FABRICATION OF PATTERNABLE NANOPILLARS FOR MICROFLUIDIC SERS DEVICES BASED ON GAP-INDUCED UNEVEN ETCHING

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ABSTRACT

In this work, a lithography-free approach for fabricating patternable nanopillars is reported. The key technique of the approach is to introduce a gap over the substrate by covering it with a cap, which contains through holes and the material on its lower surface has similar etching rate with the substrate. By this means, uneven etching of the substrate is induced under the through holes, consequently, nanopillars are fabricated into patterns corresponding to the holes. By sputtering a thin layer of Ag on the nanopillar patterns, obvious Raman enhancement can be observed. Since the large areas around the patterns are protected from anisotropic etching and metal sputtering, they are flat enough to be bonded with PDMS caps thus to form microfluidic Surface-enhanced Raman Scattering devices, and the whole fabrication process for the devices is simplified.

INTRODUCTION

Since Surface-enhanced Raman Scattering (SERS) effect was discovered, a way of trace detection, even at single molecule level [1], has been paved due to the continuous innovations and breakthroughs in research of SERS-active substrates. So far, the SERS substrates have been increasingly applied in various fields, such as biomedical, DNA sequencing [2, 3], agricultural and environmental analysis [4], in which the capability of quantitative and real-time detection is of great importance [5]. Similar to the SERS-active substrates, microfluidic SERS devices have advantages of high sensitivity, while in the mean time, they are capable of reaching a real-time detection and distributing analytes uniformly by avoiding coffee-ring effect [6] and thus to achieve relatively low measurement errors [5].

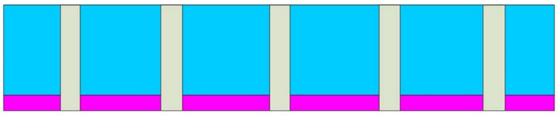
As have been reported, microfluidic SERS devices usually contain SERS-active substrates, which are covered by caps with microchannels [5, 7]. To achieve surface plasma resonance thus to realize SERS effect on the substrates as well as in the devices, nanoscale roughness or structures are required. Recently, various nanopillars are reported to function as the nanostructures, and meanwhile, preparation of the nanopillars become crucially important for the realization of high-performance microfluidic SERS devices. So far, different methods for fabricating nanopillars have been studied and applied extensively, including an oxygen-plasma-stripping-of-photoresist (OPSOP) technique [8] and other approaches which can fabricate highly repeatable nanostructures, such as electron beam (EB) lithography, focused ion beam (FIB) etching [9], nanosphere lithography (NSL) [10] and nanoimprint lithography [11]. Both EB and FIB can realize extremely tiny structures in arrays, however, the nature of serial processes demands a comparatively lengthy exposure time, thus their broader range of applications are restricted. NSL combining the advantages of both top-down and bottom-up approaches needs monolayer nanoparticles in large areas, which is of difficulty and increases complexity of the process [12]. OPSOP technique has a good controllability over dimensions and densities of the nanopillars, but the process requires several material-deposition and etching steps, which are time-consuming and also involve regions around the nanopillar patterns. As a result, bonding the substrates to PDMS caps would become difficult because of the surface roughness.

In this work, a novel, simple and lithography-free method for fabricating desirable nanopillars patterns is proposed, and the approach can provide a fairly smooth surface around the patterns. Based on this method, the bonding between PDMS caps and SERS-active substrates becomes much easier. As a consequence, a new way for fabricating microfluidic SERS devices is further developed.

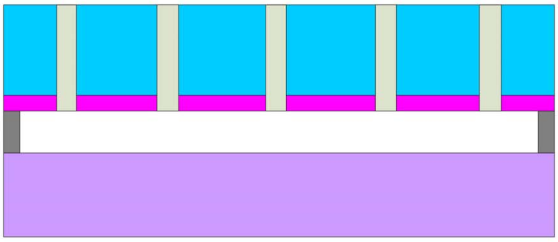
FABRICATION

In single-step experiments to figure out etching parameters, small pieces of wafers are usually attached to larger substrates and then suffered to etching processes. As taken for granted, the areas on the substrates revealed to etching gases would be etched evenly, thus a relatively smooth surface could be obtained. However, in our experiments, nanopillar patterns with certain widths were observed on the substrates around the margins of the small wafers. Based on such observations, a novel lithography-free approach for fabricating patternable nanopillars is proposed.

