

Integrated Two-Photon Polymerization with Nanoimprinting for Direct Digital Nanomanufacturing

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In this work, we demonstrate the plausibility of integrating two-photon polymerization (TPP) with nanoimprinting for direct, digital nanomanufacturing. TPP offers manufacturing of nano-molds at a low cost, while the nanoimprinting process using the nano-molds enables massively parallel printing of nanostructures. A Ti:sapphire femtosecond laser (800 nm wavelength, 100 fs pulse width, at a repetition rate of 80 MHz) was used to induce TPP in dipentaerythritol pentaacrylate to fabricate the nanoimprinting mold with 400 nm wide line array on a glass substrate. The mold surface was silanized by tridecafluoro-1,1,2,2-tetrahydrooctyl-1 trichlorosilane to facilitate the detachment of the mold from the imprinted material. This mold was then used to imprint poly (ethylene glycol) diacrylate (PEGDA). PEGDA is an important biomaterial for many applications such as tissue scaffolds for cell growth. A spectrophotometer and a scanning electron microscope (SEM) were used to characterize the materials and nanostructures.

I. Introduction

Nanoimprint lithography (NIL) techniques have been regarded as parallel nanofabrication methods for high-resolution and high-aspect-ratio features [1-3]. NIL has the potential to significantly impact many applications in areas including photonic crystals for high-brightness LEDs, biochemical sensors, and large format display polarizers [4-6]. To successfully imprint nanostructures using NIL, a rigid mold capable of nano-patterning thermal or photo-curable materials over a large area with high accuracy and repeatability is crucial. Unfortunately, fabricating nanoimprinting molds in silicon or quartz, the two most commonly used materials, usually requires costly and often unavailable cleanroom equipment and time-consuming steps, including e-beam lithography (EBL) and reactive ion etching (RIE) [7]. A recent development is to make multiple polymer molds from a single master-silicon or -quartz mold to save time and cost. Polymer molds have desirable and easily tunable bulk and surface properties that are well-suited for the nanoimprinting process [8, 9]. However, because this fabrication process requires a master mold, the whole process is still costly and time-consuming.

In this paper, we demonstrate the plausibility of creating a low-cost polymer nanoimprinting mold by using the two-photon polymerization (TPP) technique, which avoids the need of making silicon or quartz molds entirely. TPP induced by femtosecond laser irradiation in photopolymers has been demonstrated for its ability to fabricate intricate nanoscale structures [10, 11]. During TPP, the photopolymer simultaneously absorbs two photons to activate the chain reaction of polymerization. Only the central portion of the laser beam with high energy intensity is able to induce such two-photon absorption, due to the Gaussian distribution of the energy intensity over the laser beam

cross section. Therefore, TPP is able to break the diffraction limit which restrains the resolution of photo-polymerization fabrication. Sub-100 nm features have already been successfully fabricated by TPP [12]. The advantages of TPP over EBL include the low cost for capital equipment and TPP's virtual absence of any proximity effect which restrains the distance that structures can be placed from each other through the EBL process [13].

Despite its many advantages, TPP is an extremely slow serial (point-by-point) fabrication process, which has precluded it from being used in the mass production of nanostructures. This work, by using TPP to make reusable nanoimprinting molds, indirectly enables the utilization of TPP in mass production. The TPP technique does not require costly cleanroom facilities or time-consuming processes, thus costing less than the traditional mold-fabrication methods. 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 our study to demonstrate the imprinting capacity of the polymer molds made by TPP. PEGDA is a Food and Drug Administration (FDA) approved, PEG-based hydrogel that has been widely utilized in the fabrication of tissue-engineering scaffolds with microscale structures [14, 15]. However, research efforts to make nanoscale structures in tissue engineering scaffolds using PEGDA have been relatively lacking, despite of the fact that the *in vivo* stimuli of cells are in nanoscale [16]. This work will bridge this gap by transferring nanostructures into PEGDA through a polymer mold.

II. Materials and Methods

Material Preparation for TPP. The photopolymer we used for the TPP fabrication was dipentaerythritol pentaacrylate (DPPA, Sartomer Inc., Exton, PA), used as received. We chose this acrylic polymer based on several considerations. First, DPPA is fast curing, as a result of the existence of five acrylate groups in each of its molecules. Second, its abrasion resistance and flexibility with hardness characteristics make it a very suitable material for molds. Third, DPPA has one hydroxyl group in each molecule, so a fluorosilane layer, which promotes releasing in the imprinting process, can covalently bond onto its surface.

