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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]

The marine-derived deoxyribonucleic acid (DNA) biopolymer has been demonstrated in a wide range of photonic devices, including organic light emitting diodes, organic field effect transistors, and polymer electro-optic (EO) modulators.[1–4] The DNA biopolymer is an especially promising material as a cladding layer for poled polymer EO-waveguide devices. Compared to the standard cladding material UV15 commonly used in these devices, the DNA biopolymer cladding layer yields polymer waveguide devices with EO coefficients 2× greater, optical losses more than an order of magnitude lower, and increased solvent compatibility with common polymer core materials.[5,6] However, patterned EO modulators have yet to be fabricated that take advantage of these enhanced material properties due to the incompatibility of the DNA biopolymer with photolithography and chemical processing techniques. As an alternative to photolithography, thermal nanoimprint lithography (NIL) has been identified as a technique for pattering the DNA biopolymer. The NIL is a nonoptical pattern transfer method originally developed as a cost-effective alternative to electron beam lithography.[7–10] This paper outlines the techniques and procedures developed for directly imprinting optical waveguide structures on the DNA biopolymer using NIL, allowing patterned EO modulators to be fabricated using the DNA biopolymer for enhanced performance.

An inverted ridge waveguide designed for 1550 nm is patterned in the DNA biopolymer as a passive bottom cladding layer for an EO waveguide device. Unlike conventional NIL where a thermal resist layer is imprinted as an etch mask,[7,8] the waveguide pattern is directly imprinted into the biopolymer film thereby preventing damage to the material by removing exposure to resists, etchants, and solvents. The 3 in. stamps are designed to imprint channels that are 0.2-μm deep $\times$ 4-μm wide into a 2-μm thick DNA biopolymer film, with length extending over a full 3 in. wafer. After imprinting, the residual layer is retained as the bottom cladding of the inverted ridge waveguide (Fig. 1). Imprinting a depressed channel in the cladding layer as opposed to a raised ridge in the core layer displaces a smaller amount of material and improves the quality of pattern transfer.[11]

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.[12] 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 $\sim$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.[7–14] 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_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_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;
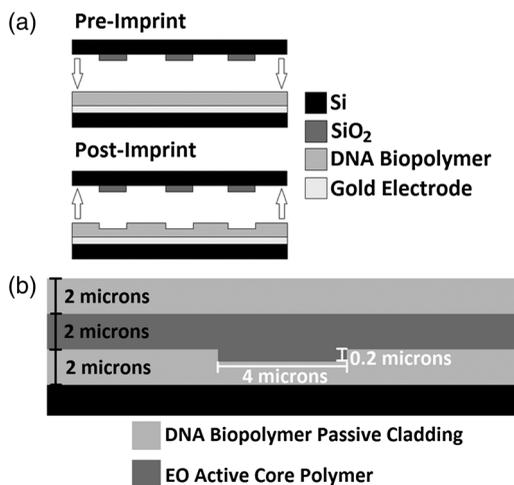
Fig. 1 (a) Schematic of the nanoimprint lithography (NIL) process showing the deoxyribonucleic acid (DNA) biopolymer film pre- and postimprint (b) the electro-optic (EO) modulator waveguide device structure with a DNA biopolymer cladding on either side of the EO active core polymer.

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) the cool down/chamber vent (imprint pressure maintained until sample is cooled) (Fig. 2).[7,8] 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
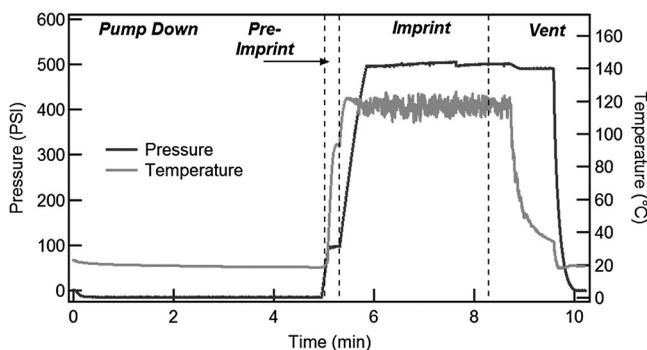

Fig. 2 Pressure and temperature cycles for the NIL process for the DNA biopolymer using the Nanonex NX-2600. The four imprint stages are: (1) pump-down where the chamber is placed under vacuum, (2) preimprint where the temperature raised to the glass transition temperature, T_g, of the material and the 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.

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.[15] An imprint temperature, ≥ 120°C and ≤ 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,[16,17] 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 1 Summary of nanoimprint lithography (NIL) recipe performance comparing Nanonex flexible membrane system and Suss rigid plate system. The imprint quality descriptors "excellent," "good," and "poor" are defined in the text.

| NIL system	Stamp material	Release coating	Susbtrate	Recipe	Imprint quality
Nanonex	SU-8 2015	None	Untreated Si	150°C, 500 psi, 5 min	Poor
Nanonex	Si	FDTS	Si/ Chrome/ Gold	150°C, 500 psi, 5 min	Good
Nanonex	Si	NXT-130	Si/ Chrome/ Gold	150°C, 500 psi, 5 min	Good
Nanonex	Si	FDTS	Si/HMDS	150°C, 500 psi, 5 min	Good
Nanonex	SiO_2	NXT-130	Si/ Chrome/ Gold	120°C, 500 psi, 3 min	Excellent
Nanonex	SiO_2	Sigmacote	Si/ Chrome/ Gold	120°C, 500 psi, 3 min	Excellent
Suss	SiO_2	NXT-130	Si/ Chrome/ Gold	150°C, 500 psi, 5 min	Excellent
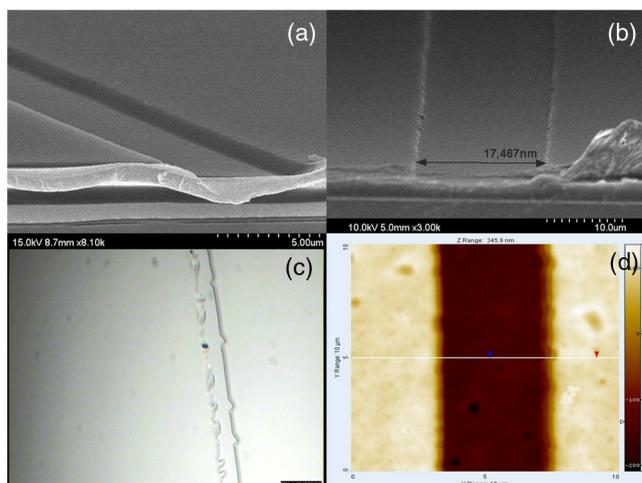
Fig. 3 The NIL-patterned waveguide channel in the DNA biopolymer with (a) "excellent" imprint quality (SEM image), (b) "good" imprint quality (SEM image), (c) "poor" imprint quality of 15-μm wide channel (micrograph), and (d) "good" imprint quality (AFM image). The imprint quality descriptors "excellent," "good," and "poor" are defined in the text.

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(d), 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.

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