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Pressure free nanoimprinting lithography using ladder-type HSQ material for LSPR biosensor chip

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ABSTRACT

We present an ingenious pressure free NIL (Nanoimprint lithography) method by simply employing a very thin PDMS mold along with a Spin-on-Glass HSQ material. Fabricating nano-patterns (i.e. nano-gratings and 2 D nano-arrays) via NIL is advantageous for LSPR based biosensors for producing large working area with high-throughput. Unlike conventional NIL and other fabrication methods, no complicated equipment is required in this work; only a simple heating plate (at 100 °C) was utilized for curing time reduction. Nano-pillar structure with definition down to 50–100 nm has been successfully fabricated using this method. After Au-deposition, mushroom like Au-capped nano-pillar chip has been successfully validated as a LSPR bio-sensor chip for IgA detection. In addition, this method provides promising features for higher dimensional structures fabrication which is considered as a beneficial tool for LSPR based biosensor sensitivity enhancement.

1. Introduction

The development of nano-fabrication techniques leads to further potential in nano-biosensing field in both sensitivity improvement matter and device integration perspective. The current trend in fabrication methods for nanostructure such as EBL (Electron-beam lithography), nanoparticle colloid assembly, etc. are either expensive, time-consuming, incompatible for large area formation, or not adaptable to various morphology design. On the other hand, since it's been firstly published by Chou et al. [1] in 1995, nano-imprint lithography (NIL) has been adopted to various electronics and photonics applications as a high-throughput nanostructure patterning method with promising fabrication resolution down to ~10 nm and also beneficial for mass production and large-area processing. NIL at room temperature (RT-NIL) has been attempted shortly after Chou's publication. Approaches to realize such process usually requires a curing method such as UV exposure [2] in order to maintain imprinted nano-pattern or demands higher pressure and immense imprint time to compensate the reduction of fluidity as a result of lower working temperature [3]. However, all features mentioned above requires a nano-imprint apparatus that makes the fabrication process limited to laboratories or facilities use only. With decades of development, NIL has entered the phase of seeking for minimal laboratory instruments and less labor involved while maintaining the high resolution and low-cost for mass production.

Slightly different from the imprint methods which use "hard mold" materials (i.e. Si, SiO_2 etc.), polydimethylsiloxane (PDMS) emerged as a soft lithography mold candidate. This is due to its flexible physical properties [4] making it adaptable for diverse nano-imprint application in planar or nonplanar situations (i.e. roll-to-roll [5]). In fact, the majority of soft nano-imprinting techniques employ a soft elastomeric stamp-like mold such as PDMS [6]. Moreover, mold-release preprocess wouldn't be necessary due to PDMS's low surface energy [7].

For RT-NIL, The fundamental idea is to vary the viscosity of the nano-imprint material without employing a thermal cycle circling around the glass transition temperature (T_g); deformation and solidification at room-temperature. The material is dissolved resulting to a gel-like fluid which enables the polymer to deform into the micro- and nano-scale surface relief features, and then the imprinted pattern is cured by evaporation. To fulfill this gelation process, the polymer material is permeated by an evaporable solvent (by solvent vapor treatment [8] or by solvent-assisted microcontact molding (SAMIM) [9]). Utilizing the air/gas permeability [10] of the PDMS mold, the solvent evaporation curing method for certain polymer resist can be done with the mold placed on top and within a relatively short imprint time.

Abbreviations: HSQ, hydrogen silsequioxane.

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Spin on glass (SOG) resist for RT-NIL was established by Matsui [11] and further improved by their group. Currently, HSQ (Hydrogen Silsequioxane), an inorganic copolymer resist consisted of repeating $HSiO_{3/2}$ units [12], collected wide attention in RT-NIL applications. Close to the idea of SAMIM, RT-NIL with liquid phase HSQ polymer could be considered as an apply-and-wick method. The polymer resist for nano-imprinting is spin-coated onto support substrates, followed by a pre-baking process in some cases. Shortly afterwards, soft PDMS molds containing nano-protrusions and channels are pressed onto the flowable polymer resist with adjusted imprinting force to ensure conformal contact. As hydraulic driven force is applied, the resist is deformed by the PDMS mold compliantly. RT-NIL using HSQ is mainly a series of gel transition events caused by polymer hydrolization, condensation, and evaporation [13].

The curing process of the resist containing HSQ molecules is based on the chemical reaction to the moisture in the air, which would cause hydrolysis while the solvent evaporates through PDMS layer. Silane groups (-Si-H) get replaced by silanol groups (-Si-OH), that follows condensation reaction which produces siloxane groups (-Si-O-Si-) causing molecule weight increase and, thus, hardening. Hence, the deformation achieved via molecule level modification of the resist ensures nano-scale patterning definition.

Adjustment of pressing force and the complying apparatus have always been the crucial parts to conduct such lithography evenly onto a planar or nonplanar substrate. Albeit room temperature nano-imprint lithography using HSQ resist with PDMS soft mold has been reported viable with relatively lower pressing force (less than 1 MPa–40 MPa [14]). Still, equipment for pressure control is essential in such cases. Therefore, in this work, a more spontaneous approach to perform this kind of nano-imprint while ensuring a fine definition is proposed. By using which, we managed to fabricate a nano-pillar array structure with under 50 nm pillar diameters and a pitch of 110 nm level resolution.

