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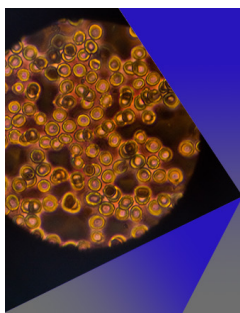
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Soft nanoimprint lithography on SiO₂ sol-gel to elaborate sensitive substrates for SERS detection

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This paper presents a new alternative fabrication of biochemical sensor based on surface enhanced Raman scattering (SERS) by soft nanoimprint lithography (S-NIL) on SiO₂ sol-gel. Stabilization of the sol-gel film is obtained by annealing which simplifies the manufacturing of these biosensors and is compatible with mass production at low cost. This detector relies on a specific pattern of gold nanodisks on a thin gold film to obtain a better sensitivity of molecules' detection. Characterizations of SERS devices were performed on a confocal Raman microspectrophotometer after a chemical functionalization. We report a lateral collapse effect on poly(diméthylsiloxane) (PDMS) stamp for specific nanostructure dimensions. This unintentional effect is used to evaluate S-NIL resolution in SiO₂ sol-gel. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5004122>

I. INTRODUCTION

Raman Spectroscopy is an efficient analysis technique to characterize chemical composition of molecules, this optical characterization is relied on inelastic light scattering^{1,2} though for low concentration it gives a weak signal. To overcome this limitation, rough metallic surfaces or metal nanostructures or both can be used.^{3,4} This method refers to surface enhanced Raman scattering (SERS) and thus allows to identify precisely the molecules with their specific peaks and high enhancement factors. The interest to develop new SERS-based spectroscopic sensors combined with other spectroscopic detections for chemical or biological applications were increased during these past few years.^{5,6} Sample design used in this work with thin gold film under nanostructures has been already reported for his interest in SERS and Surface Plasmon Resonance Imaging (SPRI).⁷⁻⁹

To pattern such device two kinds of lithographic processes can be used. The first one, referenced as conventional like electron beam lithography (EBL) requires long writing times for large areas and a significant cost for large sample productions. The second one, considered as a next generation lithography is nanoimprint lithography (NIL) which is rapid, with low cost fabrication, and allows large area structuring. The principle is to pattern a polymer with a mold which may be rigid or flexible. Two main ways in NIL have been developed, thermal process (T-NIL), commonly known as hot embossing lithography (HEL), demonstrated for the first time by S. Y. Chou in 1995¹⁰ and UV-NIL developed by J. Haisma from Philips research laboratories in 1996.¹¹ Thermal NIL

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allows high resolutions but needs high pressures (between 20 and 100 bar) and high temperatures to reach glass transition temperature (T_g) of the imprinted polymer.¹² While UV-NIL resists are liquid and UV-curable, advantages are patterning at low pressures and carried out at ambient temperature. It requires a transparent mold or substrate. With this method, mainly two techniques can be distinguished: Hard UV-NIL and Soft UV-NIL. The first uses a rigid transparent stamp, generally in quartz,^{13,14} which permits to achieve high resolutions close to those obtained by EBL. However, with a non-planar surfaces, critical resolutions cannot be reached. In this case, Soft UV-NIL is useful thanks to the use of a flexible stamp which can be conforming to the shape of the surface. A common polymer material used as flexible stamp is poly(diméthylsiloxane) (PDMS) in early works^{15–19} for its interesting physical properties such as flexibility, elasticity, low surface energy, and UV-transparency.

To improve performances of Soft UV-NIL, technological developments have mainly focused on new processes for mold's manufacture with new polymers,^{20–24} new resists and anti-sticking treatment.^{25–27}

Among recent developments for NIL resists, sol-gel resist appears as an alternative.^{28–30} Sol-gel is based on the polymerization of inorganic monomers to obtain partially or totally mineral films. The polymerization uses a soft chemistry method which relies on controlled reaction mechanisms, taking place in liquid solution and usually at ambient temperature. These mechanisms are based on the transformation of a liquid solution (sol) into a solid material (a dry gel called xerogel) via an inorganic polymerization process. Then sol-gel thin film can be stabilized and cured either by annealing^{31,32} to permit the evaporation of residual solvent still present inside the xerogel thin film or by photocuring.³³ The interest to use such inorganic polymers as material for nanoimprint lithography has been growing over the last decade.^{28–30} In another way, studies have shown the benefit of using sol-gel films directly to obtain rough surfaces which promote the production of SERS signals.³⁴

