

Nanofluidic Channel Based Single Molecular Sensors in Polymer Substrate Fabricated by Novel Nanoimprinting Processes

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ABSTRACT

A nanochannel based single molecular sensor was fabricated in poly(methyl methacrylate) substrate by a single step imprinting process with a polymer stamp. The sensor structure consists of hierarchical multiscale patterns of an array of 20 nm deep and 50 μ m long nanochannels and microfluidic networks. In contrast to nanofluidic devices fabricated by high-end nanofabrication tools such as focused ion beam milling and electron beam lithography, this direct imprint process is more desirable for efficient and low cost fabrication. Moreover, the use of high throughput molding or nanoimprint lithography process has been rather limited to the patterns in a thin polymer resist layer coated on a rigid Si or quartz substrate. In the fabrication of nanochannel sensors due to the reduction of stress generated during imprinting, this polymer stamp imprinting process can also reduce the deformation (warping) in molded substrates, and prevent the damage of expensive nanostructured stamp as well.

Keywords: nanochannel, nanoimprint lithography, polymer stamp, micro/nanofluidic system

1 INTRODUCTION

One critical challenge in developing innovative nanochannel-based sensors for bio/chemical analyses is to build multiscale structures composed of narrow, long and continuous fluidic nanochannels and microfluidic networks at low cost. High-end nanofabrication tools such as focused ion beam (FIB) milling and electron beam lithography have showed the capability to build long channels with diameter less than the persistence length of DNA [1-3]. However, the expensive equipment and complicated fabrication processes lead to high fabrication cost and therefore prevent its wide usage in large quantity. Alternative approaches to build nanochannels include sacrificial layer etching and elastic deformation of silicon [4, 5], or using the nanoscale crack and polymeric deformation of polydimethylsiloxane (PDMS) [6, 7]. With the latter methods, nanochannels with triangular cross-section were produced with the channel depth less than 30 nm, and width of 350 nm. Nanoimprinting lithography (NIL) process is a promising way to build uniform and sub-50 nm wide nanochannel

structures efficiently [8, 9]. However, most of the nanochannel structures produced by nanoimprinting process have been formed either directly in a thin polymer resist coated on a Si or fused silica substrate or in the substrate by a pattern transfer process after imprinting into the polymer resist layer [8, 9], which increases the production cost. Direct imprinting into commercially available polymer substrates such as poly(methyl methacrylate) (PMMA) or polycarbonate (PC) is most desirable for low cost fabrication, as can be seen in the fabrication of commercialized bioMEMS devices. However, the direct imprinting into polymer substrates with an inorganic Si or quartz stamp usually leads to rather severe, undesired deformation of channels such as warping and local substrate bending, making it difficult to leak-tight seal the fluidic channel with a cover slip in the subsequent bonding process [10, 11]. The expensive nanostructured stamp can also be damaged due to high stress generated during imprinting processes.

Here, we show a novel process using direct imprinting into polymer substrates to produce the nanofluidic sensor structure for single molecular analysis in a cost-effective way. The key for the process is to use polymer as stamp material. The use of polymer stamps is predicated by (1) a reduction in thermal stress generated during the cooling step due to the similar thermal expansion coefficients of stamp and substrate and (2) a reduction in adhesion at the stamp/substrate interface due to the low Young's modulus value of the stamp. Consequently, demolding becomes easier and the overall process cost can be reduced by the use of low cost polymer substrates and eliminating additional spin-coating and reactive ion etching processes which are needed when using a thin polymer resist layer coated on an inorganic substrate.

2 EXPERIMENT

2.1. Design of nanochannel sensor structures

The nanochannel-based sensor structure designed for single DNA molecular analysis is shown in Fig. 1. It consists of three parts: (1) an array of 50 μ m long nanochannels (about 15 nm depth and 200 nm width) (red area in Fig. 1), (2) microscale transport channels and reservoirs for inlet and outlet of reagents with the depth of