Our experimental results suggested that thinning the PDMS mold has facilitated efficient solvent evaporation without further concerns about the PDMS absorption saturation. By using PDMS with higher Young's modulus (hard type PDMS), the challenge of patterning fine nanostructure under 500 nm has been overcome. With the reduction of the PDMS thickness, the overall flexibility and the local contact rigidity had better outcome.

NIL has been stretching out its applications for the fabrication in various biosensor sub-categories [15]. In this study, the utility of the fabricated nanostructure for immunoassay based on LSPR detection will be disclosed. A disposable component combined with a permanent instrument [16] is considered as ideal for sensing devices with concepts like in lab-on-chip or point-of-care testing (POCT). The fabrication of the disposable component greatly influences the cost of production. Hence, in this work, our novel NIL method which is capable of being performed at room-temperature with no requirement of pressing-force can save the production time and cut the production cost greatly while still suitable for large area fabrication with high-definition.

LSPR biosensor was firstly reported by Englebienne in 1998 [17], even before then, the LSPR phenomenon occurred in the vicinity of roughened metallic surface has been studied in various prospects [18]. LSPR biosensor chips have captivated prevalent attention for a great diversity of bio-molecule detection in a label-free sensing manner [19]. It's sensitive to the permittivity changes in the vicinity of metallic nanostructure caused by bio-molecules adsorption [20].

Immunoassays performed on LSPR substrates are based on specific antibody immobilization. These pre-installed selective antibodies only bond to particular target antigen molecules. In effect, these binding events will lead to a permittivity change in the vicinity of structure metallic surface. By comparing the absorbance/extinction spectra peak position, before and after the introduction of the specimen, the presence and concentration of target antigen molecules can be determined [21,22]. Unlike conventional ELISA (enzyme-linked immunosorbent assay), of which selectivity is established by adding labelled specific antibody after sample antigen deposition, LSPR immunoassay is faster and label-free while maintaining the same level of sensitivity.

In our previous work, gold capped nano-pillar structured polymer film substrate for LSPR biosensing has already been reported. The nanostructures served as a design template leading to a relatively uniform distribution of gold aggregates. This is expected to enhance the signal-to-noise ratio [23]. However, this was done using a thermal nano-imprinting system including a vacuum chamber. To step up further from our previous study, in this work, a sub-wavelength dimension nano-pillar structure was successfully fabricated by using the pressure-free NIL method which requires neither sophisticated instruments nor long curing period. In this method, low concentrated ladder-typed HSQ resist and a thin film-like PDMS mold were utilized for the fabrication. Choosing HSQ material for our LSPR substrate preparation is also suitable due to its high transparency in UV–Vis range and preferable refractive index properties [24]. The whole procedure could be carried out in merely 40 minutes; moreover, with a little help from a simple heating plate to accelerate the solvent evaporation, the execution time can be further narrowed down to within 10 minutes. This makes it an innovative method to conventional nano-imprinting technology in both time and financial aspects. Subsequently, Au sputtering was performed to activate this nano-pillar structure into a plasmonic substrate. Optical properties were investigated via refractive index change response. And later on, the bio-sensing capability has been demonstrated through a specific antibody-antigen detection. Immunoglobulins (Igs) are a class of gamma globulins that react to specific antigens and have been studied as immunomarkers for their response to antigenic stimulations [25]. In this work, as a model for Igs immunoassay, IgA detection was successfully conducted using our Au-sputtered nano-pillar substrate while in comparison to CRP(c-reactive protein) as a negative control sample.

2. Materials and methods

2.1. Fabrication of master mold

Here, the self-organized nano-structures were prepared using anodic oxidation of aluminum. The dimensions of nano-porous structure in AAO (Anodic aluminum oxide) can be controlled by varying the anodizing conditions and preprocesses [26]. The procedure carried out with a two-stage strategy which has been reported in our previous work [23]. In order to form a regionally relative periodic hexagonal porous structure, high purity aluminum substrate was annealed, polished, acetone sonicated and, then chromic acid etched before use. A 40 V voltage was applied for 6 hours at 0 °C as the first stage of oxidization. Then, a 10 minutes chromic acid etching session at 70 °C was done right after. Another 40 V anodizing session was conducted for 150 seconds as the second stage of oxidation. Finally, a phosphate acid wet-etching process for pore widening to complete the AAO substrate was performed at 40 °C for 7.5 minutes. The resulting product served as the master mold. The nano-porous structure would be then transferred onto a COP (cyclo-olefin polymer) film (188 μm) through thermal nano-imprinting. The COP nano-pillar structured substrate was employed as secondary mold afterwards.

2.2. Fabrication of PDMS mold

A thin PDMS soft mold (width × length: 2 cm × 1.7 cm, thickness ≈ 180 μm) was fabricated with the same thermal nano-