



Large-area, cost-effective Surface-Enhanced Raman Scattering (SERS) substrates fabrication



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ABSTRACT

This work describes two low-cost, large-area fabrication techniques of SERS substrates. Both are capable of providing highly reproducible nanoscale features without any expensive masking step. The first one is based on the use of block copolymer (BCP) to pattern either nanopillars or nanospheres with controllable diameters and lattice spacing while the second one is based on the elaboration of dense and homogeneous arrays or forest of nanotips structures. For both techniques, promising SERS spectra were obtained by using Rhodamine 6G as a probe molecule. Moreover, in the case of a nanotips forest or array, the impact of features' density on the SERS signal intensity was demonstrated. It was shown that the SERS effect can be noticeably enhanced simply by tuning the plasma etching parameters.

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1. Introduction

Surface-Enhanced Raman Scattering (SERS) is a powerful detection technique allowing a strong increase of a Raman spectroscopy's sensitivity. It consists in modifying the sensing surface, on which probed molecules are adsorbed in order to boost the interaction between the incident light and the vibrational modes of the probed molecules. Signal enhancement over normal Raman scattering signals as high as 10^{14} were reported [1,2], which gives SERS spectroscopy a huge potential for various applications in the domain of chemical and biological detection.

SERS substrates are usually made of nanostructured surfaces coated with a thin noble metallic film (gold or silver). When such structures are exposed to an incident light, an electric field can be enhanced, at the substrate surface, from the interaction between the light and the electrons of the metal surface (surface plasmon resonance). This phenomenon can provide a high enhancement of the Raman signal of the molecules that are close to or have adsorbed on to the metal surface. Even though the accurate mechanisms behind this enhancement effect are not perfectly understood, the use of Surface-Enhanced Raman Scattering (SERS) substrates for detection of small amount of molecules by Raman Spectroscopy has been increasingly used during the last 5 years [3–5].

From a technology point-of-view, researchers have made great efforts in order to draw out the specs of an ideal SERS-active substrate and offer repeatable, cost-effective fabrication techniques. Most of the efforts have focused on the preparation of uniform metallic nanostructures arrays by various nano-assembly and other nanoscale top-down patterning techniques. Generally, e-beam lithography is used for the patterning of metallic nanostructures and leads to good results in terms of uniformity and repeatability of nanopatterns. Although SERS substrates fabricated by those techniques have shown good experimental enhancement factor [6], they are not suitable for large surface and low cost requirements made mandatory for real and massive introduction of SERS-based sensors in various detection domains (chemical and biomolecules detection, proteomics, cellular activities).

Indeed, the low throughput of direct e-beam writing, its high cost and its limitation to small area (few hundreds of μm^2) are serious drawbacks for its extended use for SERS-based sensors fabrication.

In this work, two low-cost, large surface fabrication techniques of SERS substrate were used. Both are derived from semiconductor processing technology and are thus compatible with a batch fabrication approach, without any lithography step.

The first processing approach is based on the use of block copolymer (BCP) and their ability to self-organize into two-dimensional patterns with well-defined dimensions and easy processing [7,8]. According to the copolymer blocks' chemistry and relative composition, various patterns (spheres, cylinders, pillars) can be

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obtained. Features' sizes obtainable are related to the copolymer block size and can reach the sub-10 nm scale.

The second approach consists in applying a reactive ion etching plasma treatment on a plain silicon wafer, without any masking level. By tuning the plasma parameters, the density and the aspect ratio of the obtained nanopillars can be tuned. The so-roughened silicon surface is called black silicon [9].

Both processing categories are compatible with large size silicon wafers (100, 200 or 300 mm diameter) and include as a final step, an e-beam evaporation of a thin gold layer.

2. Experimental details

A poly (styrene-block-dimethylsiloxane), (PS-*b*-PDMS), copolymers system was used. The selected composition was 53 kg mol^{-1} of PS and 17 kg mol^{-1} of PDMS, which is expected to organize itself into spherical patterns [10]. The flowchart of the BCP based technique is illustrated in Fig. 1a. It starts by casting a thin film of PS-*b*-PDMS onto a 100 mm silicon substrate previously coated with a 60 nm-thick Spin-on-Carbon (SoC) layer. This is done by spin coating a 1% diluted solution of PS-*b*-PDMS into PGMEA. The BCPs thickness was measured by spectroscopic ellipsometry and was found to range between 25 and 30 nm. Under these conditions, it was shown that PDMS spheres can be formed inside the PS matrix after 8 min of toluene vapor solvent annealing. The so-organized film was then treated with an extremely brief (5 s) CF_4 plasma to remove the ultra-thin PDMS surface layer. Afterwards, a 25 s, 90 W-bias O_2 plasma, which, on one hand, removes the PS matrix, and, on the other hand, oxidizes the remaining PDMS nano-spheres, was applied. The so-obtained PDMS templates were then coated with a 5 nm thick gold film and further tested as a SERS substrate. Field emission scanning electron microscopy (SEM) operating at low voltage (5 kV) was used to observe the gold coated nano-spheres distribution. Typical SEM image is shown on Fig. 2 where uniform and almost defect-free nanopatterns are reported.