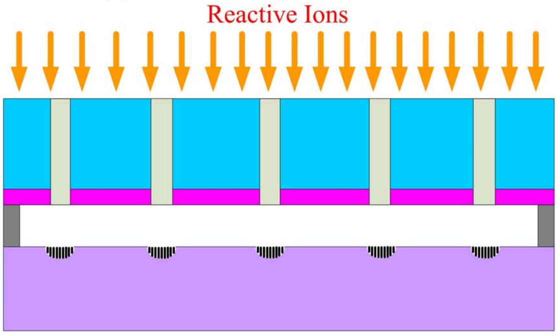
The fabrication process for patternable nanopillars is schematically depicted in Fig. 1. At the beginning of the process, through holes are perforated in a cap, and the lower surface of the cap is covered with a substrate-alike material layer, which has similar etching rate with substrate, as illustrated in Fig. 1(a). Then, the cap is attached to the substrate using adhesive tapes, which are of certain thicknesses, therefore, a gap is introduced between the cap and the substrate (shown in Fig. 1(b)). Afterwards, reactive ion etching (RIE) is adopted to etch the substrate. By this means, nanopillars are patterned within regions corresponding to the through holes (shown in Fig. 1(c)).



(a) Prepare a cap with through holes and cover the lower surface with substrate-alike material



(b) Attach the cap onto a substrate



(c) Etch the substrate using anisotropic ion etching

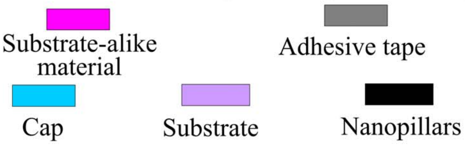


Figure 1: Fabrication process of nanopillar patterns

More specifically, in the experiment to obtain silicon nanopillar patterns, a glass wafer with through holes was used as a cap, α-Si used as the substrate-alike material and Si wafer as the substrate. When the cap was attached to the substrate, a ~200 μm gap was introduced between the two layers, and then RIE was adopted to etch the Si substrate through the holes. In the etching, RF power was 350 W, Cl_2/He flow rates were 180/400 sccm. As a result of 180 seconds of etching, patternable nanopillars were formed. Figure 2 demonstrates the scanning electron microscopy (SEM) images of the obtained nanopillars under a circular through-hole (with a diameter of ~400 μm), where, nanopillars are distributed in patterns with a width of ~60 μm along the border of a large circle (Fig. 2(a)). Figure 2(b) exhibits a top-down view of Region B in (a), where nanopillars with different densities are displayed. The margin of a pattern that has a nanopillar region inside and a slightly etched area outside is displayed in Fig. 2(c), and this figure is also a cross-section view of Region C in (a). Magnified images of the nanopillars distributed in different regions, e.g. Region E, F, G, and H, are shown in Fig. 2(d)~(h).

