NANOPILLLAR SUBSTRATE FOR SERS

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ABSTRACT

Silver coated nanoscale pillar structures are fabricated by a batch process method to serve as Surface-Enhanced Raman Scattering (SERS) substrates. In comparison to common SERS method by using colloidal silver particles in a sample solution, nanopillar SERS substrates optimized for various molecules can be fabricated by simply changing the fabrication parameters. Integrated spatially modulated SERS substrates within nanofluidic channels can be applied for ultrasensitive high-throughput screening bioassays. SERS spectra of Rhodamine 6G molecules are measured and the SERS signal enhancements can be optimized using particular substrate.

KEYWORDS: Nanoscale, SERS, Single Molecule Detection

INTRODUCTION

Ultrahigh-sensitivity and high-throughput biomolecule detection has been a research focus in recent years with the dramatically increasing demands for developing biomedical micro total analysis system (μTAS). Among numerous investigation methods, spectral analysis, especially Raman spectroscopy attracts great interests because it is a label-free process with high specificity to molecule structures; However Raman scattering signal is extremely weak. Surface-enhanced Raman scattering [1] has been widely utilized in chemical and biomedical researches as it significantly magnifies Raman scattering intensity with 6 to 7 orders of magnitude for ensemble molecules and even strikingly, 12 to 14 orders of magnitude for single molecules [2]. The conventional methods used to fabricate SERS substrates includes metal salt half-cycle oxidation, metal vapor deposition, metal colloids, electron beam or focus ion beam produced metal particle assemblies, and more recently, metal coating in porous substrates [3]. In order to obtain better geometrical configurability and compatibility to standard microfabrication techniques for making efficient and multiplexing devices in μTAS, in this paper, a batch fabrication method of creating nanoscale high-aspect-ratio pillar (NanoHARP) structure array as SERS substrate is presented. The surface properties of substrates can be controlled by slightly varying fabrication parameters. SERS spectra of Rhodamine 6G (R6G) molecules are measured and SERS enhancements are observed using different substrates.

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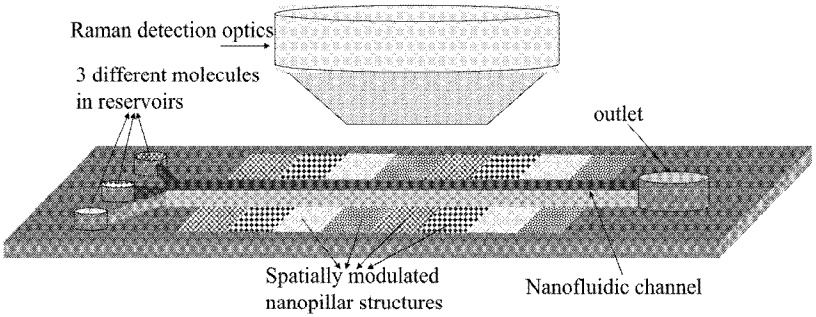

Figure 1. Conceptual schematics of multiplexed SERS detection of biomolecules transported in nanofluidic channel. The SERS substrate above is spatially modulated with variant surface densities of nanopillars and optimized for different molecules.

METHODS and MATERIALS

As shown in Fig. 1 by patterning different NanoHARP SERS substrates with different surface properties and incorporating them with sample delivery systems such as micro or nano fluidics, high-throughput multiplex screening system can be developed potentially for lab-on-a-chip single molecule detection applications.

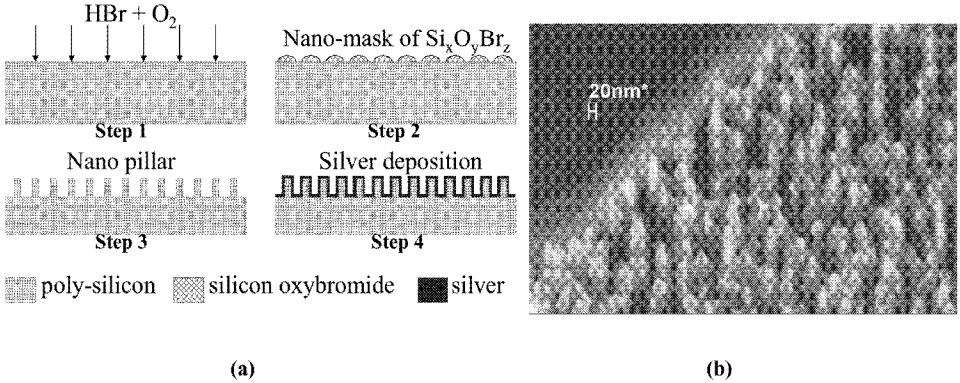

Figure 2. (a) Fabrication process of nanopillar SERS substrate. **(b)** SEM image of NanoHARP shows high-aspect-ratio pillars formed at polysilicon surface arranged in statistical orders.

