

# Surface enhanced Raman scattering silica substrate fast fabrication by femtosecond laser pulses

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**Abstract** We report the fabrication of surface enhanced Raman spectroscopy (SERS) fused silica glass substrates using fast femtosecond-laser (fs-laser) scan, followed by silver chemical plating. A cross-section enhancement factor (EF) of  $2.5 \times 10^6$ , evaluated by Rhodamine 6G ( $10^{-7}$  M solution), was obtained. The Raman mapping indicated a good uniformity over the fs-laser scanned area. The dimension and pattern of the SERS activated region can be conveniently controlled by laser 2D scanning, potentially enabling integration of SERS into a high-order optical-chemical analysis system on a glass chip.

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## 1 Introduction

Since originally discovered in the 1970s [1, 2], surface enhanced Raman scattering has been widely investigated. It was found that silver and gold nanosized particles could significantly enhance the Raman signal of molecule adsorbed onto the particle surface through the combined effects of electromagnetic and chemical enhancement. Enhancement factors (EF) as high as  $\sim 10^{14}$  on “hot spots” have been

previously reported using Rhodamine 6G (R6G) as a probe molecule showing the feasibility of single molecule detection [3].

To achieve a high EF, many methods have been studied to fabricate high-quality SERS substrates. SERS substrates are generally categorized into two main types, solid-phase patterned metallic nanoparticles or liquid-phase aggregated metallic nanoparticles from colloidal solutions. Solid-phase-based substrates have shown good stability and repeatability. SERS substrates can be made by direct physical deposition (e.g., sputtering and evaporation) of noble metals onto smooth surfaces. SERS substrates can also be made by roughening solid-state materials, including chemical etching [4], silver particles hosted by porous silicon [5], biotemplated nanostructures [6], conventional lithography [7], etc.

The latest advancement in femtosecond-laser (fs-laser) technology has opened a new window of opportunity for one-step fabrication of nano/microdevices with three-dimensional (3D) configurations. Direct exposure of most solid materials (include fused silica glass) to ultraintense fs-laser pulses results in a quick establishment of the free-electron plasma at the focal point, leading to the ablation of a thin layer of materials [8]. Fs-laser pulses with extremely high peak power produce nearly no thermal damage as the pulse duration is shorter than the thermalization time. Due to the multiphoton nature of the interaction, the ablation process can be conducted on the material surface as well as within the bulk. Fs lasers have been successfully used for directly writing optical waveguides, and machining microchannels and microchambers in glasses [9].

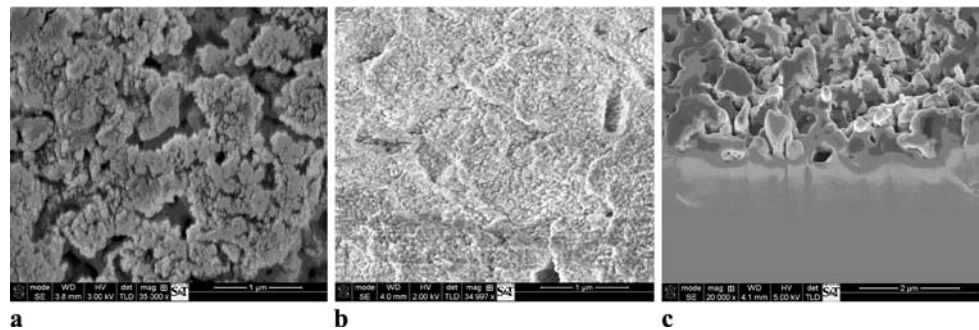
Recently, Mazur et al. reported a SERS substrate fabricated by machining nanostructures on a *n*-type silicon wafer using fs-laser pulse train with subsequent silver deposition by thermal evaporation [10]. Cheng et al. wrote a waveguide-like microwire on  $\text{Ag}^+$ -doped glass and then

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**Fig. 1** SEM images of fs-laser-fabricated SERS silica glass substrates, (a) nanostructured substrate before chemical plating, (b) top view of a 5-min silver chemically plated substrate, and (c) side view of a 5-min silver chemically plated substrate



grew the photoreduced silver particles into a SERS suitable size by chemical plating [11]. This may provide a way to integrate “fingerprint” SERS analysis into microfluidics system with one-step fs-laser micromachining. Fused silica glass substrates, well known for their bio-compatibility and low cost, are one of the most competitive candidates for bioassay application. A wild variety of optical devices (e.g., waveguides and resonators) can be integrated with SERS to further enhance the analysis capability. In 2007 Fan et al. demonstrated that an optical resonator could significantly enhance SERS signal through excitation laser multi-interaction with target molecules enabled by a tubular microresonator [12]. Fs laser is one of the few flexible techniques for micromachining silica glass substrates with high accuracy and full controllability offering a path to fabricate lab-on-a-chip and micro-total-analysis system [11].