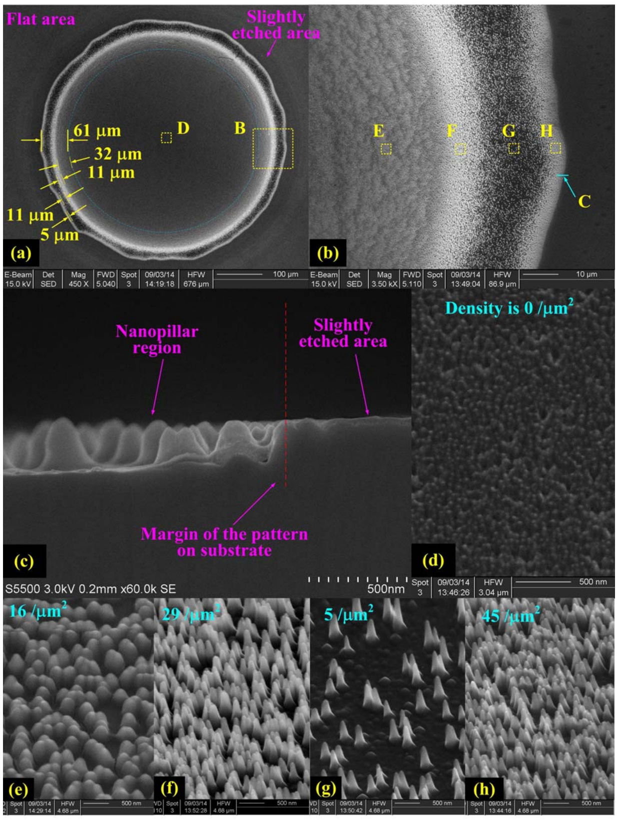


Figure 2: SEM images of a nanpillar pattern and magnified images at different positions of the pattern. (a) large circular pattern with nanopillars; (b) top-down view of Region B in (a); (c) cross-section view of Region C in (b); (d)-(h) magnified images of nanopillars in regions from D to H in (a) and (b), in which the bar is 500 nm.

METHODOLOGY

The mechanism for forming the nanopillars can be ascribed to the varying and non-uniform ion distributions caused by the gap and the substrate-alike material, the details are illustrated in Fig. 3. On account of the reason that almost every ion going directly through the center of the holes reacts with the substrate, the concentration of the etching ions that reach the hole centers is maintained at a high level, thus at these positions, the etching rate reaches its highest. Near the hole-edges, nevertheless, the substrate-alike material and the substrate surface are revealed to etching gases, thus part of the ions would transfer laterally into the gap, then the ion concentration at these positions is decreased, which, as a result, gives rise to a slower etching rate. Simultaneously, ion concentration near the hole-edges is non-uniformly distributed for the same reason. Consequently, an uneven etching of the substrate leading to nanopillars is achieved. Figure 3 also shows a magnified graph of nanopillars distributed within a region corresponding to a perforation. As shown in Fig. 3, Region 1 presents the very short and sparse nanopillars around the central areas of the circle where the material is almost fully removed. Conversely, Region 2 demonstrates an inadequate reaction between the Si substrate and the ions, therefore, obvious nanopillars are observed in this region where the ions are non-uniformly distributed. Within the gap, on the other hand, the anisotropic features of the ions is reduced, thus the etching rate in this region decreases rapidly, subsequently, nanopillars are generated only within small regions near the hole-edges. This is also the reason for the generation of nanopillars in Region 3. In this way, by adjusting sizes and profiles of the perforations, nanopillars with desirable patterns can be obtained.

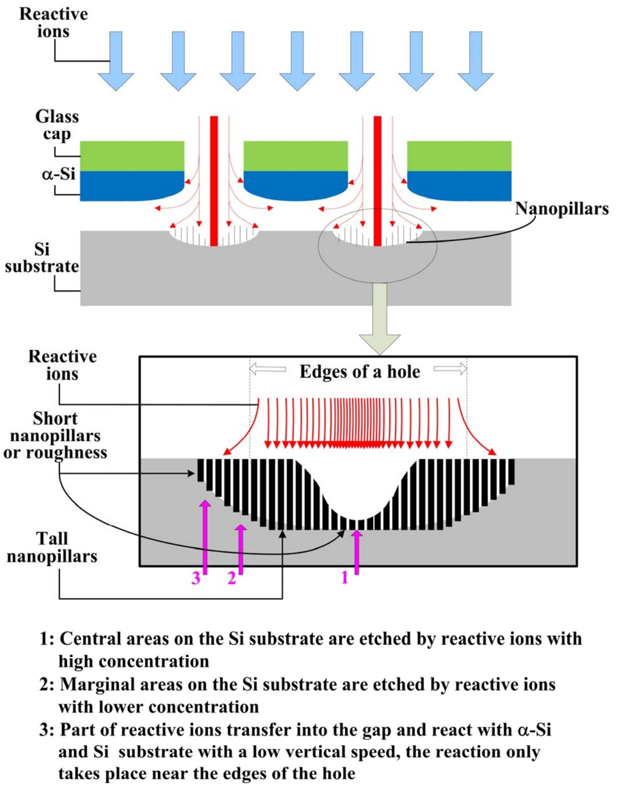


Figure 3: Schematic graph for the mechanism of the gap-induced-uneven-etching approach, by using glass with through holes as a cap, α-Si as the substrate-alike material, Si as the substrate. Nanopillar morphologies are different at different positions, but can be controlled by adjusting width of the holes in the cap.