An optional second step of this BCPs based technique consists in transferring the oxidized PDMS nano-spheres into the underlying Si/SoC stack (cf. Fig. 1b). To do so, a hydrogen bromide/oxygen (HBr/O_2) pulsed plasma (200 sccm $\text{HBr}/5 \text{ sccm } \text{O}_2$, pressure: 20 mTorr, 250 W source power, 750 W bias power, pulse 1 kHz at 20% duty cycle) was applied [11] for 120 s using the same ICP plasma reactor (Applied Materials Centura 300). As a result, uniform arrays of 120 nm high silicon/SOC nano-pillars were obtained and finally coated with a 5 nm thick gold film deposited by e-beam evaporation with a rate of 2 Å/sec (cf. Fig. 3).

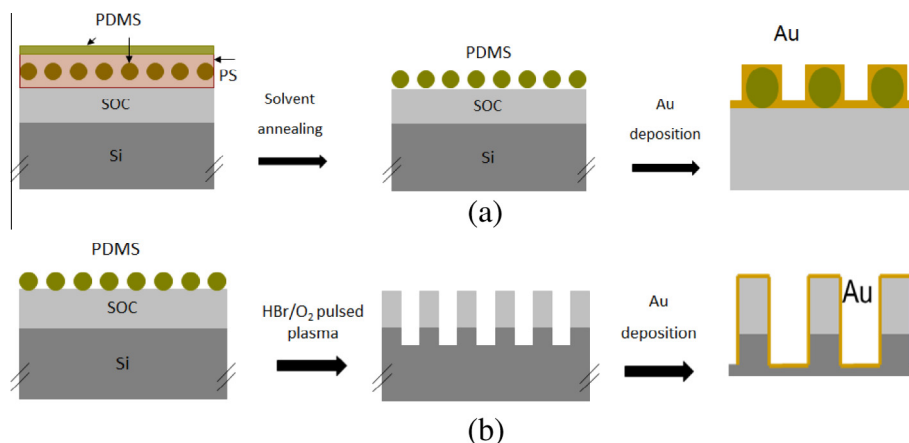


Fig. 1. Fabrication flowchart, (a) of nano-spheres arrays of PDMS with a lateral dimension of 25–30 nm, assembled from PS-*b*-PDMS, after removal of the PS matrix, (b) of nano-pillars obtained by the transfer of PDMS nano-spheres into a Si/SoC stack by HBr/O_2 pulsed plasma.

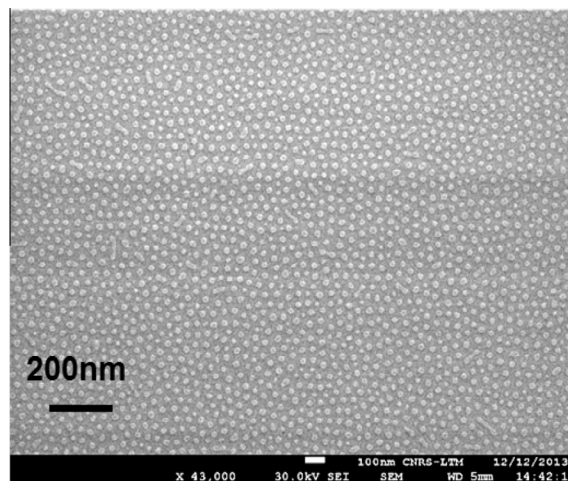


Fig. 2. Scanning electron microscopy top-view of nano-spheres arrays of PDMS coated with 5 nm thick gold with a lateral dimension of 25–30 nm.

The second low-cost, large surface SERS substrates fabrication process consists in etching plain 200 mm silicon wafers without any masking patterns. The etching reactor used was an ICP type Centura 5200B from Applied Materials using a chlorine/oxygen mixture. Preliminary works consist in adjusting the coil and plate's applied powers as well as the plasma pressure to initiate the etching process on the silicon surface. The optimum values of those parameters were the following: 800 W coil source power, 200 W bias power and 30 mTorr for the reactor pressure.

Then, the Cl_2 flow rate was set to be 200 sccm while the O_2 flow rate was tuned between 20 and 30 sccm. Thanks to this last knob, it was possible to vary the density of nanopillars etched over the silicon surface as illustrated on two SEM images on Fig. 4.

It is worth noticing that the etching procedure does not use any fluorocarbon passivating step usually applied in deep reactive ion etching process. By doing this, we avoid any contamination with carbonaceous species during further SERS analysis.

3. Results and discussion

Raman analysis was carried out by using microscopic Raman system (Renishaw Raman spectroscopy) with 514 and 785 nm wavelengths excitations. The laser is focused on the substrate with a $50\times$ objective, the measured laser power at the SERS surface level was 1 mW, and the accumulation time was set at 10 s.

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