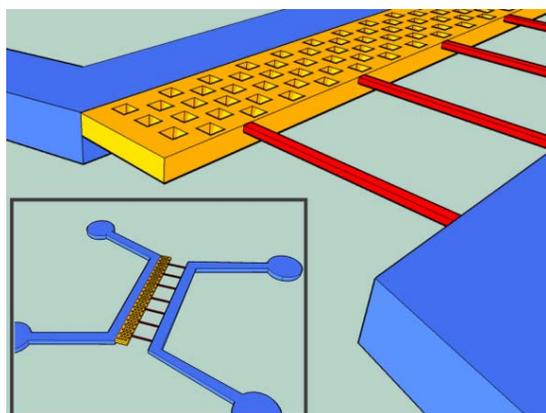


Fig 1. A schematic picture of the design of fluidic system. Inset: Top view of the whole structure

10 μm (blue area in Fig. 1), and (3) gradient interface and micropillars in the inlet of the nanochannels (yellow area in Fig. 1) where the microchannel depth reduced from 10 μm to 500 nm. The micropillars were added in the gradient interface in order to reduce the entropic gap of DNA molecules entering into the nanochannel from microscale transport channels.

2.2. Fabrication

The fabrication process consists of four major steps: (1) fabrication of the original master stamps with recessed micro- and nanochannel structures on Si substrates; (2) pattern transfer to a UV-curable resin by UV nanoimprinting to achieve polymer stamps with protruded structures; (3) nanoimprinting from the cured polymer stamp to PMMA substrates; (4) bonding with thin PMMA sheet. Figure 2 shows schematics of the fabrication process for direct imprinting into polymer substrate using a polymer stamp.

2.2.1. Master stamp fabrication

Silicon wet etching, dry etching and FIB milling were combined to build a hierarchy fluidic networks on the silicon stamp (Fig 2. (a)). First a Cr layer with thickness of 60nm was deposited on $\langle 100 \rangle$ surface of silicon wafer as etching mask. With conventional positive-photoresist photolithography and Cr wet etching procedure, etching windows were opened for reservoirs and transport channels. The exposed areas were then anisotropically etched to 10 μm in depth by 30% KOH solution, while the remaining Cr layer served as the mask during wet etching. After rinsed with DI water and dried by compressed nitrogen, the inlet of nanochannel and micropillars' pattern was defined by photolithography. The Cr layer in these areas was removed and reactive-ion etching (RIE) was used to etch 500 nm in depth. After removing the residual Cr layer and exposing the original silicon substrate, nanochannel arrays were milled with FEI Quanta 3D FEG. Finally, a monolayer of 1H,1H,2H,2H-perfluorodecyltrichlorosilane is coated from gas phase under vacuum condition in a vacuum chamber.

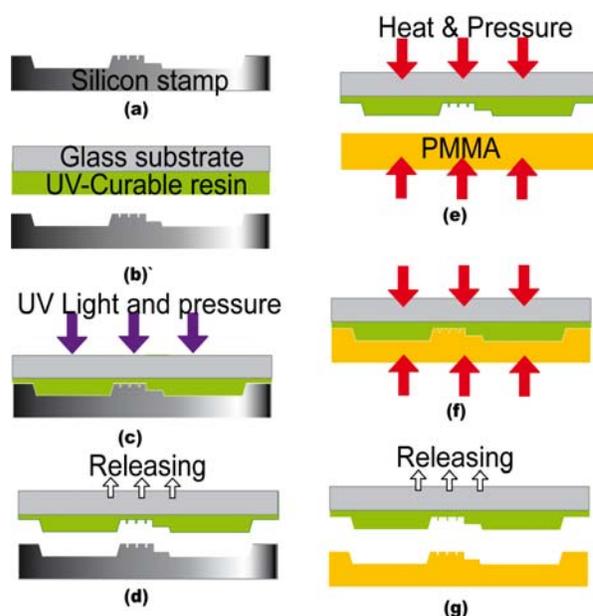


Fig 2. The Pattern transfer from silicon stamp to PMMA. (a)~(d) make protrusive stamp on UV-curable resin by imprinting from the silicon stamp; (e)~(g) Get nanofluidic structures on PMMA by imprinting from the UV-curable resin stamp

This layer acts as the anti-adhesion layer on the mold to facilitate the following demolding processes.

