

Polybenzoxazine as a Mold-Release Agent for Nanoimprint Lithography

Chih-Feng Wang,[†] Shih-Feng Chiou,[‡] Fu-Hsiang Ko,[§] Jem-Kun Chen,^{||} Cheng-Tung Chou,[‡]
Chih-Feng Huang,^{||} Shiao-Wei Kuo,^{||} and Feng-Chih Chang^{*,||}

Department of Materials Science and Engineering, I-Shou University, 84008 Kaohsiung, Taiwan,
Department of Chemical & Materials Engineering, National Central University, 32001 Taoyuan, Taiwan,
and Institutes of Nanotechnology and Applied Chemistry, National Chiao-Tung University,
30050 Hsinchu, Taiwan

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One of the most important tasks remaining to be resolved in nanoimprint lithography is the elimination of the resist sticking to the mold during demolding. Previously, the main approach was to apply a thin layer of fluorinated alkyl silane mold-release agent on the surface of the mold; however, this involves complicated steps and high costs. The low surface free energy material polybenzoxazine provides an efficient mold-release agent for silicon molds that is easier to process, costs less, and has no side reactions.

Introduction

Polybenzoxazine is a recently discovered class of low surface free energy materials that possess neither fluorine nor silicone.¹ The surface free energy of polybenzoxazine is 16.4 mJ/m², which is lower than that of pure poly(tetrafluoroethylene) (PTFE) by 21 mJ/m².² PTFE is an important material in bioscience and medical applications because of its special biocompatible, nonflammable, antistick, and heat-resistance characteristics. The low intermolecular forces present in fluorinated polymers have been recognized to account for the relatively low surface free energy. Because of their wide availability, PTFE-based materials comprise the most convenient approach to reduce the problem of adhesion between surfaces.³

Nanoimprint lithography (NIL), a high volume and cost-effective patterning technique, is a potential candidate for next-generation lithography.^{4,5} In NIL, a mold with a protruding/recessed surface pattern is pressed onto a preheated thin resist film coating on the substrate. Through compression and demolding (detachment of the mold), the “negative” of the mold pattern is imprinted onto the polymer layer. Compared to other previously developed lithography tools with nanoscale resolution, such as electron beam lithography and extreme ultraviolet lithography, the advantage of NIL is its ability to pattern structures from micrometer to nanometer scales at low cost. Its potential applications have been demonstrated in optics,^{6,7} nanoelectronics,⁸ biodevices,⁹ and high-density storage devices.¹⁰

Essentially all imprint techniques involve contact between the mold and the resist polymer, and the adhesion characteristic between polymer materials and the mold is a critical factor in

the process. One of the most important problems that is usually encountered with NIL is the tendency for the resist polymer to adhere to the mold surface during the demolding process. Sticking effects will reduce the lifetime of molds, downgrade the quality of the replication, and complicate the processing procedure. One approach to reduce the resist polymer adhesion is to apply a self-assembled monolayer (SAM) of a fluorinated alkyl silane release agent onto the surface of the mold by immersing the mold in a solution containing the release agent.¹¹ Jung et al.¹² found that the solution-based process for developing the SAM antisticking layer on the mold does not perform well for molds with sub-100-nm pitch with high aspect ratios. However, the silane coupling agent tends to polymerize in solution, and the oligomeric precursor can also react with the silanol and covalently attach to the mold surface, leading to a highly nonuniform film.^{13,14} In this letter, one method of applying the polybenzoxazine as a release agent onto the mold was evaluated by means of surface characterization and nanoimprinting technologies.

Experimental Section

2,2-Bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazine) propane (BA-m benzoxazine) was supplied by Shikoku Corp. Monomer stock solutions were prepared by dissolving BA-m benzoxazine in tetrahydrofuran at various concentrations. The solution was filtered through a 0.2 μm syringe filter before spin coating onto a 6 in. Si wafer. The selected monomer solution (5 mL) was applied to the Si mold covering the whole surface, which was followed by immediate spinning at 1500 rpm for 45 s. The sample was left to dry at 60 °C for 1 h and then cured on a digital hot plate for another 1 h at 200 °C. The chemical structures of the BA-m benzoxazine monomer and BA-m polybenzoxazine are shown in Scheme 1.

