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Improved PDMS mold fabrication by direct etch with nanosphere self-assembly mask for Soft UV-NIL subwavelength metasurfaces fabrication

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Abstract

With the increased relevance of metasurface for optical applications, a fabrication method that allows for both large surface and sub-100nm dimensions at a low cost is required for their development. Due to its high throughput and small structuration capabilities, Soft Nanoimprint Lithography is a good candidate as fabrication method for these type of devices. But its application for metasurfaces at visible wavelengths has been hindered by the necessity to use low-viscosity polymers in order to reach the dimensions required, making the final stamp more fragile and the process more expensive and complicated. Here we propose a PDMS mold fabrication method which relies on self-assembly masking of the PDMS followed by direct etching of the mold, decorrelating the minimum dimension attainable from the polymer viscosity. We characterize a metasurface fabricated using a mold obtained with our method validating its use for nanofabrication of large surface devices.

Keywords: Soft UV-NIL, PDMS etch, self-assembly, metasurfaces

1. Introduction

In the recent years, devices with the capacity to control and manipulate light-matter interaction have attracted the attention of the research community. This type of devices was made possible thanks to metasurfaces whose optical properties are not achievable in conventional materials. Metasurfaces are made of subwavelength elements that are repeated all over the surface. By changing these elements composition, size, shape and periodicity

we can control the properties beyond what is possible with natural materials. Many applications that make use of these exotic properties have been demonstrated, from holography [1] to color generation [2, 3, 4] or even metamaterials [5]. One of the limitations of these structures is their fabrication over a large surface required to use them in real-world applications. In this context Nano-Imprint Lithography (NIL) is a very good solution to fabricate them since the nanostructured pattern can be reproduced several times on the same substrate. NIL was first proposed by S. Chou et al [6]. The process consisted in using a hard mold to imprint onto a thermoplastic material which was heated up. In 1996 a method using a UV-curable polymer [7], instead of a thermoplastic material, was proposed solving the problems brought about by the thermal expansion and contraction of the materials. Works have shown that this technique can reach the sub-10nm range [8, 9]. In order to improve the molds conformity to rough or even curved surfaces a method called Soft UV-NIL was created with replacement of the hard mold by a polymer based soft mold [10, 11]. This version of NIL is the one that shows the most promise of use in large scale fabrication of metasurfaces due to its capacity to produce subwavelength structures over a large area with a high throughput. An important step of this technique is the polymer mold fabrication which is usually obtained using a molding technique. A silicon master, which is the negative of the final mold desired, is fabricated, often by using e-beam lithography. The polymer is molded onto the silicon master and reticulated by heating. Polydimethylsiloxane (PDMS) is considered as the standard transparent flexible material for Soft NIL processes due to its UV-transparency, its mechanical properties, and its simplicity for casting. The main factors limiting the smallest dimensions attainable with this technique are related to the smallest feature size that the PDMS can fill due to its viscosity [12] and to the wettability of the master [13]. Solutions to this issue have been proposed like using Hard PDMS [14] which has a lower viscosity, by diluting PDMS in a solvent [15] or using a combination of hard and soft layers [16, 17]. However, these solutions result in more fragile molds that can be used less times, and finally require the fabrication of new molds increasing the overall cost of fabrication. In this work we propose a novel mold fabrication method which bypass several costly or risky technological steps. The mold is done by direct nanostructuring of a polymerized PDMS layer: PDMS is etched through a mask obtained by self-assembly polystyrene (PS) nanoparticles [18]. This technique is suitable for low-cost and large surface fabrication of nanostructures. We first detail the self-assembly technique of

monolayers of polymer nanoparticles and their deposition onto a PDMS film. This technique has been improved to maximize the surface of the obtained monolayer and to minimize the disorder during the self-assembly and deposition. We then present the process for direct nanostructuring of the PDMS by etching and lastly, we demonstrate the use of the obtained PDMS mold for fabrication of large surface plasmonic metasurfaces by Soft UV-NIL.

2. Fabrication

The overall fabrication process is composed of 3 steps: (1) the deposition of a monolayer of PS particles onto a PDMS film, (2) the mold fabrication by etching the PDMS film, and (3) the Soft UV-NIL process using the realized mold to fabricate large area metasurfaces. The full process is schematized in Figure 1, and detailed in the next three subparts.