In order to make high-aspect-ratio nanopillar structures, an etching-passivation [4] method (Fig. 2a) is used. First, by using mixed HBr and O_2 gases, a polysilicon substrate is etched by HBr and oxidized by O_2 simutaneously. In 7 seconds a nano-mask made of silicon oxybromide natually forms , and then HBr gas is used to etch uncovered polysilicon substrate. HBr has a high etching selectivity of polysilicon to oxide (200:1), therefore high-aspect-ratio nano pillar structures can be created. Then a 50~100 nm thin

film of silver is thermally deposited to form metallic pillar array. The scanning electron microscopy image of nanopillar structure is shown in Fig. 2b. The density and aspect ratio of nanopillars can be controlled by O_2 passivation time, flux rate, and HBr etching time. The pillar density and height are charaterized using an Atomic Force Microscope (AFM). Table I shows the NanoHARP surface properties created with different fabrication parameters. As shown a wide range of nanopillar array configurations can be made by simply modifying fabrication parameters.

Oxidation flux rate (sccm)	3	6	8	10
Pillar density (um^{-1})	55	518	768	1296
Etching time (min)	1	2	3	4
Pillar height (nm)	300	360	540	720

Table I. NanoHARP surface properties with different fabrication recipes. First two rows show the relationship of O_2 flow rate and average pillar density, and last two rows show the relationship of HBr etching time and average pillar height

EXPERIMENTS and RESULTS

1 nM R6G molecule suspensions are prepared and coated on the SERS substrates. A Raman spectrometer R2001 (Raman System, NY) with a 2048-pixel CCD detector is used to measure SERS signal. The Raman spectrometer is equipped with a bifurcating fiber optics sampling probe (InPhotonics, CA) that can apply 785 nm focused laser excitation on the sample, and collect light in the same optical path. The focal length and focal spot size are respectively 5 mm and 90 μm.

Different nanopillar devices are tested in the experiment and SERS spectra of R6G molecules are shown in Fig. 3. The characteristic peaks of R6G molecule can be clearly identified. Raman scattering enhancement factor is larger than 10^4 times for the optimal substrate as shown in our results. It should be noted the enhancement factor varies over several orders of magnitude depending on the pillar density of NanoHARP devices. The substrate fabricated with 6sccm O_2 passivation and 50 nm thick Ag coating has the largest SERS enhancement. Measured by an AFM, the average pillar density and pillar diameter of this substrate are about 43.9 nm and 40nm. All the substrates tested have the same average pillar height around 250 nm. Fairly large background fluorescence spectrum can also be observed, and the suppression methods of fluorescence are under investigation.

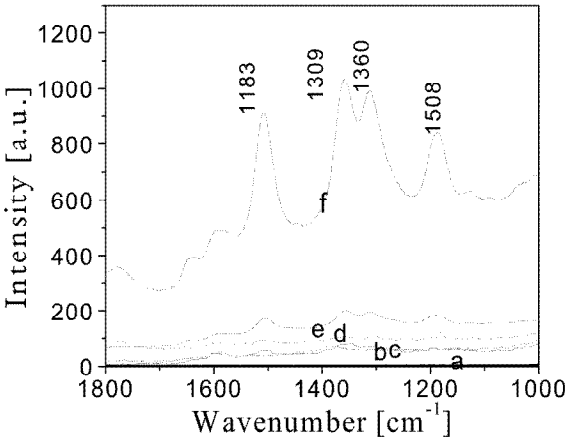

Figure 3. The Raman spectra of R6G molecule were acquired using different substrates which are marked as their fabrication recipes, e.g. 3 sccm O_2 -50nm Ag stands for the substrate passivated by O_2 with flux rate at 3 sccm and coated with 50nm-thick silver film. The shown substrates are (a) Ag on silicon, (b) 8 sccm O_2, 50 nm Ag, (c) 10 sccm O_2, 50 nm Ag, (d) 3 sccm O_2, 50 nm Ag, (e) 4 sccm O_2, 50nm Ag (f) 6 sccm O_2, 50 nm Ag.

CONCLUSIONS

Batch fabricated NanoHARP structure allows to create spatially modulated SERS substrates by simply changing the fabrication parameters. Therefore they can be used for multiplexed high-throughput screening to detect single biomolecules. So far 1 nM R6G molecules are detected. High SERS enhancement has been achieved and different SERS enhancements of different substrates have been shown.

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