The advancing contact angle of the polymer surface was measured at 25 °C using a Krüss GH-100 goniometer interfaced with image-

* To whom all correspondence should be addressed. E-mail: changfc@mail.nctu.edu.tw. Tel/Fax: +886-3-5131512.

[†] I-Shou University.

[‡] National Central University.

[§] Institute of Nanotechnology, National Chiao-Tung University.

^{||} Institute of Applied Chemistry, National Chiao-Tung University.

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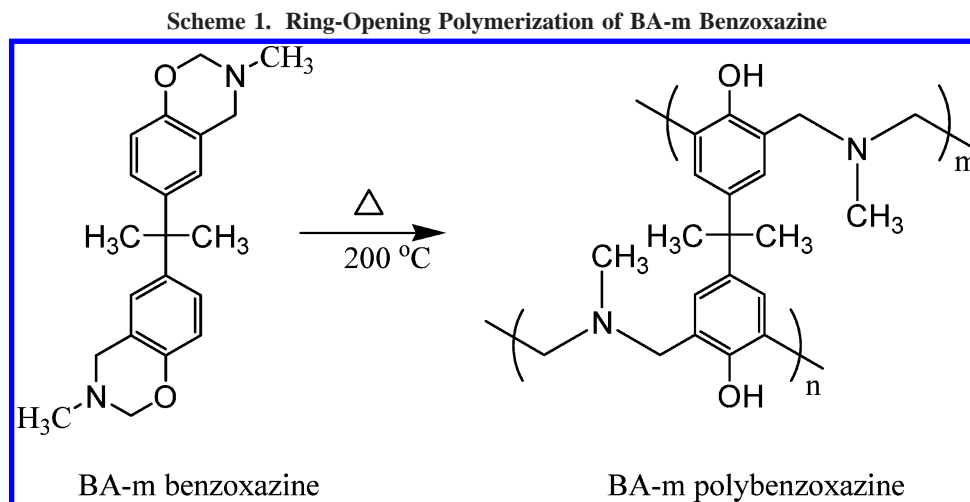


Table 1. Glass-Transition Temperature (T_g) and Advancing Contact Angles for Water,^a Ethylene Glycol (EG),^b and Diiodomethane (DIM)^c on BA-m Polybenzoxazine Film Structures^d

thickness (nm)	T_g (°C)	contact angle (deg)			surface free energy (mJ/m ²)		
		H ₂ O	EG	DIM	γ_s^{LW}	γ_s^{AB}	γ_s
449.3	179	112.1	91.7	81.7	16.6	0.1	16.7
79.3	180	111.7	91.6	81.3	16.8	0.0	16.9
13.5	174	112.8	93.1	82.0	16.5	0.0	16.5
11.8	176	112.3	93.0	82.3	16.3	0.0	16.3
8.8	178	113.1	92.8	82.8	16.1	0.1	16.2
6.3	176	112.7	93.3	82.5	16.2	0.0	16.2

^a $\gamma_L = 72.8$, $\gamma_L^{LW} = 21.8$, $\gamma_L^+ = 25.5$, and $\gamma_s^- = 25.5$. ^b $\gamma_L = 48$, $\gamma_L^{LW} = 29$, $\gamma_L^+ = 1.92$, and $\gamma_s^- = 47$. ^c $\gamma_L = 50.8$, $\gamma_L^{LW} = 50.8$, $\gamma_L^+ = 0$, and $\gamma_s^- = 0$. ^d The corresponding surface free energies (γ_s) are also given.

capture software by injecting a 5 μ L liquid drop. Deionized water, ethylene glycol ($\geq 99\%$, Aldrich), and diiodomethane (99%, Aldrich) were used as standards to measure the surface free energies.

The thickness measurement of the polybenzoxazine films was performed using a Sopra SE-5 ellipsometer. The radius of curvature and the stress variation of the polybenzoxazine thin film coated on the Si wafer during a heating procedure were measured by a stress measurement instrument (Tencor, FLX-2320). The heating rate was held at 3 °C/min under the ambient air atmosphere. The wafer was not clamped onto the heating chuck in order to allow for free curvature motion.

