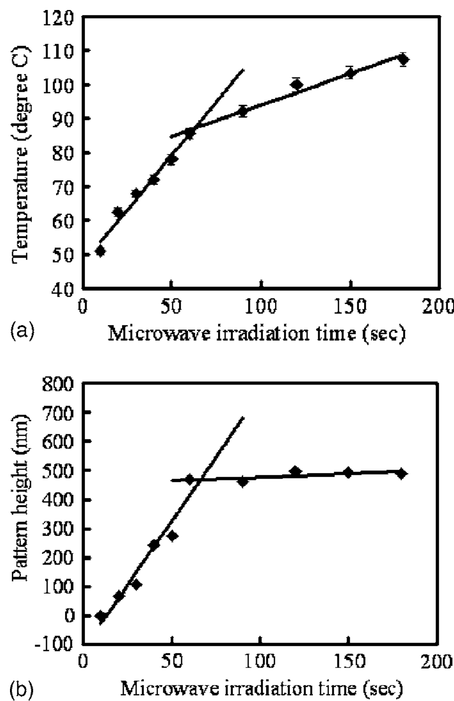

FIG. 3. Relationships between the microwave irradiation time and (a) the temperature of the polymer film and (b) the pattern height after SMISC.

terms than does the PDMS surface coated with the antisticking agent. During the SMISC process, the total surface energy of the PDMS surface coated with the antisticking agent is only one quarter that of the novolak polymer. Thus, thermodynamically, a driving force arises to minimize the surface tension of the novolak polymer by adsorption onto the surface of the PDMS mold. In addition to the electrostatic attraction, the surface tension—mainly from the Lifshitz-van der Waals interaction—also contributes to the pattern formation.

Figure 3(a) depicts a plot of the temperature of the polymer film with respect to the microwave irradiation time. The temperature increased linearly with the time (slope: 0.638 °C/s) during the first stage (10–60 s) of microwave irradiation. The heating rate decreased, however, to 0.184 °C/s during the latter stage (60–180 s). We attribute this behavior to the intrinsic property of the dissipation factor for the novolak resist. The efficiency of microwave absorption during the first stage (10–60 s) was approximately 3.5-fold higher than that during the latter stage (60–180 s). This phenomenon is related to the solvent effect: the coexisting solvent in the film evaporated rapidly at higher temperatures and, therefore, the polymer film's dissipation factor reduced accordingly. The film's solvent had evaporated totally after approximately 60 s of microwave irradiation.

Figure 3(b) displays a plot of the pattern height obtained through SMISC as a function of the microwave irradiation time. The pattern height increased gradually with linearity (at a rate of 8.89 nm/s) with respect to the irradiation time during first stage (10–60 s), but leveled off during the latter stage (60–180 s) as a result of the pattern reaching its physical limits. We note that no pattern formed after irradiation for 10 s because the film's temperature was only 51 °C, whereas a 20 s irradiation (equivalent to 62.5 °C) produced a 67 nm polymer pattern through the synergetic effects of the electrostatic and surface tension forces. This temperature after 10 s of microwave irradiation was lower than the T_g of the novolak resist (i.e., 60.5 °C); thus, it could not induce pattern formation. The great advantage of microwave irradiation is that a 471-nm-high pattern can be grown after irradiation for only 60 s, which is a significantly shorter time than those reported previously.[7–10] The step height of the pattern gradually closed in on the mold depth upon increasing the irradiation time from 60 (471 nm) to 180 s (489 nm). This result suggests that most of the surroundings of the novolak pattern surface after 60 s were stabilized by the PDMS surface, greatly reducing the surface tension forces for the growing pattern. Once pattern growth had concluded, demolding of the polymer pattern from the flexible PDMS mold was favorable because of the low surface tension of the PDMS mold modified with the antisticking agent.

In summary, we have developed a rapid (1 min) technique for soft-mold-induced pattern growth under a microwave field. Both electrostatic forces and surface tension effects contribute to the origin of pattern growth. The low surface tension of the mold surface, which had been modified with an immobilized antisticking agent, facilitated the demolding process.

This study was supported financially by the National Science Council, Taiwan, through Contracts Nos. NSC 95-2120-M-009-003 and NSC 95-2113-M-009-032-MY3.

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