CHARACTERIZATION AND APPLICATION

SERS features of the nanopillars formed in this work were tested by sputtering a thin Ag layer (50 nm) on them and using R6G solutions with different concentrations as analytes. A 1 µL droplet of R6G analyte with concentration of 1 µg/L (Analyte A) was dropped on a nanopillar-based SERS substrate, and the substrate was with a surface area of 1.0×1.0 cm^2. The SERS spectrum of Analyte A at the position of Region B in Fig. 2 (a) is illustrated as Curve 1 in Fig. 4. As for comparisons, a 1 µL droplet of R6G analyte with concentration of 2 mg/L (Analyte B) was dropped on a glass slide with the same surface area. Curve 2 in Fig. 4 represents the spectrum of Analyte B. By comparing these two curves, an enhancement factor around 10^7 can be obtained, demonstrating potential applications of nanopillars in microfluidic SERS devices.

In conventional fabrication processes for nanopillar-based SERS-active substrates, it is difficult to get a very smooth surface around the patterns, as these areas are also suffered to anisotropic etching processes. Therefore, bonding the substrates to particular caps seems to be uneasy.

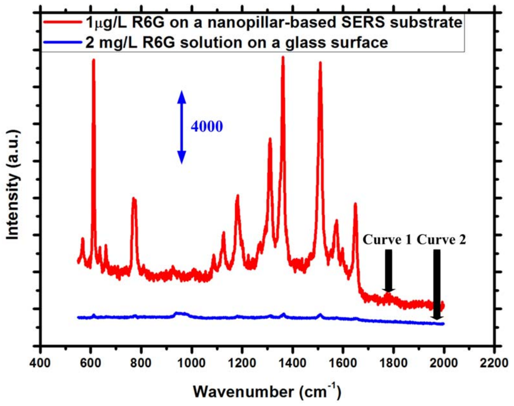


Figure 4: SERS measurement results, with an enhancement factor around 10^7, demonstrating potential applications of nanopillars in microfluidic SERS devices.

Fortunately, the method proposed in this work provides a way to obtain a very flat surface around the nanopillar patterns, thus it has potential to overcome the problem. To testify the smooth features of the areas beside the nanopillar patterns, atomic force microscopy (AFM) was adopted to analyze the roughness, for comparison, a polished Si wafer was also detected. The AFM images are shown in Fig. 5, which demonstrates that the surfaces of the areas are as smooth as the polished Si wafer. Therefore, the bonding in fabrication of microfluidic SERS devices would be easily achieved.

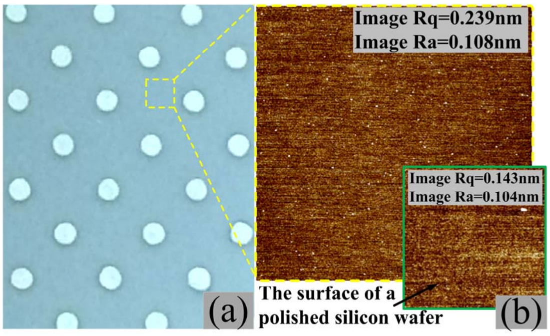
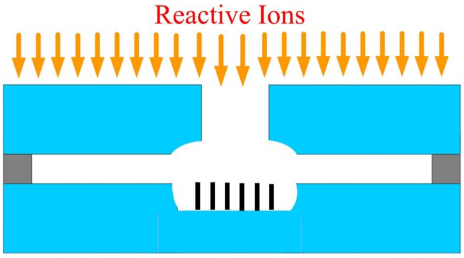


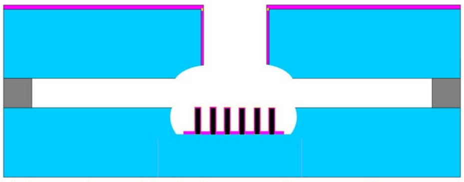
Figure 5: (a) Ag patterned in nanopillar regions realized by the gap-induced-uneven-etching approach; (b) roughness comparison between areas around the Ag patterns and surfaces on a polished Si wafer.

