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PRINTED BIOPOLYMER-BASED ELECTRO-OPTIC DEVICE COMPONENTS

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14. ABSTRACT
The major accomplishments during the tenure of this proposal include: Designed target test patterns of optical grating devices and fabricated e-beam lithography-based master molds. Printed micro and nanostructures using a newly developed spin-on nanoprinting (SNAP) technique. SNAP is a simple and easy technique to print any optical structures. The contractor demonstrated that this technique can be used to print grating structures on a silicon substrate.

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1. Introduction

Soft patterning of polymeric materials for developing photonic, electronic, microfluidic and optical applications are becoming increasingly popular because of its ease of fabrication and low cost [1]. However, extension of these patterning techniques to biopolymers has been hardly explored but is capable of providing entirely new horizons for new opto-electronic devices. Biomaterials are of particular interest because they often show unusual properties which are not easily replicated in conventional polymeric materials. Among the natural biopolymers, deoxyribonucleic acid (DNA) is an attractive material which can be used to make electronic and photonic devices [2, 3]. If patterned on the micro and nanoscale using a soft lithography technique, high quality biodegradable optical devices can be developed.

Integrated photonic devices are an ever-growing field which finds applications in optical communication networks as well as many other modern technologies [4]. Biopolymer materials like DNA are a viable candidate material for making these optical and photonic devices. These materials can be used for a large range of operating wavelengths due to low material dispersion and optical losses [5]. Biopolymers of interest include marine-based DNA purified from waste products of the Japanese fishing industry. These biopolymers are either naturally occurring or synthetically developed. There are many recent reports showing that they produce enhancements in device performance due to its unique electronic and optical properties [6]. Moreover, their distinctive double helical structures hold the potential for increased nonlinear chromophore alignment if used in a device like electro-optic (EO) modulator resulting in increased EO activity. These materials are completely environmental friendly since they are biodegradable. Biopolymers are also actively investigated for several applications like electron blocking layer in organic light emitting diode (LED), low gate voltage bio-field effect transistors and chemical sensors [7].

The inherent requirement of devices used in integrated optics is high resolution in their patterning. Electron beam lithography is the preferred technique to accomplish this high resolution. However, the basic process of point-by point fabrication is a major limitation of e-beam lithography compared to other imprinting lithographic techniques [8]. Substantial time and expenses are required to fabricate these devices. This time-consuming procedure and limited throughput oftentimes negates the use of e-beam lithography in industrial settings as a tool for mass fabrication of optical and photonic devices. Even though, photolithographic process can be used for many device fabrications, its application is limited due to the resist material used, size of the features and operating cost. Thus, new cost effective processing techniques are essential for the widespread application of polymer/biopolymer based photonic and opto-electronic devices. Moreover, developments in the commercial marketplace for compact waveguide based micro-optics make this an appropriate time to develop low-cost, high throughput lithography free device manufacturing processes.

Following are the major accomplishments during the tenure of this proposal:

1. Designed target test patterns of optical grating devices and fabricated e-beam lithography-based master molds.

2. Printed micro and nanostructures using a newly developed spin-on nanoprinting (SNAP) technique.

2. Results

2.1. SNAP Technique to Print DNA-Cetyltrimethylammonium (CTMA)

The nanoimprinting technique we developed for casting nanostructures and devices on DNA-CTMA is outlined in Figure 1. The process is developed by modifying our recently reported SNAP technique [9, 10]. The first step is the fabrication of a mold which is a rigid and inert material which carries the inverse of the nanofeatures to be transferred on to a polymer film surface. These nanofeatures are prepared on the surface of the mold by e-beam or photolithography. The mold is usually made up of silicon or SiO_x. The silicon master mold was then wetted with a commercially available anti-adhesive agent (Rain-X®). Rain-X® is an isopropanol-based cocktail of quaternary ammonium and fatty acid siloxanes and imparts a good degree of hydrophobicity on SiO_x on Si or SiO_2 surfaces. The DNA-CTMA solution was filtered (0.2μm filter) and degassed for 5 minutes before use to prevent bubble formation during printing. SNAP technique for DNA-CTMA involves spin-coating or blade-casting of a layer of DNA-CTMA solution on the surface of the mold. Spin-coating results in the complete penetration of the DNA-CTMA solution into the nanocavities of the mold. This process is clearly different from the conventional nano-imprinting lithography (NIL) technique in which nano-structuring is done by pressing a template at high temperature and pressure onto a resist deposited on a substrate. In the NIL process, high temperature and pressure, or ultraviolet (UV) light, are necessary to produce nano-structures. However, in our SNAP process, nano-structuring can be done without using any of the above conditions. SNAP printing requires the starting material to be sufficiently fluid to flow into the nano-concavities in the mold. The thin film is then transferred to the required substrate.