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). To activate the chain reaction of TPP, the photopolymer must simultaneously absorb two photons, whose effect is equivalent to absorbing a single photon of half the wavelength. Besides, the photopolymer must be transparent to the laser beam to eliminate single photon polymerization which may reduce the fabrication resolution. Therefore, a suitable photopolymer for TPP induced by an 800 nm laser should have high absorption at 400 nm and negligible absorption at 800 nm. To verify that DPPA with 1% photoinitiator is such a suitable photopolymer, the absorption spectra of DPPA with 1% photoinitiator and 0% photoinitiator, respectively, were measured by a spectrophotometer (Cary 5000 UV-Vis-NIR, Varian, Inc., Palo Alto, CA). As Figure 1 shows, DPPA with 1% photoinitiator had a high absorption rate at a wavelength of 400 nm, a fact apparently attributable to the photoinitiator because DPPA with 0% photoinitiator did not exhibit such a strong

absorption rate at 400 nm. In addition, both DPPA with 1% and 0% photoinitiator had no natural absorption at the spectral region near 800 nm, which demonstrated that the single photon polymerization could not occur in these materials under near infrared (NIR) femtosecond laser irradiation.

The DPPA structures produced by TPP need to adhere onto a glass substrate--the mold substrate--during the TPP process in order to be used as the imprinting mold. The mold substrates (Fisher Scientific Inc., Pittsburgh, PA) were cleaned for 8 minutes in piranha solution consisting of a 2:1 mixture of sulfuric acid and hydrogen peroxide, washed by deionized (DI) water, and dried by high-pressure nitrogen. To enhance the adhesion with DPPA, the substrates were then treated for 5 minutes in a 1-mM 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). Subsequently, 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. Figure 2 shows the experimental setup for TPP fabrication. The excitation source for TPP was 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. The laser beam was expanded by a 2X beam expander to overfill the incidence aperture of a 100X oil-immersion objective lens (N.A. = 1.3, Fluar, Carl Zeiss MicroImaging, Inc., Thornwood, NY) which focused

the laser beam into the volume of DPPA. The laser power employed for the fabrication was 5 mW, measured by a power meter (PowerMax 500D, Molectron Detector Inc., Portland, Oregon) before the laser beam entered the objective lens. The power switch of the laser beam was controlled by an electrical-motorized shutter (Edmund Optics Inc., Barrington, NJ). The vertical position of the laser focal point was controlled by the movement of a vertically-mounted step-motor (Newport Inc., Irvine, CA). The fabrication process was monitored *in situ* by a charge-coupled device (CCD) camera (CV-S3200, JAI Inc., San Jose, CA). The mold structures were generated by moving a motorized stage (Newport Inc., Irvine, CA), which held the glass substrate, at a speed of 50 $\mu\text{m}/\text{second}$.

Post-treatment of the Mold. Within 5 minutes of being fabricated by TPP, the mold was developed in ethanol (Decon Labs Inc., King of Prussia, PA) for 3 minutes to wash away uncured photopolymer. After the development process, there were still some residual acrylate groups on the surface of the mold that might bond with the imprinted material and hinder mold detachment. To remove these acrylate groups, the mold was then soaked in a solution of 1% 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.

To facilitate detachment of the mold during the imprinting process, it was crucial to grow a releasing layer on the mold surface. Fluorosilane was chosen as our releasing-layer material because it is highly hydrophobic, as a result of its low surface energy. Figure 3 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 3 (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 3 (b) shows. This replacement greatly increased the number of hydroxyl groups on the mold surface, making it easier for fluorosilane molecules to bond onto it. 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, as illustrated in Figure 3 (c). Next, a layer of fluorosilane -- 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. Finally, the mold was again soaked in DI water for 2 minutes and baked on a hot plate at 100 °C for 10 minutes. Figure 3 (e) and (f) illustrate the reactions that occurred in those two steps. After the fluorosilane had been successfully grown on the mold, the mold was stored in a vacuum desiccator (Desi-Vac, Fisher Scientific Inc., Pittsburgh, PA).