2.2.2. Fabrication of polymer stamp

A UV-curable polymeric blends containing 78% polypropylene glycol diacrylate (PPGDA), 20% trimethylolpropane triacrylate (TMPTA), and 2 wt% Irgacure 651 as the base, crosslinking agent and photo-initiator, respectively, were used as the UV resist to fabricate polymer stamps. After blending, those components were well mixed with a magnetic stirrer. Glass used as substrate was treated with oxygen plasma at 150 W for 3 min to enhance adhesion at the UV resin/substrate interface. The glass surface was coated with the UV resin by dispensing by a pipette (Fig. 2(b)). Then, the stamp was placed on the UV resin-coated substrate and gently pressed on it in order to ensure complete filling of the resin into stamp cavities. This was followed by an expose of UV light for 30 sec for curing. The UV lamp used for curing has an intensity of 1.8 W/cm^2 and the broadband wavelength with a cutoff angle of 400 nm and the maximum wavelength intensity at ~ 365 nm.

After curing, the UV-curable resin was gently demolded from the silicon stamp to get the negative copy on UV-curable resin (Fig. 2 (d)).

2.2.3. Imprinting in polymer substrate with polymer stamp

Nanoimprinting lithography procedure was carried out at 130 $^{\circ}\text{C}$ and 10 bar for 5 min, the demolding temperature is 70 $^{\circ}\text{C}$ (Fig. 2 (e~f)).

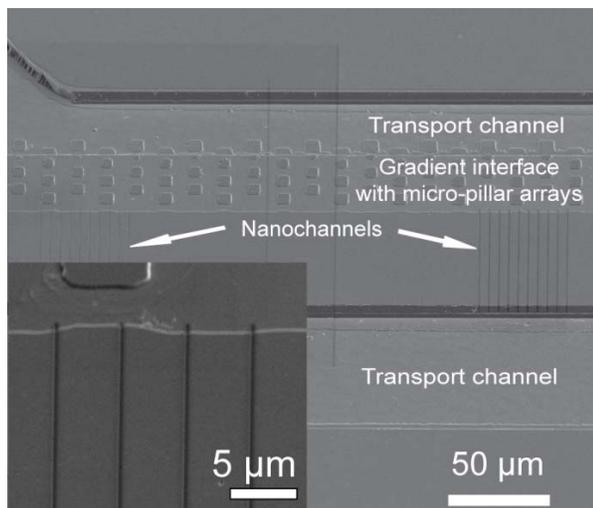


Fig. 3. The top view SEM image of the silicon stamp. Notice it is the same as the final structure on PMMA. Inset: Magnified view of nanochannels.

When the sample has been totally cool down, demold the PMMA substrate from the UV-curable-resin stamp, get the positive copy on PMMA. (Fig. 2(g))

2.2.4. Bonding

The PMMA sheet with pattern and another blank thin PMMA sheet (150um in thickness) was treated by oxygen plasma under 20W for 15s and then bonded together at 87°C under pressure of 20 bar for 30 min. The NIL machine was used for get a homogeneous pressure for the bonding process.

3 RESULTS AND DISCUSSION

Fig 3 shows an SEM image for the structure in original silicon master. The structure has the same pattern polarity

as the pattern in PMMA, where the designed nanochannels and microfluidic networks are patterned as recess, surrounded by a large unstructured area. This is made possible because the original master is copied twice to produce patterns in PMMA. Such process is advantageous over the stamp fabrication with protrusive nanowire structures to build nanochannel [8, 9]. First, the structuring of negative nanowires (or nanochannels) requires significantly less process time for FIB. Second, hierarchical photolithography and the subsequent Si etching processes (either RIE or wet chemical etching) can easily be applied to produce recess structures with different depths. Third, surface roughness produced in the stamp surface during Si etching is confined to the small structured areas, which will improve the subsequent UV-NIL process significantly by reducing adhesion at the stamp/resin interface.