With all these features, a process for fabricating SERS devices based on our approach is proposed, which is quite simple and can be easily managed, as is schematically depicted in Fig. 6. Firstly, the method described in Fig. 1 is utilized to generate nanopillar patterns (shown in Fig. 6(a)). Subsequently, the cap with perforations is further used as masks in Ag sputtering. For the substrate with nanopillars, only regions corresponding to the perforations are revealed, thus only these regions are covered with Ag, and the surface beside them are well protected (Fig. 6(b)). In this way, lithography and lift-off technique for patterning the Ag layer become unnecessary. Finally, the cap is taken off from the substrate, and a PDMS cap with microchannels is bonded to the substrate. Consequently, a microfluidic SERS device is achieved (Fig. 6(c)).

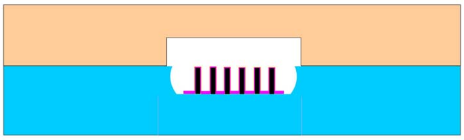
Moreover, such a gap-induced-uneven-etching approach can also be applied to produce nanopillars of other materials, including SiO_2, Si_3N_4, metal, glass and others. Figure 7 shows SiO_2 nanopillars generated by using a glass cap over a Si substrate covered with SiO_2. The average diameter of the SiO_2 nanopillars is about 100 nm, and the density is about 30 /μm^2. Since the features of glass are similar to those of SiO_2, thus it is possible that nanopillar patterns can be obtained on glass substrates. Therefore, transparent SERS devices become realizable.



(a) Fabrication of nanopillar patterns on a Si substrate



(b) Sputtering a thin Ag layer on the nanopillar patterns



(c) Bonding the SERS substrate to a PDMS cap with microchannels

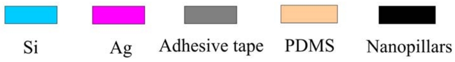


Figure 6: Fabrication process of microfluidic SERS devices.

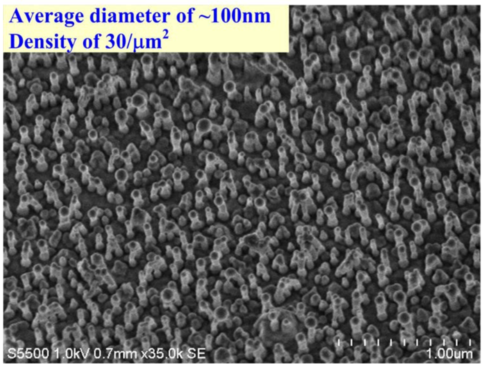


Figure 7: A large area of SiO_2 nanopillars achieved by the gap-induced-uneven-etching approach. In the fabrication, a SiO_2 layer covered by a glass cap with through holes is etched.

CONCLUSIONS

A gap-induced-uneven-etching technique for fabricating patternable nanopillars is proposed, which is simple, fast and lithography-free. Based on this approach, a simplified fabrication process for microfluidic SERS devices is further developed. Similarly, such an approach can be applied to other materials, including SiO_2, which makes transparent SERS devices possible. Meanwhile, based on this approach, a new route for nanopillar patterns to be applied in other fields is opened up.

ACKNOWLEDGMENT

This work was supported in part by Jiangsu Natural Science Foundation (Grant No. BK20131098), the National Natural Science Foundation of China (Grant No. 61401458, 61335008 & 61176114). Special acknowledgements are due to Prof. W.G. Wu and Mr. Y. F. Mao from Institute of Microelectronics, Peking University for their help with the experiment and preparation of SEM images.

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