

## FABRICATION OF NANOIMPRINTING MOLDS WITH ACRYLIC POLYMER BY TWO-PHOTON POLYMERIZATION

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### Abstract

We demonstrate the plausibility of making low-cost nanoimprinting molds with acrylic polymer using femtosecond-laser-induced two-photon polymerization (TPP) technique. A Ti:sapphire femtosecond laser was used to induce TPP in dipentaerythritol pentaacrylate to make nanostructures, the nanoimprinting mold, on pretreated glass substrate. A layer of fluoro-silane was then grown on the surface of the mold to promote the release of the mold after imprinting. To test the imprinting capacity of the mold, poly (ethylene glycol) diacrylate was patterned by the mold and the results were analyzed by a scanning electron microscope (SEM).

### I. Introduction

Nanoimprinting lithography (NIL) is a low-cost, high-resolution, and parallel nanofabrication technique that has been intensely studied in recent years. NIL is capable of fabricating nanoscale structures, which, due to diffraction limit, cannot be accomplished by most other parallel fabrication methods such as the commonly-used photolithography process [1, 2]. Furthermore, because of its parallel fabrication mode, NIL could fabricate samples much faster than could other nanofabrication methods such as Electron Beam Lithography (EBL). Unfortunately, fabricating nanoimprinting molds usually requires numerous costly and often unavailable cleanroom equipments and time-consuming steps, including EBL and reactive ion etching (RIE) [3].

In this report, we demonstrate the plausibility of creating a low-cost polymer nanoimprinting mold by using the two-photon polymerization (TPP) technique. TPP fabrication technique has already made sub-100 nm features by breaking the diffraction limit which used to restrain the resolution of photo-polymerization fabrication. However, TPP is an extremely slow serial (point-by-point) fabricating process, which has precluded it from being used in the mass production of nanostructures. Our project, by using TPP to make reusable nanoimprinting molds, indirectly enables the utilization of TPP in mass production. Moreover, a variety of polymers can be used to make such molds, which ensures that it is relatively easy to obtain the desirable bulk and surface properties for polymer molds suitable for different imprinting projects. Poly (ethylene glycol) diacrylate (PEGDA) was patterned in the study to demonstrate the imprinting capacity of the polymer molds made by TPP.

## II. Materials and Methods

**Acrylic Polymer Preparation for TPP Fabrication.** The acrylic polymer we used for the TPP fabrication was dipentaerythritol pentaacrylate (DPPA, Sartomer Inc. Exton, PA), which was used as received. To increase the TPP rate of DPPA, 1% photoinitiator (Irgacure 819, Ciba Specialty Chemicals, Tarrytown, NY) was thoroughly mixed with DPPA by heating the mixture in 80 °C silicone oil (Fisher Scientific Inc. Pittsburgh, PA).

The acrylic polymer should adhere on a glass substrate in order to be used as a mold. To enhance the adhesion with DPPA, the glass substrates were treated for 5 minutes in a 1mM solution of 3-trichlorosilyl propyl methacrylate (TPM, Fluka Chemicals, Milwaukee, WI) in a 4:1 mixture of heptane (Fisher Scientific Inc. Pittsburgh, PA) and carbon tetrachloride (Sigma-Aldrich Inc. Milwaukee, WI). Then the substrates were washed by carbon tetrachloride and dried by nitrogen. Finally, in order to get rid of the chlorhydric acid generated in the previous step and the residual water on the surface, the substrates were soaked in DI water for 2 minutes and then baked on a hot plate (Super-Nuova, Barnstead Thermolyne Corporation, Dubuque, IA) at 100 °C for 5 minutes.