Imprinting in PEGDA. The imprinting process was conducted in a mask aligner (SUSS MA-6, SuSS Microtech, Munich, Germany), following the procedure outlined below. The procedure is discussed in detail in Ref [17]. 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. The glass sample substrate was treated with TPM to improve its adhesion with PEGDA, following the same procedure as the one used to treat the mold substrate during the material-preparation stage. Next, the mold was secured on the sample stage of the mask aligner by two strips of 100- μ 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. The tapes on the mold and the sample substrate also served as spacers that protected the mold from being damaged during the imprinting process by preventing their direct contact with each other. Subsequently, 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 each other. Due to the mold's hydrophobic surface, PEGDA could not immediately fill in the nanoscale structures on the mold immediately after the contact, so it was allowed to spread for 3 minutes before the application of UV irradiation. PEGDA 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

A scanning electron microscope (SEM, Supra 40VP, Zeiss, Carl Zeiss SMT Inc., Peabody, MA) was employed to examine the mold and the PEGDA structures obtained by the imprinting process. The parallel lines--the patterns of the mold--remained intact

and firmly attached to the mold substrate after having completed multiple imprinting processes, as figure 4 (a) shows. The width and height of each line is 400 nm and 1.2 μm , respectively, and the distance between adjacent lines is 5 μm . The width and depth of the structures fabricated by TPP is determined by the laser power, the laser scanning speed, the concentration of photoinitiator in photopolymer, and the molecular structure of photopolymer. Figure 4 (b) presents a side view of the parallel lines and provides a direct view of the height of the lines. Figure 4 (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 4 (c), the height of the trench cannot be obtained that way. Nor can it be obtained by an atomic force microscope (AFM) scan 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, as shown by Figure 4 (d) was needed. The trenches were perpendicularly cut by a scalpel to expose their cross section. Because cutting on bare PEGDA surface will generate debris near the cut that may obstruct the cross-sectional view of the trench, a 6 nm-thick layer of Pt/Pd alloy was deposited on the PEGDA surface before cutting to prevent debris.

Our work demonstrates that imprinting molds made by TPP could successfully transfer nanoscale patterns to photo-curable hydrogel—PEGDA. In order to pattern PEGDA in mass production with high fidelity, the mold must be able to detach easily and completely from the imprinted sample with no residual PEGDA left on it after each imprinting. This

goal was achieved in our work by the pre-treatment of the mold substrate that enhances its adhesion with DPPA and by the post-treatment of the mold which prevents its adhesion with PEGDA during the imprinting process. During the post-treatment of the mold, to facilitate the detachment of the mold from the imprinted structures, it was crucial to grow a layer of silicon tetrachloride on the mold surface before growing the releasing layer of fluorosilane. This is because silicon tetrachloride tripled the number of hydroxyl groups on the mold surface so that a much denser layer of fluorosilane was able to bond onto it. Whitesides et al. reported another method to increase the number of hydroxyl groups on the polymer surface by transforming some methyl groups of the polymer to hydroxyl groups via RIE [18]. This technique promises to be an alternative for the post-treatment of the polymer mold surface since it is simpler than the silicon tetrachloride treatment used in our experiment.

Our TPP imprinting technique could be used to make nanoimprinting molds from a variety of materials. Most acrylic photopolymers whose surface properties could be modified by the post-treatments can be patterned by TPP to create nanoimprinting molds. Moreover, 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 [19, 20]. We purpose that PFPE can also be patterned by TPP to make nanoimprinting molds, which will further simplify the fabrication procedures depicted in this paper.

IV. Conclusions

A polymer nanoimprinting mold was created by the femtosecond laser induced TPP. Because the etching step is removed from the mold fabrication process and no costly EBL facility is employed, TPP method is faster, easier, and less costly than the fabrication processes using the traditional silicon or quartz molds. The mold was treated with a series of silanization processes to facilitate the detachment of the mold from the imprinted materials. PEGDA was patterned by the mold to demonstrate its imprinting capacity. 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 with high accuracy over a large area, thus demonstrating the feasibility of making nanoimprinting molds by TPP. More intricate nanoimprinting molds can be made by the TPP technique because it is relatively easy for TPP to create smaller features with arbitrary geometry. We believe the integration of TPP with NIL will significantly reduce the cost and time-to-production for direct, digital nanomanufacturing.

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Figure 1. Absorption spectra of DPPA with 1% photoinitiator and with 0% photoinitiator. There is no absorption near 800 nm in either solution and there is strong absorption in DPPA with 1% photoinitiator near 400 nm.

Figure 2. Experimental setup of two-photon polymerization.

Figure 3. Schematic diagram of the post-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 and the number of hydroxyl groups on the mold surface greatly increased as the chlorine ions of silicon tetrachloride were replaced by hydroxyl groups in water molecules; (c) the mold was annealed on a hot plate at 100 °C to stabilize the layer of hydroxyl groups by forming -Si-O-Si- bonds between adjacent silicon tetrachloride molecules; (d) tridecafluoro-1,1,2,2-tetrahydrooctyl-1 trichlorosilane reacted with the hydroxyl groups on the mold surface, $R_F = (CH_2)_2(CF_2)_5CF_3$; (e) the mold was once again soaked in DI water; (f) the mold was annealed on a hot plate at 100 °C.