Once the original master is fabricated, the hierarchical nanochannel sensor structure can be easily transferred twice into UV curable resist and then into PMMA by single step imprinting. Our results show that, regardless of the pattern size, all the structures in the original master and polymer stamp are well transferred. The fidelity of the pattern transfer was studied by atomic force microscopy (AFM), focusing on the changes in the dimensions of nanochannels. Figure 3 compares the AFM images of a nanochannel on the original Si master, cured polymer stamp, and imprinted PMMA substrate, respectively. The original channel fabricated by FIB on silicon is 212 nm in width and 15 nm in depth. After transferred to the UV resist, variations in the width and depth of the channel were negligible within 5%. The small change can be attributed to the relaxation of cured UV resist after demolding. The dimensional changes for the PMMA nanochannels produced by thermal NIL were rather significant. The variations in width and depth amount to 6.5% and 12.5%, respectively. We attribute it to the deformation of the cured UV resin in the stamp

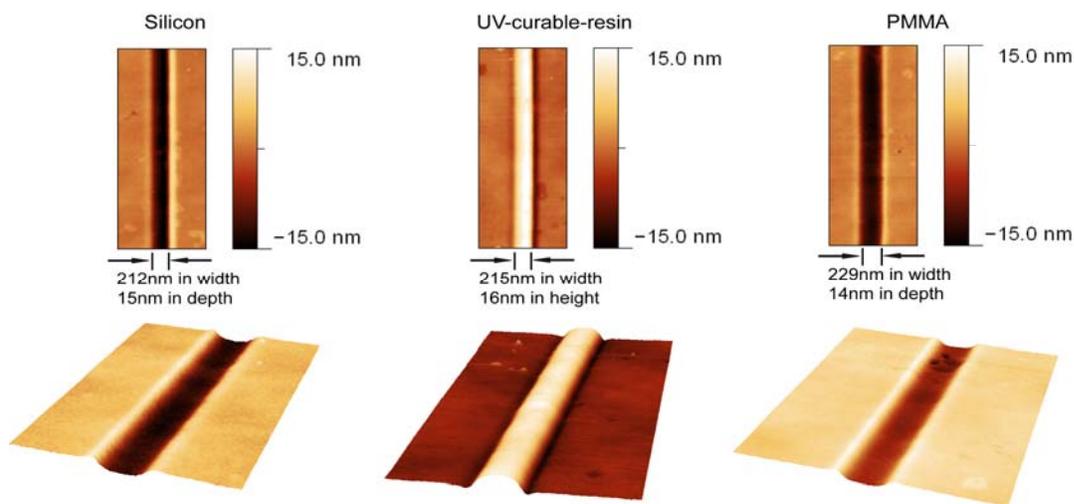


Fig 4. AFM image of nanochannel in silicon, UV-curable-resin and PMMA and the respective 3D patterns. Notice that on UV-curable-resin the structure is protrusive, while on silicon and PMMA the structure is concave. The lost of dimension in NIL process is less than 8% in depth and 4% in width.

structures upon high temperature and pressure applied during thermal NIL. The deformation became larger if thermal imprinting was operated under a lower temperature or shorter time. When using 300 μm thick glass slides as substrate of UV-curable-resin, 70% of pattern will not be transferred if temperature is less than 115°C and imprinting time is less than 3 min. On the other side, relatively higher imprinting temperature and longer imprinting time will improve the pattern fidelity from the cured UV-resist stamp to PMMA. Significant deformation (warping) in molded substrates did not occur during cooling and demolding unless the molding temperature is higher than 150 °C and pressure is larger than 20 bar. When the depth of the stamp structure was low (~ 20 nm), it was observed that the stamp becomes spontaneously separated from the molded substrate even without applying any forcible demolding. In addition, the breakage of the stamp, which is often observed in imprinting into polymer substrates, did not occur with the cured UV resist stamp and the stamp could be used multiple times without any damage.

With plasma treated glass as the substrate of the UV-curable-resin stamp, the stamp can be used for pattern transfer for many times. Most of the failures occurring in our process was peeling of UV resin from the glass substrate during demolding. This is due to insufficient adhesion between the UV resin and glass substrate. By treating the glass substrate with oxygen plasma for longer time and with high power, the adhesion at the UV resin/glass interface was improved and as a result, we could use a stamp more than ten consecutive imprinting processes.

4 CONCLUSION

We developed a novel fabrication process using a polymer stamp to direct imprint into PMMA substrate to produce hierarchical, multiscale structures. A nanochannel-based single molecular sensor with complex microfluidic networks was fabricated by this cost-effective method. Experiments showed good replication fidelity for the multi-replication processes. We also found that the undesirable deformation in the molded polymer substrate can be significantly reduced by using the polymer stamp.

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