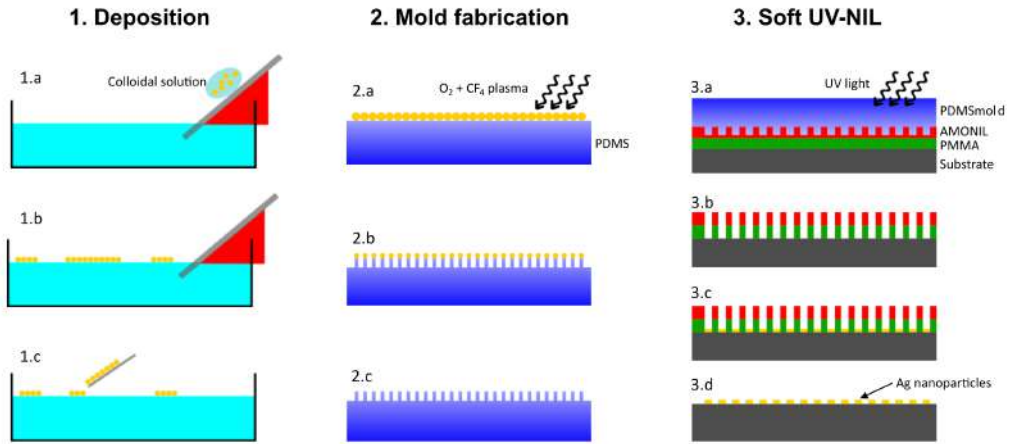


Figure 1: Full fabrication process. 1) Particle deposition process 1.a) The PS particles in a colloidal solution are deposited onto the blade 1.b) Particles go from the blade to the water surface 1.c) The particles are deposited onto the PDMS film 2) Stamp fabrication process 2.a) The self-assembled particle structure is transferred onto the PDMS with an $O_2 + CF_4$ plasma etch 2.b-c) After an acetone cleaning we obtain a PDMS stamp for NIL 3) Soft UV-NIL process 3.a) The stamp is placed on the substrate recovered by a layer of PMMA and Amonil. The sample is exposed to UV light to reticulate the Amonil resist 3.b) The residual layer of Amonil and the PMMA layer are etched away 3.c) An Ag layer is deposited onto the sample 3.d) The PMMA is removed leaving only the substrate with Ag NPs (lift-off.)

2.1. PS nanoparticles monolayer deposition onto PDMS film

In order to have a deposition of the PS nanoparticles with the lowest amount of disorder, our PDMS film must have the minimum amount of surface irregularities possible. In consequence a layer with the RTV 615 from ELECO PRODUITS composed of a specific dilution of 93wt% PDMS and 7wt% of reticulating agent is obtained by spin-coating at 200 rpm on a silicon wafer. The PDMS is then degassed at room temperature of 1h and baked at 80°C for 30 minutes to reticulate. The film is then inverted to do the deposition on the smoother surface which was in contact with the silicon. The samples are cleaned in an ultrasonic bath with ethanol for 20 minutes and then put in an O₂ plasma for 20 minutes to make the surface hydrophile for the PS deposition. To obtain a self-assembled structure with sub-wavelength dimensions we use a 50:50 solution of DI and ethanol with a concentration of 13g/l of PS nanoparticles with 200nm in diameter [19]. The particles are deposited on to the surface of a DI solution with Sodium dodecyl sulfate (SDS) through a glass blade tilted at 45° degrees, which is placed on a blade holder fabricated specifically for this purpose to insure stability. The self-assembled layers we have obtained with this method have, consistently, over 1cm² in area. The hydrophile layer of PDMS is then dipped into the water solution, placed under a nanoparticles layer and removed from the solution, recovering the layer on its surface. The whole process was done by hand which further demonstrates the simplicity of this process. In Figure 2(a) we can see the resulting structure deposited onto the substrate. We have obtained many areas with a perfect hexagonal structure on several tens of μm² and with a few defects between those areas. The homogeneity of the structure was good across most surface with more defects appearing close to the edge of the deposited surface.

2.2. Structure transfer by PDMS direct etch

The PDMS is then etched through the PS NP mask by RIE, with 40sccm of CF₄, 20sccm of O₂, 50W and 100mTorr. After the etch, the remaining PS particles are removed in a ultrasonic bath with acetone for 5 minutes. The resulting PDMS mold was characterised with AFM measurements in tapping mode (Figure 2(c)). The pattern transferred into the PDMS presents good homogeneity over many mm². The mold presents a vertical feature size of over 60nm across most of the surface.