Figure 4. SEM images of the imprinted PEGDA structures and the DPPA mold after imprinting: (a) DPPA mold of 400 nm-wide lines with a pitch of 5 μm, (b) side view of the DPPA mold, (c) imprinted PEGDA structures of 400 nm-wide trenches with a pitch of 5 μm, (d) perspective view of the PEGDA trench cross section; the inset is the vertical view of the trench cross section.

fig1.tiff

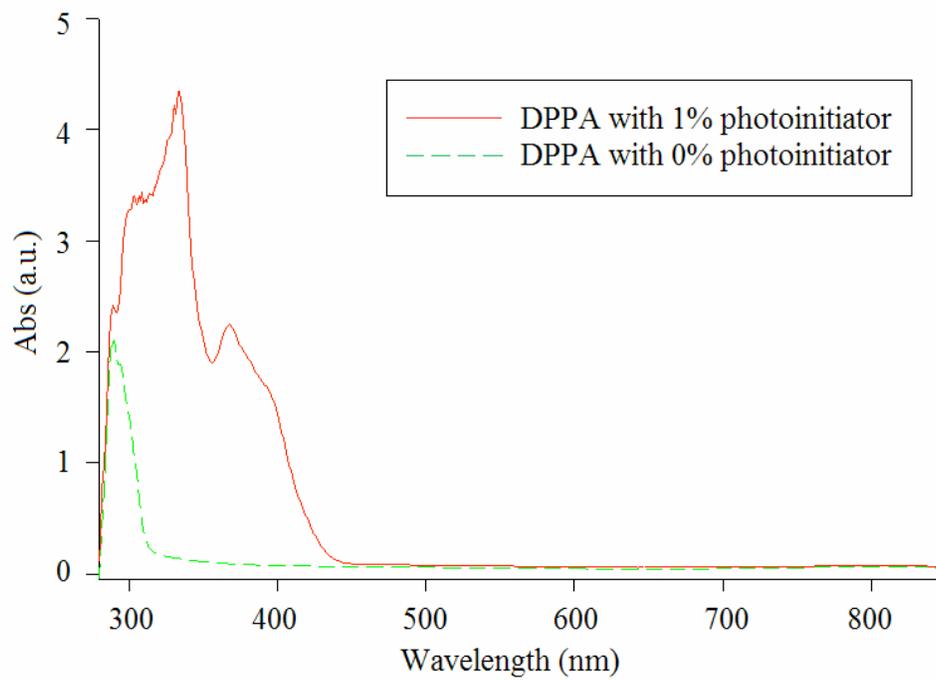


fig2.tiff

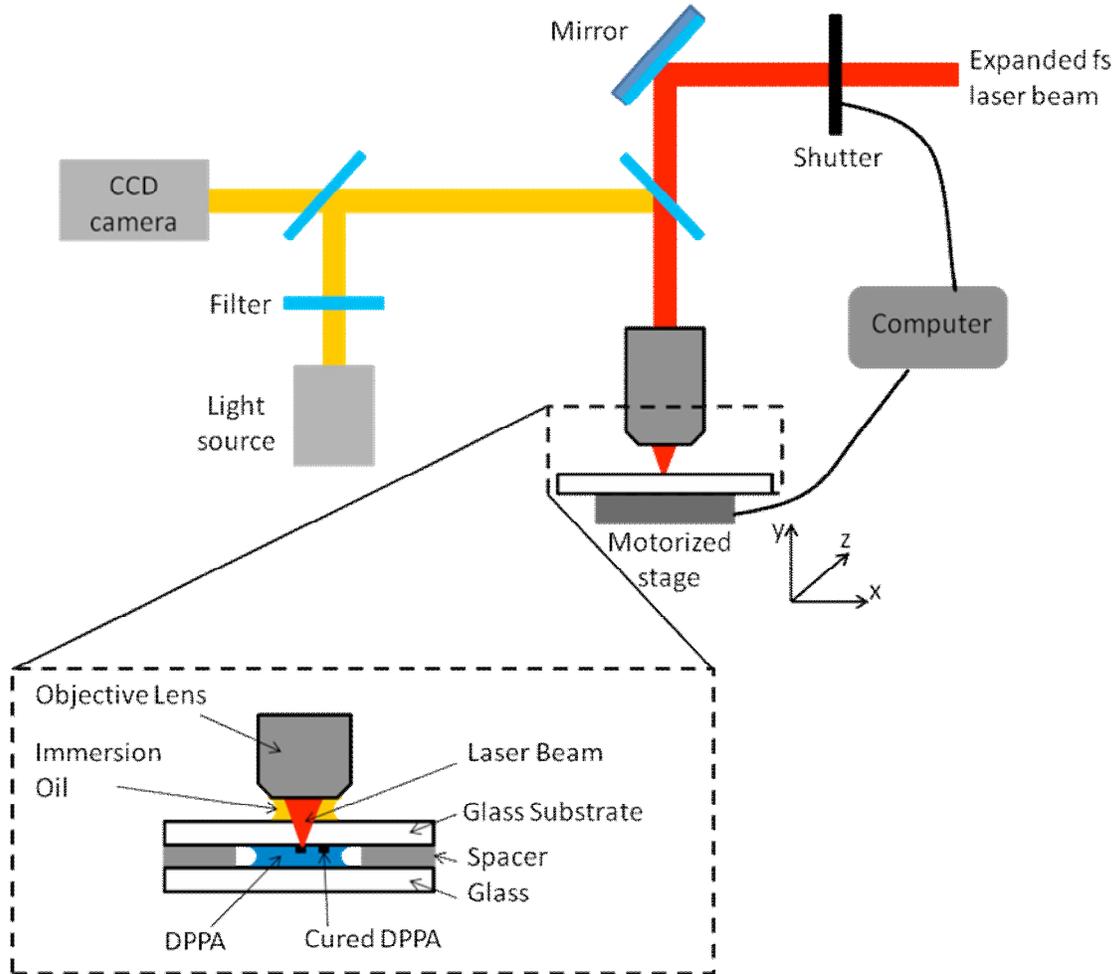


fig3.tiff

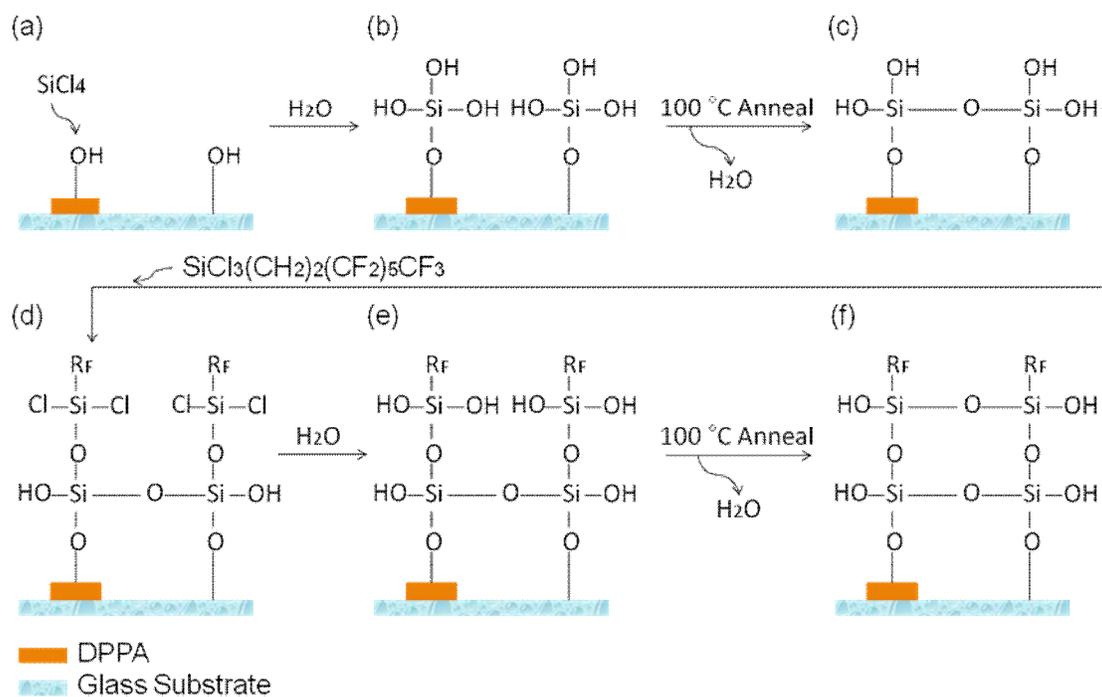


fig4.tiff