The resist polymer purchased from Sumitomo Chemical Company (NEB22) was used for nanoimprinting. Imprinting experiments were carried out on molds with and without polybenzoxazine surface treatment using an imprint tool developed by Nanonex (model NX-1000). The mold consists of 25 reticles with each reticle measuring 0.8×1.0 cm² in footprint on a 6 in. wafer. Each mold includes four kinds of lines (line width from 145 to 640 nm) or four kinds of cylinders (diameter from 140 to 615 nm). The pattern height is 300 nm for lines, and the pattern height for cylinders is 240 nm. The resist and mold were contacted at a preprint pressure of 200 psi at 110 °C, and an imprint force of 380 psi was then used to press the mold into a 400-nm-thick resist over a period of 5 min at 130 °C.

The microstructures of the polymer surface and the mold were characterized using a Hitachi S-6280H scanning electron microscope (SEM). Atomic force microscopy (AFM) data were acquired using a MultiMode scanning probe microscope from Digital Instruments. Damage to both the tip and the sample surface were minimized by employing the AFM in tapping mode.

Results and Discussion

A bifunctional benzoxazine monomer, 2,2-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazine) propane (abbreviated as BA-m), was employed as the target monomer in this study. The BA-m benzoxazine monomer possesses excellent characteristics for film formation upon spin coating on a silicon wafer. After spin coating, cross linking of the benzoxazine film was performed by placing it on a digital hot plate for 1 h at 200 °C. Table 1 lists the surface and thermal properties of polybenzoxazine thin films with different thicknesses.

Although the surface free energy of a solid can be used as a guide or indicator of its relative adhesive properties, it is difficult to measure the surface free energy of a solid directly. For practical reasons, procedures based on contact angle measurements are commonly employed.^{15,16} The advancing contact angle is relatively less sensitive to surface roughness and heterogeneity than is the receding angle. Therefore, the advancing angle data are commonly used to calculate the components of surface and interfacial energy.¹⁷

The water advancing contact angles vary insignificantly upon decreasing the thickness of the polybenzoxazine films as shown in Table 1. Similar trends are also found for the advancing contact angle of both diiodomethane and ethylene glycol on the polybenzoxazine surface. The surface free energy was evaluated using van Oss and Good's three-liquid acid–base method.¹⁸ According to this approach (refer to eq 1), the surface free energy of a solid, γ_s , can be calculated from a combination of three factors:

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (1)$$

where γ_s^{LW} is the Lifshitz/van der Waals component, γ_s^{AB} is the acid–base component, γ_s^+ is the Lewis acid component, and γ_s^- is the Lewis base component. Values of γ_s^{LW} , γ_s^+ , and γ_s^- can be calculated from eq 2 after measuring the liquid–solid contact angles (θ) of these three characterizing liquids.

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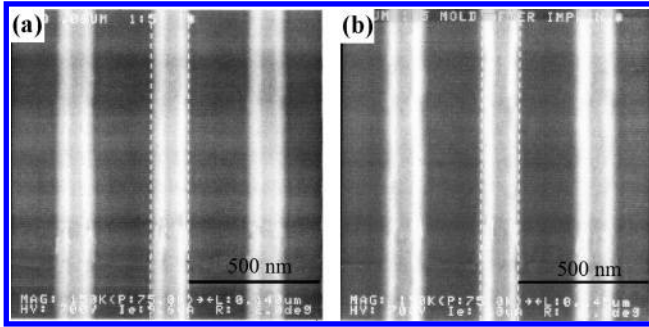


Figure 1. SEM images of polybenzoxazine-untreated (a) and -treated (b) molds with a line width of 145 nm.