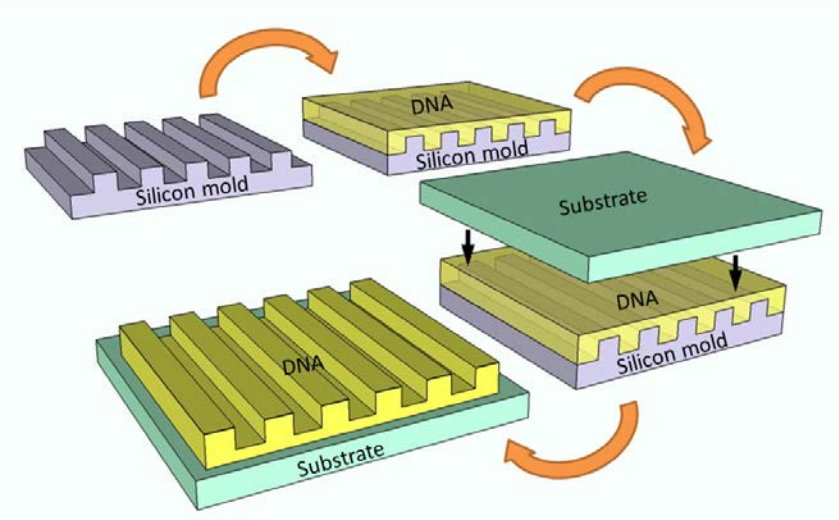

Figure 1: Steps Involved in the SNAP Technique

2.2. Mold Fabrication

In order to optimize the grating dimensions and shrinkage of the printed DNA-CTMA, we designed and fabricated a trial mold. This mold carries an inverse grating pattern to be transferred on to the DNA-CTMA. The fabricated mold was used to print several grating structures.

We prepared 5 different samples to test the shrinkage. To compare the dimensions of the mask and the printed structures, we used Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). Figures 2 (a) and (b) show the top and cross-sectional views of the mask. The width and depth of the channels on the mold are 1.8 μm and 600 nm, respectively. The printed DNA structures are shown in Figure 2(c) and (d). Table 1 lists the dimension of the printed structures. The shrinkage was calculated to be ~15-20% in width and ~10-15% in height. The thickness of the DNA film was about 15 μm.

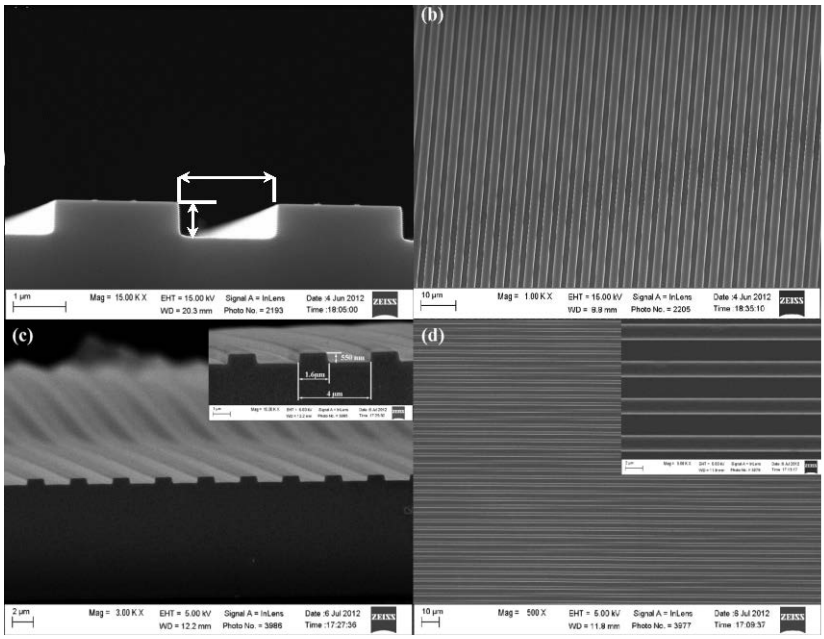

Figure 2: SEM Images show (a) Cross-sectional and (b) Top Views of our Mask; Printed DNA Waveguides are shown in (c) and (d)

The inset in (c) and (d) provide high magnification images of the printed structures.