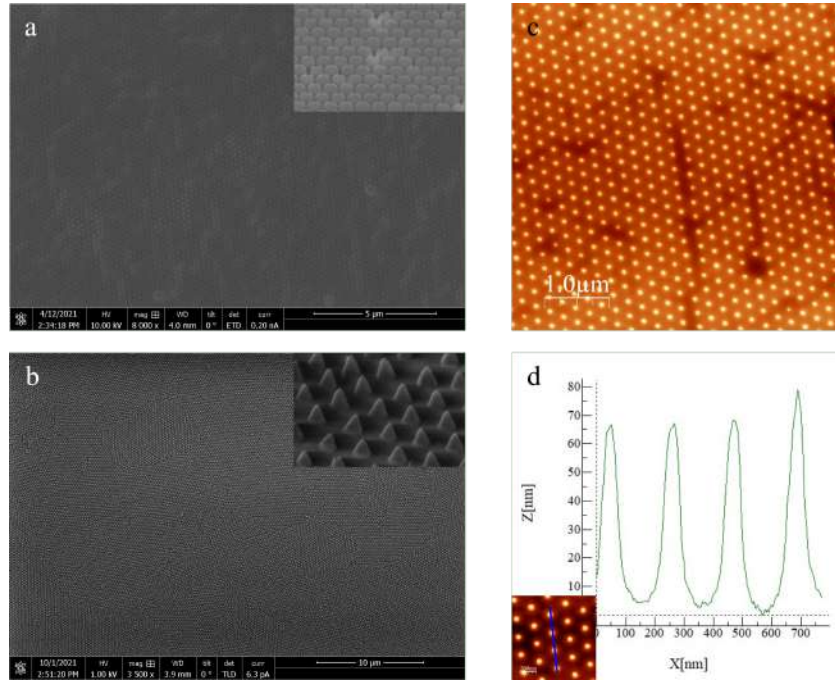


Figure 2: a) SEM image of PS NP after deposition onto the substrate, b-c) PDMS substrate after etching with MEB and AFM respectively d) PDMS mold profile

2.3. Fabrication of the metasurface

The design of the metasurface is inspired from Bertin et al.[4] where the plasmonic resonance of the Ag nanoparticles was used to control the reflectance and transmittance spectra of a glass substrate. Here we first consider a silicon substrate. A Si wafer was cleaned for 5 min in an ultrasonic bath with acetone and dehydrated in a heating plate at 90°C for 10 min. PMMA is used as a lift-off layer. It was spun at 3000 rpm followed by a bake at 180°C for 10 min to obtain a 180 nm layer. The top resist for the UV-NIL process is Amonil, a UV-curable resist from AMO-GmbH, which we spin at 8000 rpm to obtain a 110 nm layer. The PDMS mold is placed on top of the Amonil/PMMA layer. Only the weight of the stamp ensures the imprint pressure. The sample is then exposed to UV light (Hamamatsu LC8 at 365nm) for 2 min to reticulate the Amonil resist layer. The residual layer of the Amonil is removed with a RIE etch with 2sccm O₂, 20 sccm CHF₃, 25W and 7mTorr. PMMA is then etched away with 10 SCCM O₂, 15W and 4mTorr. The last step is the metallic evaporation of 1nm of Ge at a rate

of 0.01nm/s followed by 30nm of Ag at a rate of 0.1nm/s. The PMMA is then lifted off with butanone. The largest metasurface fabricated with this technique had an area of 0.67cm².

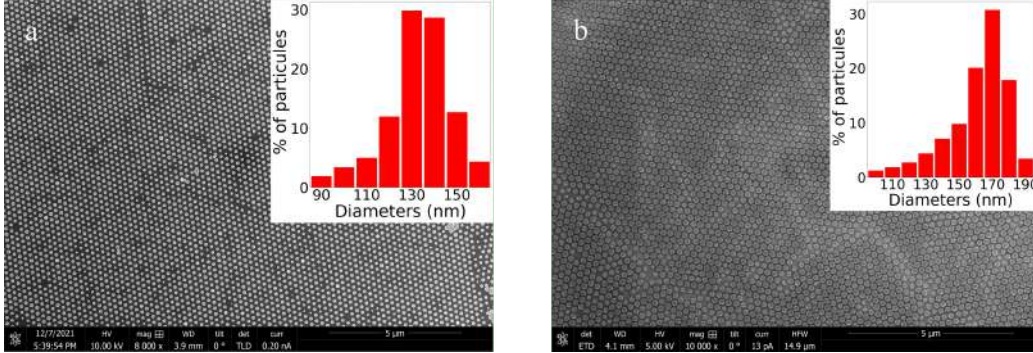


Figure 3: a) Metasurface obtained from Soft UV-NIL with PDMS mold on silicon substrate (inset) Histogram of particle size distribution. b) SEM image of the metasurface on glass (inset) Histogram of particle size distribution,