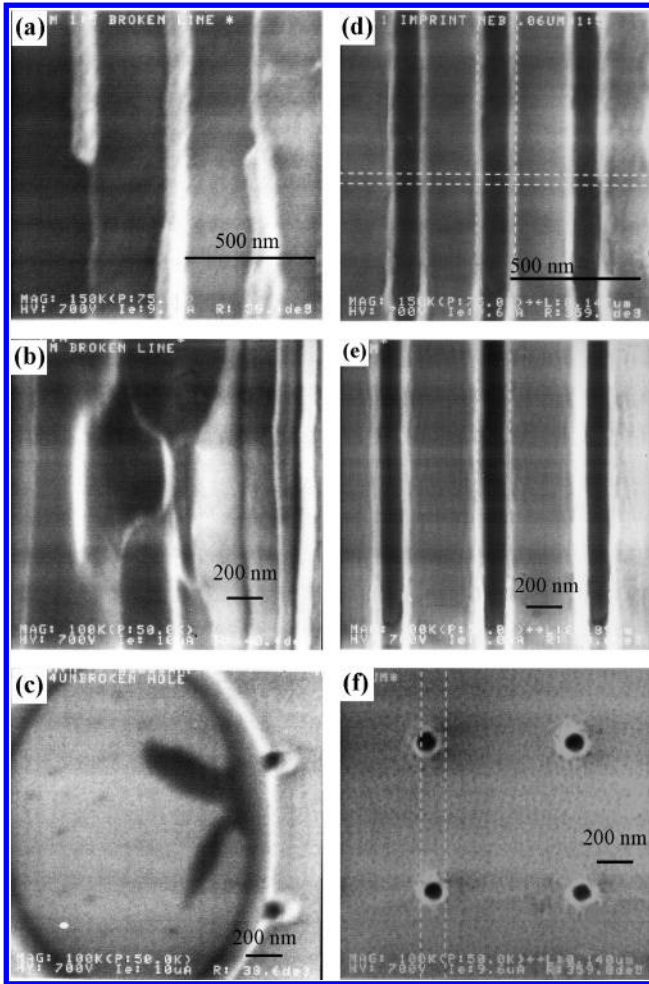


Figure 2. SEM images of trenches and holes transferred by imprinting with lines and cylinders using molds in the absence of polybenzoxazine films (a–c) and in the presence of polybenzoxazine films (d–f). (a, d) Line width 147 nm; (b, e) line width 189 nm; (c, f) diameter 140 nm.

$$\begin{aligned} \gamma_{L1}(1 + \cos \theta_1) &= 2(\sqrt{\gamma_S^{LW} \gamma_{L1}^{LW}} + \sqrt{\gamma_S^+ \gamma_{L1}^-} + \sqrt{\gamma_S^- \gamma_{L1}^+}) \\ \gamma_{L2}(1 + \cos \theta_2) &= 2(\sqrt{\gamma_S^{LW} \gamma_{L2}^{LW}} + \sqrt{\gamma_S^+ \gamma_{L2}^-} + \sqrt{\gamma_S^- \gamma_{L2}^+}) \quad (2) \\ \gamma_{L3}(1 + \cos \theta_3) &= 2(\sqrt{\gamma_S^{LW} \gamma_{L3}^{LW}} + \sqrt{\gamma_S^+ \gamma_{L3}^-} + \sqrt{\gamma_S^- \gamma_{L3}^+}) \end{aligned}$$

In eq 2, γ_L is the surface tension of the liquid, and subscripts S and L refer to solid and liquid, respectively. Diiodomethane was selected as the apolar liquid, and water and ethylene glycol were selected as the polar liquid pair. The calculated surface free energies of polybenzoxazine thin films follow similar trends to