In our study, we have developed a new method for the manufacturing of SERS sensors with different sizes and pitches of gold nanodisks on gold film. This alternative technique is based on a soft nanoImprint lithography (S-NIL) in SiO_2 thermo-curable sol-gel deposited on a sacrificial resist layer and a lift-off process to obtain gold nanodisks. The added value of this fabrication method with respect to classical UV-NIL process is the replacement of an UV-curable resist by a thermo-curable one. This offers the possibility for other applications requiring a stamp and substrate together opaque to UV light. Thereby this method makes it possible to produce easily sensor with large quantity comparable to previous soft method.³⁵ Hence, we have patterned various holes' diameters (150–400 nm) with a periodicity of 400 nm and 600 nm on the bilayer resists (SiO_2 sol-gel/PolyMethyl Methacrylate A2) with a flexible stamp and without external pressure. PMMA resist is used for the lift-off process after gold deposition. Then we report on optical characterizations of the device with thiophenol molecules ($\text{C}_6\text{H}_6\text{S}$) by SERS measurements. For specific dimensions, we obtained a lateral collapse of pillars on PDMS stamp. This unintentional effect has been used to evaluate print resolution in SiO_2 sol-gel.

II. EXPERIMENTAL

A. PDMS stamp fabrication

First step to obtain soft NIL stamp is the silicon master mold fabrication using an electron beam lithography system (NB4 from NanoBeam Limited, UK). Exposure was performed on PMMA A4 resist (200 nm) using an accelerating voltage of 80 kV and a current of 2 nA. After development in methyl isobutyl ketone/ isopropanol (MIBK/IPA) (1/3, 1min 30sec) and a rinse in IPA (30 sec) a reactive ion etching (RIE) process has been optimized to transfer nanoholes into a silicon substrate. To compare SERS intensities versus structures' density several holes' patterns were designed (300 μm *300 μm of lateral dimensions) with diameters (D) ranging from 150 nm to 350 nm for two periods (P) 400 nm and 600 nm on the same master mold. Before cast molding, an anti-adhesion layer treatment based on trimethylchlorosilane (TMCS) was used to reduce surface energy of the silicon and make easier the demolding step. Then to reduce PDMS's viscosity and improve the penetration of the polymer in nanoholes, we used 5% hexane diluted standard PDMS (RTV615). The mixing

solution with his curing agent (1 curing agent : 5 PDMS) ration by weight, is deposited on Si master mold and cured at 60°C during 4 h.

B. Gold nanodisk fabrication and thiophenol molecules deposition

Gold nanodisks on continuous film were obtained by a nanoimprint lithography in SiO₂ sol-gel and lift-off process with the bilayer resist method. As sol-gel is an inorganic thermo-curable polymer we have used a sacrificial PMMA A2 layer spinned on a glass substrate previously covered with 2 nm of Ti and 30 nm Au layers. These metallic layers were obtained using a Plassys evaporator equipment. The sol-gel used in these researches provides from SILSEF Company. 90 nm thick layer was deposited by spin coating on 120 nm PMMA layer before manual imprint with the flexible stamp. An annealing at 110°C during 10 sec was done before demolding. Etching process of the sol-gel and sacrificial layer have been performed by a RIE equipment (STS). RIE process for sol-gel was based on 50 sccm CHF₃, at low pressure (15 mTorr) and 325 W power. For PMMA resist, etching was adjusted with 10 sccm O₂, a chamber pressure of 4.7 mtorr, and 10 W power and stopped when the level of gold film is achieved. Then, an Au layer (30 nm) is evaporated and sol-gel was removed by a lift-off process in acetone thanks to the PMMA underlayer. To test SERS sensitivity of this substrate, functionalization was performed with thiophenol (C₆H₆S) molecules before characterizations. Samples were immersed in 0.1 mM solution of thiophenol for 2.5 h and rinsed in ethanol for 5 min before dried up with nitrogen.

III. RESULTS AND DISCUSSION

A. Flexible stamp

As describe above the flexible stamp was obtained by a molding process on a silicon master mold on which several holes networks with different diameters have been patterned by E-beam lithography. Figure 1(a) shows an AFM view of PDMS stamp with dots. They have a conical shape with a diameter (D) of 200 nm at half of their height (h= 210 nm) and a periodicity of 600 nm. This shape is the result of an optimized etching process in Si master mold.

In Figure 1(b) AFM view for diameter 200 nm and periodicity of 400 nm shows a lateral collapse effect where PDMS pillars stick to each other randomly. Dilution has permitted to obtain aspect ratio (h/D) 1.4 but greater than critical aspect ratio.²³ This unintentional collapse effect was particularly interesting because it allowed us to evaluate ultimate imprint resolution in sol-gel resist.