Table 1. Dimensions Collected from 5 Different Printed DNA Patterns

SAMPLE#	W (μm)	H (nm)	WIDTH DIFF. (μm)	HEIGHT DIFF. (nm)
Mask	1.8	600		
1	1.60	550	0.19	50
2	1.63	545	0.17	55
3	1.69	568	0.11	32
4	1.63	575	0.17	25
5	1.59	535	0.21	65

Based on the shrinkage results, we designed the actual molds required to print the grating structures (schematic) as shown in Figure 3 and the dimensions calculated are given in Table 2. It was also our intention to reduce the thickness of the DNA residual film. Photolithography was used to develop a second silicon mold based on the optimized dimensions given in Table 2. Top and cross-sectional SEM views of the mold developed (for printing the actual grating structures) are shown in Figure 4.

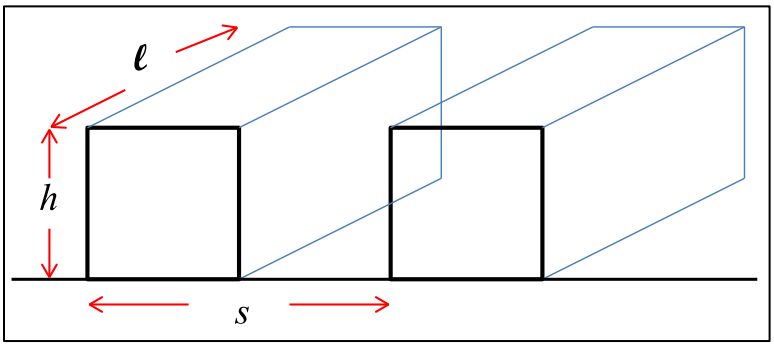

Figure 3: Grating Structure Designed
Based on the shrinkage of the DNA-CTMA structures developed using the first generation mold

Table 2. Detailed Dimensions for Printed Structures and Masks

Required dimensions			Mask dimensions		
l (mm)	h (μm)	s (μm)	l (mm)	h (μm)	s (μm)
10	1 & 2	1.8	10	1.2 & 2.4	2

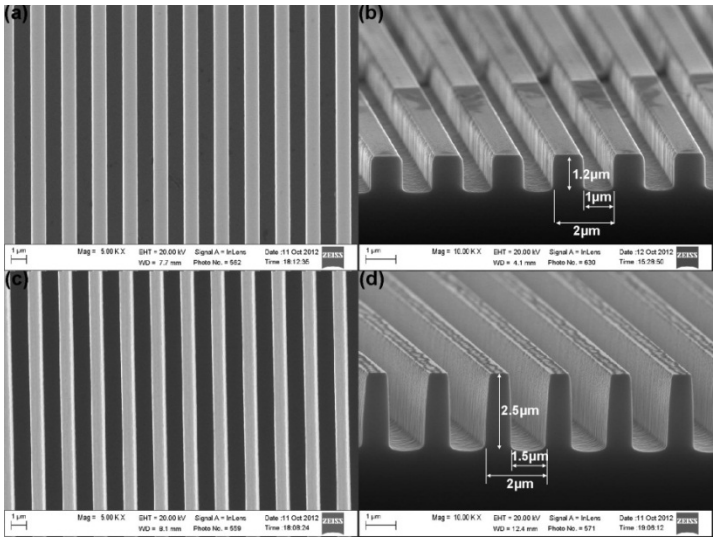

Figure 4: SEM Images Showing Top and Angled View of the Mold
Fabricated for printing DNA-CTMA grating structure

2.3. Nanoimprinted Structures for Light Coupling

Coupling light into planar waveguide structures using optical fiber or prism coupler is a slow and tedious process. The goal of this project was to print DNA-CTMA grating structures on top of the waveguide structure to couple light as shown in Figure 5. University of Central Florida (UCF) has been focusing on printing grating structure on top of the waveguide structures provided by Air Force Research Laboratory (AFRL).

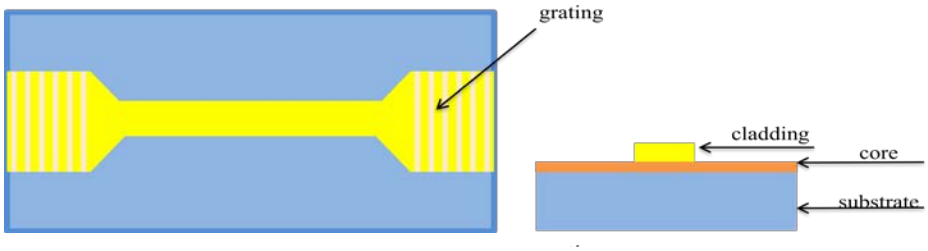

Figure 5: Schematic Diagram of the Waveguide Structure with Grating Couplers

2.4. Printing DNA-CTMA Grating Structure

The device configuration proposed by Dr. Heckman's group at AFRL for coupling efficiency measurement is given in Figure 6. The substrate required for making this device configuration was received from AFRL. The substrate provided was a Silicon (with oxide layer) wafer with about 2µm thick oxide layer on the top. As directed by AFRL, we have spin coated a layer of amorphous polycarbonate (APC) film on top of this substrate. A 12 percent by weight of APC in cyclopentanone was used to make a ~2µm thick APC film.