**TPP Fabrication Process.** A Ti:sapphire femtosecond laser (Vitesse, Coherent Inc. Santa Clara, CA) producing 100-femtosecond duration pulses with a central wavelength of 800 nm at a repetition rate of 80 MHz was used as the excitation source for TPP. To use the full capacity of the large numerical aperture oil-immersion objective lens, the laser beam was expanded by a 2X beam expander to overfill the incidence aperture of the 100X oil-immersion objective lens (N.A. = 1.3, Fluor, Carl Zeiss MicroImaging, Inc. Thornwood, NY) which focused the laser beam into the volume of DPPA. The laser power we used in the mold fabrication was 5 mW, measured by a power meter (PowerMax 500D, Molelectron Detector Inc. Portland, Oregon) before the laser beam entering the objective lens. The mold structures were generated by moving a motorized stage (Newport Inc. Irvine, CA), which held the glass substrate, at a speed of 50  $\mu\text{m}$  / second. The fabrication process was monitored *in situ* by a charge-coupled device (CCD) camera (CV-S3200, JAI Inc. San Jose, CA). The mold was developed in ethanol (Decon Labs Inc. King of Prussia, PA) for 3 minutes to wash away uncured DPPA after TPP fabrication.

**Treatment of the Mold after the TPP Fabrication.** To get rid of the unreacted acrylate groups on the mold surface, the mold was soaked in a solution of 1 wt% photoinitiator (Irgacure 2959, Ciba Specialty Chemicals, Tarrytown, NY) in DI water and was irradiated with a UV lamp (OmniCure S2000, Exfo Life Sciences & Industrial Division, Mississauga, Ontario, Canada) for 2 minutes. After that, a fluoro-silane based releasing layer was grown on the mold surface to facilitate detachment of the mold during the imprinting process. Figure 1 shows the schema of the silanization process. First, two glass petri dishes, containing several drops of silicon tetrachloride and the mold, respectively, were placed in a vacuum oven (Isotemp Vacuum Oven Model 280A, Fisher Scientific Inc. Pittsburgh, PA) for 2 hours. During this process, a layer of silicon tetrachloride (Acros Organics, Morris Plains, NJ) was grown on the mold surface, as Figure 1 (a) illustrates. Then the mold was soaked in DI water for 2 minutes, during which time the chlorine

ions of silicon tetrachloride were replaced by hydroxyl groups of water molecules, as Figure 1 (b) shows. This replacement greatly increased the number of hydroxyl groups on the mold surface, making it easier for fluoro-silane molecules to bond onto. After that, the mold was baked on a hot plate at 100 °C for 10 minutes to strengthen the newly formed layer of hydroxyl groups by forming -Si-O-Si- bonds between adjacent silicon tetrachloride molecules. Next, a layer of fluoro-silane -- tridecafluoro-1,1,2,2-tetrahydrooctyl-1 trichlorosilane (TFTT, United Chemical Technologies Inc. Bristol, PA) was grown on the mold surface following similar steps as the ones used for growing silicon tetrachloride, with the only difference being that TFTT, instead of silicon tetrachloride, was placed onto one of the two glass petri dishes. Figure 1 (c) illustrates the reactions occurred in this step. Finally, the mold was again soaked in DI water for 2 minutes and backed on a hot plate at 100 °C for 10 minutes. Figure 1 (d) shows the final result. After the fluoro-silane had been successfully grown on the mold, the mold was stored in a vacuum desiccator (Desi-Vac, Fisher Scientific Inc. Pittsburgh, PA).