B. Nanoimprint in sol-gel and gold nanodisks

Printing tests were performed by placing gently the flexible stamp on top of SiO₂ sol-gel layer, without any additional pressure.¹⁷ An annealing at 110°C during 10 sec was used to cure the resist. After annealing, stamp was released leaving the sol-gel patterned. Figure 2 shows SEM views of the imprint results.

Figure 2(a) is a SEM tilted view of the imprint in SiO₂ sol-gel. The residual layer thickness obtained was lower than 10 nm. When diameter increases to 200 nm with the same period, we obtain figure 2(b) result which corresponds to the imprint with the PDMS stamp having lateral collapse

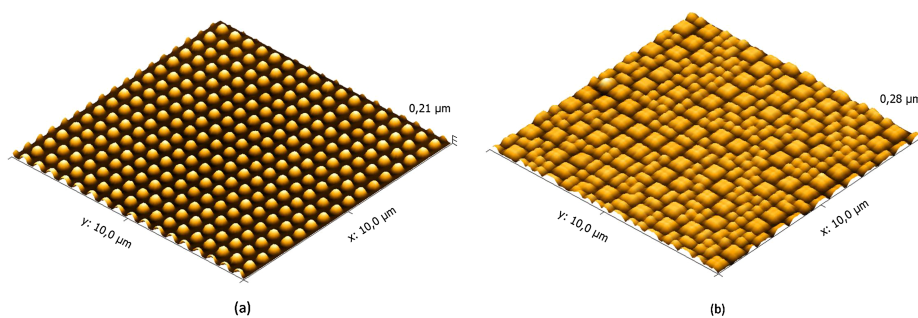


FIG. 1. AFM images of stamp PDMS: with diameter 200 nm pitch 600 nm (a), diameter 200 nm pitch 400 nm (with collapse effect of simultaneously 2 or 4 dots) (b).

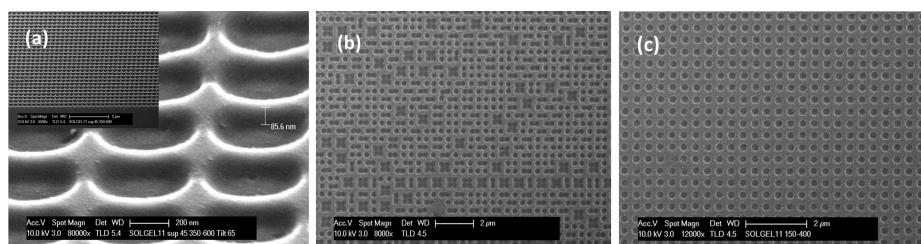


FIG. 2. SEM images of the imprint in SiO₂ sol-gel: diameter 350 nm and periodicity 600 nm (a), diameter 200 nm and periodicity 400 nm with a collapse effect (b), diameter 150 nm and periodicity 400 nm (c).

effect. Figure 2(c) shows an imprint with diameter 150 nm and pitch 400 nm. Diameter 150 nm is the lower limit that we can obtain in a reproducible manner with a PDMS. We can notice a consistent transfer with the stamp. Etching processes of sol-gel and PMMA was performed as described in “EXPERIMENTAL” section and stop at gold film. A gold deposit (30 nm) and lift-off process in solvent with ultra sonic were performed to obtain gold nanodisks as shown in Figure 3. Figure 3(a) shows regular dot arrays with diameter 230 nm and pitch 600 nm. A certain roughness around gold nanodisks is attributed to the RIE process of SiO₂ sol-gel, this was confirmed by a SEM observation after etching step. This process step also induces also the widening of the nanostructures.

Figure 3(b) shows gold nanodisks for diameter 200 nm and pitch 400 nm. We can notice a gold nanostructure randomization due to the lateral collapse effect in PDMS which has been transferred until this last step. Some discs can touch each other with a random distribution. As shown in black square, others are very close with a gap smaller than 50 nm. Hence, this result shown in Figure 3(b) makes possible to evaluate a print resolution in SiO₂ sol-gel around this value.

C. Optical characterizations

To characterize the performance of substrate as a sensor, SERS measurements were performed on several nanostructured areas functionalized by thiophenol molecules. Some Raman characteristic peaks of thiophenol molecules are 419, 1000, 1075, 1575 cm⁻¹. These Raman spectra were recorded using a XploRA spectrophotometer from Horiba Scientific. The acquisition time was fixed to 30 s. A 638 nm laser was used for these measurements with a power of 2.6 mW. The laser excitation was focused on the substrate using a microscope objective (x20, N.A.= 0.7). The same objective was used to collect the Raman signal from the SERS substrates in a backscattering configuration. SERS spectra were recorded with a spectral resolution under 4 cm⁻¹.

