Nanoimprint lithography of deoxyribonucleic acid biopolymer films

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Abstract. Thermal nanoimprint lithography (NIL) is presented as an alternative fabrication technique for patterning deoxyribonucleic acid (DNA) biopolymer films for photonic device applications. The techniques and procedures developed for directly imprinting optical waveguide structures on a DNA biopolymer using NIL, bypassing the use of a resist layer and any chemical processing, are outlined here. The fabrication technique was developed with a Nanonex NX-2600 NIL flexible membrane system. Additionally, a process for using a Suss MicroTec ELAN CB6L substrate bonder is discussed as an alternative to commercially available NIL systems. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: 10.1117/1.JMM.12.4.040501] \\

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The DNA used in this study was derived from salmon and precipitated with a surfactant, hexadecyltrimethylammonium chloride (CTMA), to form the water-insoluble biopolymer, DNA-CTMA. Details of the DNA-CTMA processing technique can be found in prior publications. The DNA biopolymer is dissolved at 14 wt% in butanol, spin coated on gold-coated Si substrates, and cured in vacuum at 80°C to produce ∼2-μm-thick films. The evaporated gold film on the Si substrate serves the dual purpose of an adhesion coating and a bottom electrode for the EO modulator. The edge bead on the DNA-CTMA, an artifact from spin coating, was removed with a razor blade to provide a level surface for NIL.

NIL stamps have been developed using various materials, including silicon, glass, SU-8, and polymers. Electron-beam writing is often used for stamps with submicron scale features and photolithography is used for larger-scale features. For this study, the minimum feature sizes were large enough that photolithography was used to fabricate the stamp. Three stamp materials (plasma etched Si, plasma etched SiO\textsubscript{2} on a Si substrate, and the negative UV curable resist MicroChem SU-8 2015 on a Si substrate) were initially compared for compatibility with the DNA biopolymer. However, because SU-8 2015 was found to aggressively stick to the DNA biopolymer, it was not pursued as a stamp material. All stamps were 3 in. wafers, and were used in conjunction with film samples on 3 in. substrates.

Three release coatings were investigated for use on the Si and SiO\textsubscript{2} stamps: perfluorodecyltrichlorosilane (FDTS), chlorinated organopolysiloxane Sigma-Aldrich (St. Louis, Missouri) Sigmacote, and the chlorosilane Nanonex (Monmouth Jct., New Jersey) NXT-130 mold release agent. For the FDTS coating, 1 g of FDTS was diluted in 75 mL of n-heptane, the stamp was submerged for 4 min, rinsed in a bath of n-heptane for 20 s, rinsed in a fresh bath of n-heptane for 5 min, then dried on a hotplate at 130°C for 10 min. For Sigmacote, a pipette was used to fully cover the surface of the stamp, it was rinsed with deionized water after 2 s, then baked in a vacuum at 130°C for 1 h.

The Nanonex NXT-130 was applied by vapor coating with the Nanonex Ultra-100 Molecular Vapor Coater for 25 min at 90°C. All of the release coatings performed equally well;
Fig. 1 (a) Schematic of the nanoimprint lithography (NIL) process showing the deoxyribonucleic acid (DNA) biopolymer film pre- and postimprint (b) the electro-optic (EO) modulator waveguide device structure with a DNA biopolymer cladding on either side of the EO active core polymer.

however, due to the ease of application, Sigmacote is the preferred release coating.

The Nanonex NX-2600 NIL system was used in this work and its performance is compared with a Suss MicroTec (Garching, Germany) ELAN CB6L substrate bonder. Although the Suss bonder is not an NIL system, it performs similarly by applying high pressures and temperatures through parallel plates. The NIL process for both systems involves four steps: (1) the chamber pump-down (NIL performed under vacuum), (2) preimprint step (temperature raised to the glass transition temperature $T_g$ of material to be imprinted and pressure gradually increased), (3) imprint step (imprint pressure and temperature applied for set time), and (4) cool down/chamber vent (imprint pressure maintained until sample is cooled) (Fig. 2). The stamp and sample are then separated manually, assisted by wedging a thin blade between the wafers and blowing compressed air between the wafers. A temperature $\geq T_g$ of the polymer material is used as the NIL imprint step temperature. The $T_g$ of the DNA biopolymer was measured to be 90 to 110°C for a 1-μm-thick film by shear force modulation spectroscopy. The DNA biopolymer is thermally stable to 200°C. An imprint temperature, $\geq 120°C$ and $\leq 200°C$, was necessary for 1:1 pattern transfer. Since DNA-CTMA is a highly viscous polymer, the maximum pressure setting of 500 psi for the Nanonex tool was used. Pressures less than 500 psi resulted in partial pattern transfer from the stamp to the polymer film characterized by soft edges and reduced feature depth. The imprint step time was 3 to 5 min to allow the DNA biopolymer adequate time to flow into all parts of the stamp, creating a 1:1 pattern transfer.