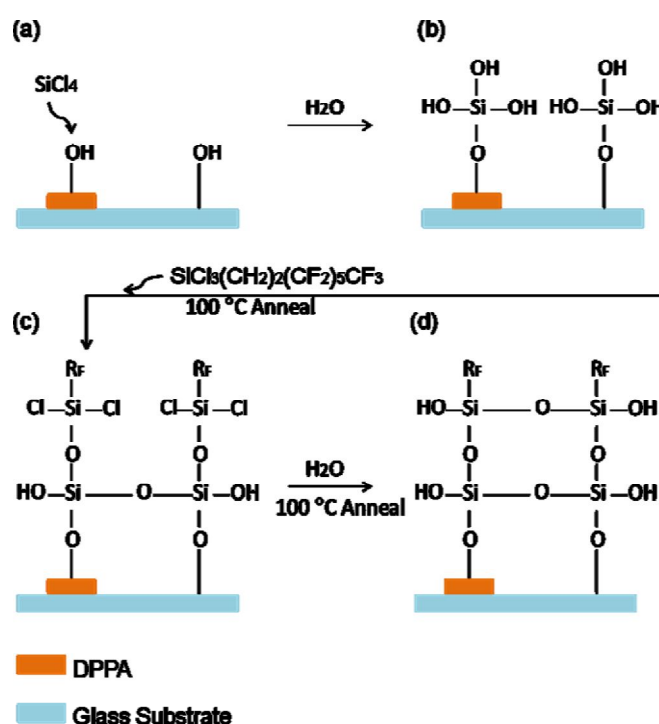


Figure 1. Schematic diagram of the treatment of the mold surface: (a) silicon tetrachloride reacted with the hydroxyl groups on the mold surface; (b) the mold was soaked in DI water to form more hydroxyl groups on its surface; (c) tridecafluoro-1,1,2,2-tetrahydrooctyl-1 trichlorosilane reacted with the hydroxyl groups on the mold surface,  $\text{RF} = (\text{CH}_2)_2(\text{CF}_2)_5\text{CF}_3$ ; (d) a fluoro-silane layer was formed on the mold surface.

**Imprinting in PEGDA.** The imprinting work was conducted in a mask aligner (SUSS MA-6, SuSS Microtech, Munich, Germany), following a procedure outlined below. A more detailed discussion regarding the procedure was described in our previous study [4]. Firstly, PEGDA (MW 258, Sigma-Aldrich Inc. Milwaukee, WI) was thoroughly mixed with 1% Irgacure 2959 through 5-minute sonication (Branson Ultrasonics Corporation, Danbury, CT) to increase its cross-linking rate. Next, the mold was fixed on the sample stage of the mask aligner by two strips of 100  $\mu\text{m}$ -thick sticky tapes. The sample substrate that served as a transparent dummy mask was similarly affixed onto a glass dummy plate by two sticky tapes. After that, the glass dummy plate with the sample

substrate affixed on it was mounted to the mask holder of the mask aligner by vacuum suction so that the glass substrate was directly above and facing the mold. Lastly, a drop of PEGDA was deposited on the mold surface by a glass pipette. The sample stage was then lifted upwards until the tapes on the mold and on the sample substrate contacted with each other. The PEGDA was allowed to spread for 3 minutes and was then irradiated by 365 nm UV light for 30 seconds. After the exposure, the mold was detached from the sample substrate by the automatic descent of the sample stage. After the imprinting process, the mold was taken from the sample stage and could be used in subsequent imprinting processes without any further surface treatment.

### III. Results and Discussion

The mold and the imprinted PEGDA structures were examined by a scanning electron microscope (SEM, Supra 40VP, Zeiss, Carl Zeiss SMT Inc., Peabody, MA). As figure 2 (a) shows. The width and height of each line on the mold is 400 nm and 1.2  $\mu\text{m}$ , respectively, and the distance between adjacent lines is 5  $\mu\text{m}$ . Figure 2 (b) presents a side view of the parallel lines and provides a direct view of the height of the lines. Figure 2 (c) and (d) show that the imprinted PEGDA structures consist of parallel trenches of the same dimensions and spacing as the parallel lines on the mold, thus demonstrating that our imprinting process accurately transferred the patterns on the DPPA mold to PEGDA over a large area. While the widths and the spacing of the trenches can be easily measured from the top-view SEM image on figure 2 (c), the height of the trench cannot be obtained that way. It cannot be obtained by an atomic force microscope (AFM) scanning either because the trench is too narrow for the AFM tip to approach. Therefore, to measure the height of the trenches, the cross-sectional view of the trenches, figure 2(d), was needed.