3. Characterization of the metasurface

To characterize the optical response of the structure the process described above was also done with a glass substrate, with the same stamp. In order to compare the sample fabricated on glass with the one on Si, the sizes of the silver particles of each structure were measured using an image processing program. We used SEM images of each sample with a resolution of 3nm/pixel. For the Si sample a total of over 49k particles were measured (for a total surface of 2300 μm^2). The histogram of diameter distribution is presented in Figure 3(a): the maximum of occurrence is at 130 nm with an average of 132.4 nm. The same measurement was done with the structure fabricated on glass considering a total of 55k particles (for a total surface of 2760 μm^2). The histogram of size distribution is presented in Figure 3(b). Here the histogram maximum is at 170nm, but the average diameter is 160.9 nm. The average is shifted down from the maximum of the histogram because of breakage of the silver particles which, in certain areas, made their diameter smaller. When compared to each other we can observe that the glass sample particle diameter is shifted to higher values and has a higher size dispersion. These two differences are likely related to the nature of the substrate, possibly during the resists etch step, since both of the samples

were fabricated from the same PDMS mold. The sample fabricated on glass was characterized in an angulo-spectral transmittance measurements bench. A Tungsten-Halogen (Horiba LSH-T250) was used as a light source coupled to a monochromator (Horiba iHR 320). The measurements were done with a slit opening in the monochromator of 1 mm, at normal incidence. In Figure 4 we present the measured and simulated transmittance. The simulations were done using the commercial software Ansys Lumerical FDTD Solution, considering Ge and Ag optical data from CRC Handbook of Chemistry & Physics [20]. We simulated the optical response of a ‘single domain’ hexagonal structure with 210 nm particle distance (real distance after fabrication) composed of NPs with 160 nm diameter, 1 nm Ge thickness and 30 nm Ag thickness. The transmittance spectra have similar widths, which means that the silver nanoparticles sizes must be quite homogeneous in the test area (corresponding to the test light beam section). However, by considering different test areas, the transmitted dips values oscillate from 21% down to 12% for wavelength between 590 to 650 nm. This inhomogeneity is attributed to spatial density and size variations over the whole structure. Indeed, the interval of wavelength values for the dips correspond to the resonant wavelengths for particles with diameters between 160 and 185 nm which corresponds to the diameter values with higher percentage in the histogram of particle size.

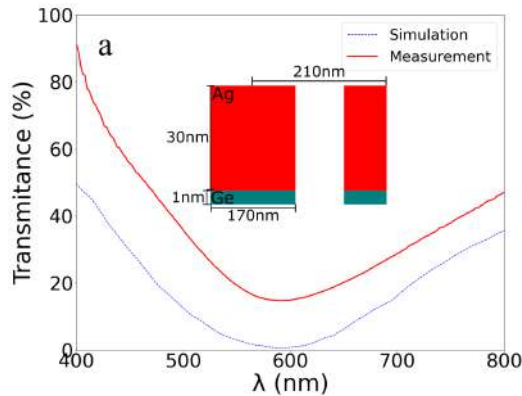


Figure 4: Measured and simulated transmittance (right).

4. Conclusion

A new method to fabricate nanostructured PDMS molds has been demonstrated. The use of direct etching makes the dimension limit decorrelated

from the viscosity of the mold substance, unlike usual mold fabrication method. This method enables to fabricate structures with dimensions in the 100nm range with the potential to reach even smaller sizes with further improvements. Additionally, we have shown that self-assembled PS NP layer pattern can be also transferred directly into PDMS films: this technique is low-cost and can produce large surface devices using standard techniques and machines that can be found in most cleanrooms, making it compatible with industrial fabrication. Moreover, the presented process could be generalized by using other types of mask fabrication on PDMS allowing for more complex structures to be fabricated with this method.

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