A summary of the NIL results are shown in Table 1. Although NIL patterned surfaces are often characterized by cross-sectional scanning electron microscope (SEM) images, profile scans, and atomic force microscope (AFM) surface scans, this was not possible with the DNA biopolymer since the film tends to tear at the cleaved edge and obscures the cross-sectional view. Therefore, a qualitative classification method of “excellent,” “good,” or “poor” was used to describe the imprinted NIL pattern. Excellent indicates a 1:1 pattern transfer with straight sidewalls, minimal roughness, and fully developed corners; this was achieved with the Nanonex system using a NIL recipe of 120°C at 500 psi for 3 min with a release coated SiO$_2$ stamp. Scattering loss for surface roughness $<100$ nm is expected to be negligible due to the 1550-nm operating wavelength. Additionally, slightly rounded corners are expected due to the viscous nature of the biopolymer which is unable to fully conform to the sharp stamp features. For excellent pattern transfer, the pattern appears to be complete and uniform along the full length of the waveguides (2 to 3 in.). Good indicates correct imprint depth but with overly rounded corners and rough sidewalls due to incomplete filling of the stamp pattern. Poor indicates that the

<table>
<thead>
<tr>
<th>NIL system</th>
<th>Stamp material</th>
<th>Release coating</th>
<th>Substrate</th>
<th>Recipe</th>
<th>Imprint quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanonex SU-8</td>
<td>None</td>
<td>Untreated</td>
<td>Si</td>
<td>150°C, 500 psi, 5 min</td>
<td>Poor</td>
</tr>
<tr>
<td>2015 Chrome/</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanonex Si</td>
<td>FDTS</td>
<td>Si/Chrome/Gold</td>
<td>Si</td>
<td>150°C, 500 psi, 5 min</td>
<td>Good</td>
</tr>
<tr>
<td>Nanonex Si</td>
<td>FDTS</td>
<td>Si/Chrome/Gold</td>
<td>Si</td>
<td>150°C, 500 psi, 5 min</td>
<td>Good</td>
</tr>
<tr>
<td>Nanonex Si</td>
<td>FDTS</td>
<td>Si/HMDS</td>
<td>Si</td>
<td>150°C, 500 psi, 5 min</td>
<td>Good</td>
</tr>
<tr>
<td>Nanonex SiO$_2$</td>
<td>NXT-130</td>
<td>Si/Chrome/Gold</td>
<td>Si</td>
<td>120°C, 500 psi, 3 min</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nanonex SiO$_2$</td>
<td>Sigmacoate</td>
<td>Si/Chrome/Gold</td>
<td>Si</td>
<td>120°C, 500 psi, 3 min</td>
<td>Excellent</td>
</tr>
<tr>
<td>Suss SiO$_2$</td>
<td>NXT-130</td>
<td>Si/Chrome/Gold</td>
<td>Si</td>
<td>150°C, 500 psi, 5 min</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

Fig. 2 Pressure and temperature cycles for the NIL process for the DNA biopolymer using the Nanonex NX-2600. The four imprint stages are: (1) pump-down where the chamber is placed under vacuum, (2) preimprint where the temperature raised to the glass transition temperature, $T_g$ of the material and the pressure is gradually increased, (3) imprint where the imprint pressure and temperature are applied for a set time, and (4) cool down/chamber vent where the imprint pressure is maintained until the sample is cooled.
biopolymer film adhered to the sidewalls or other features of the stamp resulting in tearing of the film. This qualitative pattern transfer classification is demonstrated by the SEM, micrograph, and AFM images (Fig. 3). As shown in Fig. 3(c), some pitting defects occur in the spaces between the waveguide features, another indication of incomplete filling of the stamp.

Excellent pattern transfer was also achieved with the Suss MicroTec substrate bonder. However, to achieve uniform pattern transfer, it was necessary to sandwich the stamp and polymer film wafers between two 0.020-in.-thick sheets of Teflon polytetrafluoroethylene (PTFE) (McMaster-Carr, Aurora, Ohio) inside the parallel plates to compensate for nonplanarities of the rigid plates and mimic the pressure-equalizing effect of the flexible membranes of the Nanonex system. An NIL recipe of 150°C at 500 psi for 5 min using the Suss bonder with PTFE sheets resulted in excellent pattern transfer, of the same quality achieved on the Nanonex system.

In summary, an NIL process was developed and characterized for directly imprinting photonic waveguide structures in a DNA biopolymer using both a commercial NIL system and an in-house adapted NIL system using a Suss substrate bonder. Identifying NIL as a patterning method for DNA biopolymer photonic structures allows for fabricating a wide variety of photonic and electronic devices that are unattainable using conventional wet photolithographic techniques. It has been shown that micron-scale features that are traditionally achievable only by photolithography can be successfully transferred to the DNA biopolymer through NIL. Future work using stamps fabricated by e-beam lithography has the potential to push the feature sizes to the nano-scale for DNA biopolymer devices.

References