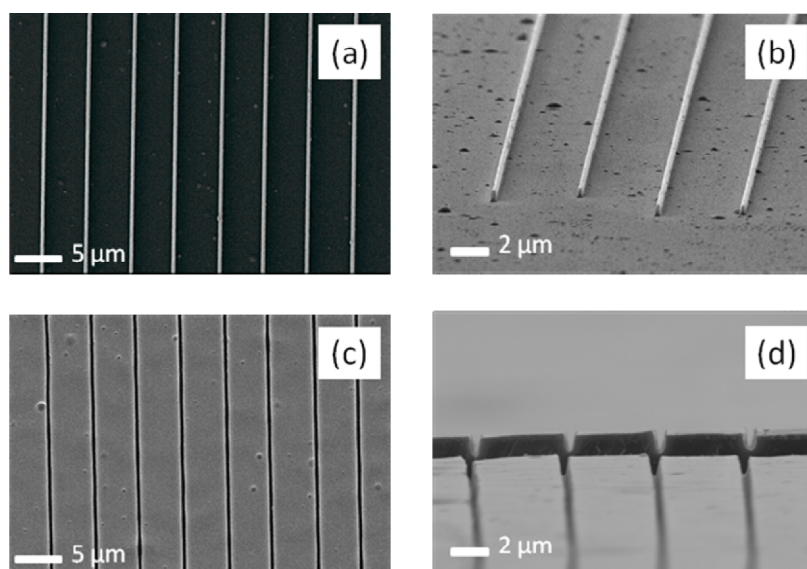


Figure 2. SEM images of the imprinted PEGDA structures and the DPPA mold after imprinting: (a) DPPA mold of 400 nm-wide lines with a period of 5  $\mu\text{m}$ ; (b) side view of the DPPA mold; (c) imprinted PEGDA structures of 400nm wide trenches with a 5 $\mu\text{m}$  period; (d) cross-sectional view of the PEGDA trenches, which were perpendicularly cut to expose the cross-sections.

Our work demonstrates that imprinting molds made by TPP could successfully transfer nanoscale patterns to PEGDA. To successfully transfer the patterns, the mold must be easily detached from the imprinted materials after imprinting. Thus it was crucial to grow a layer of silicon tetrachloride on the mold surface before growing the releasing layer of fluoro-silane. This is because silicon tetrachloride tripled the number of hydroxyl groups on the mold surface so that a much denser layer of fluoro-silane was able to bond onto it. Another method to increase the number of hydroxyl groups on the polymer surface is by transforming some methyl groups of the polymer to hydroxyl groups via RIE [5]. This technique is a promising alternative treatment for the mold surface since it is simpler than the silicon tetrachloride treatment used in our experiment. It is also noteworthy that some fluoro-based polymers such as perfluoropolyether (PFPE) have intrinsic ultralow surface energy, as a result of which molds made of such materials have inherent anti-attaching ability so they can imprint without any surface treatment. Previous studies have demonstrated the superior imprinting capability of PFPE nanoimprinting molds made from a master silicon mold by UV polymerization [6]. We think PFPE can also be patterned by TPP to make nanoimprinting molds, which will further simplify our fabrication processes.

#### **IV. Conclusions**

An acrylic polymer nanoimprinting mold was generated by TPP fabrication using a femtosecond laser. The mold was treated by silanization steps to promote detachment of the mold from the imprinted materials. The SEM images of the mold and the imprinted PEGDA patterns show that a group of 400 nm-wide parallel lines were successfully transferred to PEGDA, which demonstrates the imprinting capacity of the mold. The fabrication process of the acrylic polymer mold was simpler than that of the traditional silicon/quartz mold. We boldly expect that the TPP technique will be widely used in making nanoimprinting molds in future.

#### **V. Acknowledgements**

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