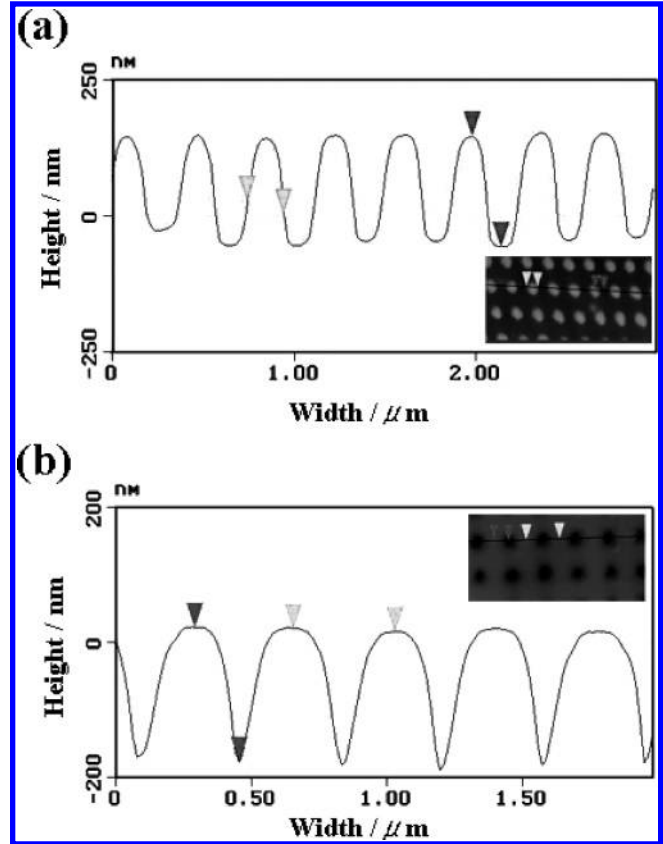


Figure 3. AFM images of (a) the polybenzoxazine-treated mold (cylinders) after imprinting 13 times. (b) Resist pattern (holes) on the substrate after imprinting with polybenzoxazine-treated molds.

those observed for the advancing contact angles. The observed surface free energy of the polybenzoxazine film is fairly independent of its film thickness (surface free energy of 17 mJ/m² at a thickness of 449.3 nm, surface free energy of 16 mJ/m² at a thickness of 6.3 nm).

The glass-transition temperature (T_g) of the polybenzoxazine thin film was estimated by the wafer-curvature measurement that is usually performed with a stress measurement instrument to measure the radius of curvature and the stress variation of the polymer thin film coated on the substrate during a heating procedure.¹⁹ Upon heating under controlled conditions, the induced stress starts relaxing when the temperature of the polymer/wafer stack reaches the T_g region of the polymer material. Thus, the T_g of polymer materials can be determined by the wafer-curvature measurement technique. The observed T_g of the film is nearly constant even when the film thickness is only 6.3 nm. The polybenzoxazine thin film is suitable for the antisticking application of hot embossing nanoimprint lithography because of its high glass-transition temperature. Results from the surface free energies and the glass-transition temperatures clearly indicate that the polybenzoxazine ultrathin film (6.3 nm) possessed a low surface free energy (about 16 mJ/m²) and a high T_g (about 176 °C) that are similar to those of thick films.

The use of polybenzoxazine as a spin-coatable release agent for silicon molds is reported in this study. A 1 mg/mL solution of benzoxazine monomer dissolved in tetrahydrofuran was applied to the Si mold covering the whole surface, which was followed by immediate spinning. The sample was left to dry at 60 °C for 1 h and then cured as above. The resultant film thickness achieved was 5.7 nm as measured by an ellipsometer. The scanning electron

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microscopy (SEM) images of the untreated (Figure 1a) and the polybenzoxazine-treated (Figure 1b) molds do not show any significant difference. NIL was performed using an imprint tool developed by Nanonex (model NX-1000) using untreated and polybenzoxazine-treated Si molds. Figure 2 displays SEM images of the trenches and holes that were transferred by imprinting with lines (line widths of 147 and 189 nm) and cylinders (diameter of 140 nm). Figure 2a–c shows SEM images of NIL using the untreated mold. Severe damage to these trenches and holes is found and is attributable to the sticking problem during the process of mold separation. In addition, a small quality of the resist may stick to the mold surface during the process of mold separation. Without proper mold surface treatment, the lithography process would fail, and the mold has to undergo a complete cleaning process to remove the residual resist for the next imprint step. The defect caused by the adhesion of the resist disappears after precoating the mold with the polybenzoxazine thin film (Figure 2d–f). Figure 3a shows the atomic force microscopy (AFM) image of the polybenzoxazine-treated mold (cylinders) after imprinting. The polybenzoxazine-treated mold was clean after imprinting 13 times. Figure 3b is the AFM image of the resist pattern on the substrate imprinted with polybenzoxazine-treated molds, showing that the patterns are nearly identical to the original

structure of the mold. This low surface free energy material polybenzoxazine has been demonstrated to be applicable to NIL antisticking applications.

Conclusions

Polybenzoxazine has recently been discovered to be a low surface free energy polymer material since the discovery of well-known fluoropolymers and silicones. The ultrathin film of this polybenzoxazine still possesses a lower surface free energy and a higher glass-transition temperature than its thicker film. The pattern transfers of various diagrams using the polybenzoxazine-treated mold resulted in reproducible performance without any resist adhering to the surface of the mold. Polybenzoxazine not only possesses low surface free energy but also performs well in the antisticking application of NIL. In addition, polybenzoxazine has a low cost, is easy to process, and creates no side reactions during mold modification.

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