Figure 4 shows an increasing SERS signal versus nanostructures density as expected. We calculated enhancement factor (EF) defined by the following equation:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}} \quad (1)$$

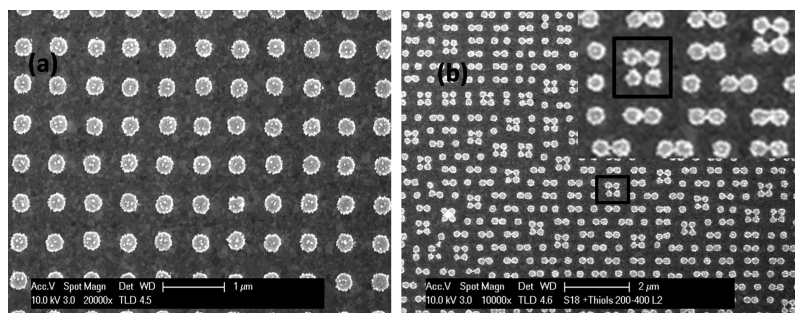


FIG. 3. SEM image of gold nanodisks on gold film after lift-off process: (a) diameter 230 nm and periodicity 600, (b) diameter 200 nm and periodicity 400 nm.

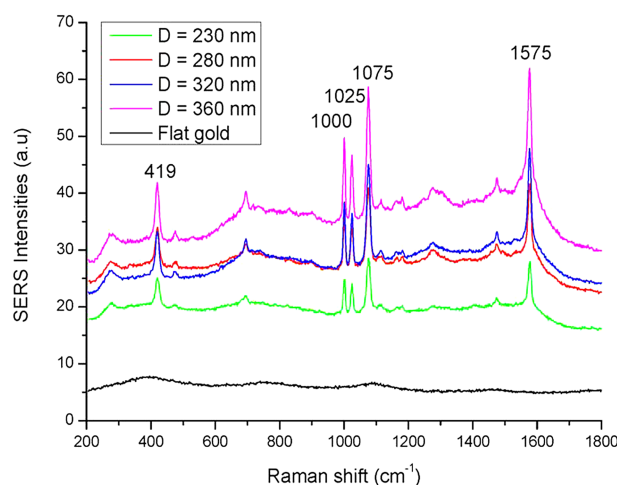


FIG. 4. SERS measurements with pitch 600 nm and diameters 230-360 nm (a).

Where I_{sers} and I_{Raman} are respectively the SERS and Raman intensities. N_{Raman} and N_{sers} are defined as the number of excited molecules in Raman and SERS experiments, respectively N_{Raman} is obtained from Ref. 35 and estimated to 4.22×10^{15} . N_{sers} is evaluated from the following equation: $N_{sers} = N_A \times S_{collected} \times \sigma_{Surf} \times \frac{S_{structures}}{p^2}$ with N_A the Avogadro's number (mol^{-1}), $S_{collected}$ the illuminated area around $7 \mu\text{m}^2$, σ_{Surf} is the surface coverage of thiophenol molecules and is approximately around $0.544 \text{ nmol}/\text{cm}^2$,^{36,37} $S_{structures}$ is the sum of the lateral and top surface of nanodisks. p corresponds to the periodicity of the nanostructures array.

SERS EF are between 2.6×10^6 and 3.1×10^6 depending of the nanodisks' sizes for the period 600 nm. The order of magnitude of 10^6 agrees with characterization of gold nanostructures functionalized on gold film.^{8,9} SERS measurements have also been performed for 400 nm period nanodisks and shown due to collapse effect lower peak intensities.

IV. CONCLUSIONS

In this work we have presented an original fabrication process for biochemical surface enhanced Raman scattering sensor based on soft nanoimprint lithography (S-NIL) on thermo-curable SiO_2 sol-gel at low temperature. This soft nanoimprint method, mainly manual, and the lift-off process with sacrificial layer under SiO_2 sol-gel permit to product easily sensors at low cost, thereby this method is compatible with mass production. Otherwise for a periodicity of 400 nm we have obtained a collapse effects of the pillars on PDMS stamp. We used this effect to evaluate the resolution of the imprint in sol-gel. SERS characterization with thiophenol were performed with spectrophotometer. An evaluation of SERS intensities on various structures' density has been shown with the periode 600 nm. This new alternative manufacturing provided devices with specific coupling properties due to the periodicity and the size of gold nonodisks on a gold film underlayer. These results consistent with previous studies validate this new sol-gel-based process.

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