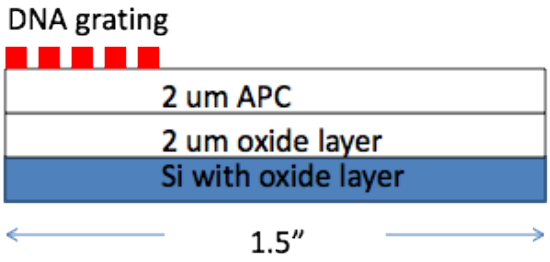

Figure 6: Schematic of a Test Device for Coupling Efficiency Measurement

For printing DNA-CTMA grating structures for coupling efficiency measurements, we have received three different batches of DNA-CTMA. The first batch was labeled as lot 08063 (bag 2, 200kDa 10cyl-7July11-1 AL). We were able to make good films using this batch of materials. The second batch was 6/19/12 (BT+EH, purified sonicated). Films made from this batch were quite brittle. The third batch received was HP-AJ0118 (Bag 3, 6 cyl, 26June12-2) and the films prepared were so brittle that the film separation from the mold was not at all possible. These three samples have the same molecular weight of 200kDa. The difference between the first batch and the other two batches was in the rinsing procedure used during the purification of DNA-CTMA. The latter two samples were produced using a thorough rinsing technique to remove

excess ions and excess CTMA from the DNA-CTMA product. Since the films prepared from the latter two batches were brittle, we have focused on the optimization of printing using DNA-CTMA, which was prepared using the "old" rinsing process (first batch). We were able to print and remove DNA-CTMA films easily. We optimized the curing time and successfully printed high quality DNA-CTMA grating structure on the substrates provided. The printed film was about 1 cm × 1.5 cm on top of the silicon mold as shown in Figure 7. AFM images of the printed structure are shown in Figure 8.

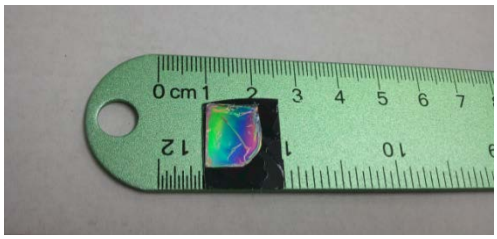

Figure 7: Photograph of Printed DNA-CTMA Film on Silicon Substrate

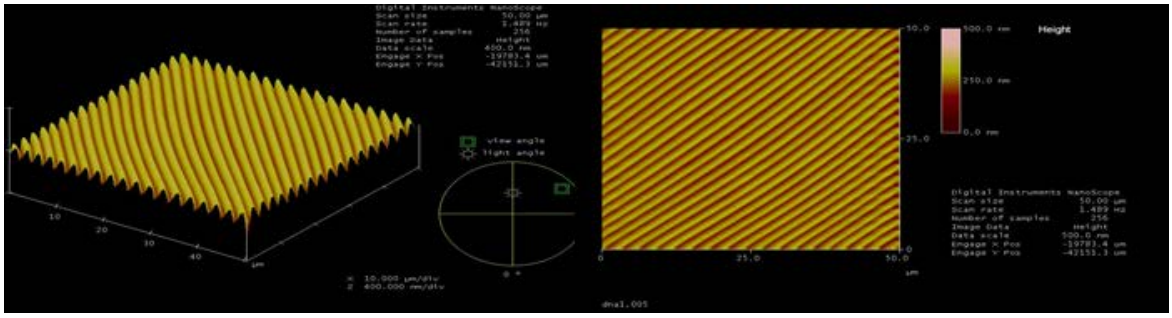

Figure 8: AFM Images of the SNAP Printed DNA-CTMA Grating Structures

3. Conclusion/Acknowledgement

SNAP is a simple and easy technique to print any optical structures. We have demonstrated that this technique can be used to print grating structures on a silicon substrate.

UCF principal investigator, Dr. Jayan Thomas, acknowledges University of California, Santa Barbara Nanofabrication facility for mold fabrication.

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LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ACRONYM	DESCRIPTION
AFM	atomic force microscope
AFRL	Air Force Research Laboratory
APC	amorphous polycarbonate
CTMA	cetyltrimethylammonium
DNA	deoxyribonucleic acid
EO	electro-optic
LED	light emitting diode
NIL	nano-imprinting lithography
SEM	scanning electron microscope
SNAP	spin-on nanoprinting
UCF	University of Central Florida
UV	ultraviolet