In this paper, we report a fused silica glass-based SERS substrate fabricated by fs laser. Using a fs-laser scanning method to nanostructure a designated area on the glass substrate, followed by a silver chemical plating process, we obtained a high-performance SERS substrate with a consistent EF of  $\sim 10^6$  covering the interacted area using R6G as analyte molecule at the excitation wavelength of 632.8 nm. It is worth noting that chemical plating alone can make good quality SERS substrate on silica glass [13]. However, this process lacks the controllability of shape and dimension of the SERS-active area causing it unsuitable to be further integrated into high-order systems.

## 2 Experiment

**Laser nanostructuring** SERS substrates were fabricated on fused silica glass using a home-integrated fs-laser 3D micromachining system. The repetition rate, center wavelength, and pulse width of the fs laser (Legend-F, Coherent, Inc.) were 1 kHz, 800 nm, and 80 fs, respectively. The attenuated laser beam (0.7 nJ) was directed into an objective lens (Olympus UMPLFL 20 $\times$ , NA 0.46) and focused onto the upper surface of silica glass slide mounted on a computer-controlled five-axis translation stage (Aerotech, Inc.). The computer-controlled stage moved the sample at a speed of

1 mm/s, spacing the neighboring laser ablation points at a distance of 1  $\mu\text{m}$ , considering a 1 kHz repetition rate. Upon finishing a line scan, the fiber was stepped transversely by 1  $\mu\text{m}$  to start another line scan. A 1500  $\mu\text{m}$   $\times$  100  $\mu\text{m}$  rectangular substrate on the glass took about 5 min to complete.

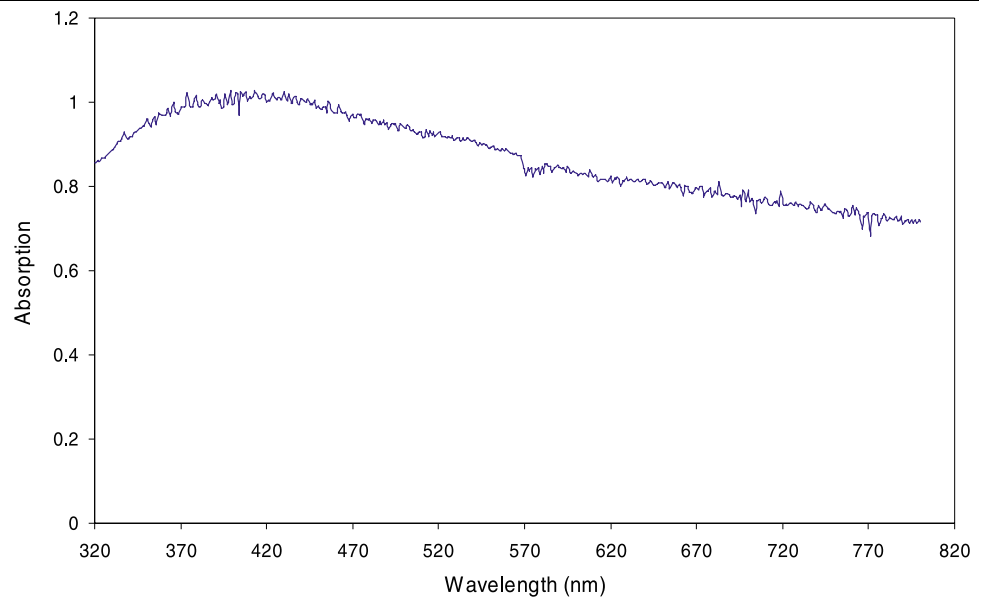
**Chemical plating** Formation of silver nanoparticles on the laser-scanned substrate proceeded as follows. The laser scanned substrate was clean carefully in an ultrasonic ethanol bath, rinsed with deionized water, and dried in nitrogen environment. A container cleaned with concentrated  $\text{H}_2\text{SO}_4$  was well rinsed using deionized water to hold the plating solution. The plating solution was prepared by mixing 30 ml of 0.3 M silver nitrate aqueous solution with 30 ml of 0.2 M NaOH to obtain a fine brown precipitate of  $\text{Ag}_2\text{O}$ . A 0.4 M ammonia solution was then added into the mixture drop by drop until the precipitate completely dissolved to form  $[\text{Ag}(\text{NH}_3)_2]^+$ . A 0.3 M silver nitrate solution was added until the solution became pale brown. After 1 drop of 0.4 M ammonium was added, the solution became transparent again, and the dried glass substrate was then fully immersed into the solution. A 30 ml of 0.1 M  $\alpha$ -lactose was then added into the solution to reduce the silver ions to form silver particles.

**SERS measurement** Characterization of pristine SERS substrates was carried out on a commercial Raman spectroscopy system (Horiba Jobin Yvon). A 632.8-nm He–Ne laser was used to excite the Raman signal. Raman spectra were recorded through a 10 $\times$  microscope objective (NA 0.25) and projected onto a charge-coupled device (CCD) array using a 1200 g/mm grating with an integration time of 5 s.

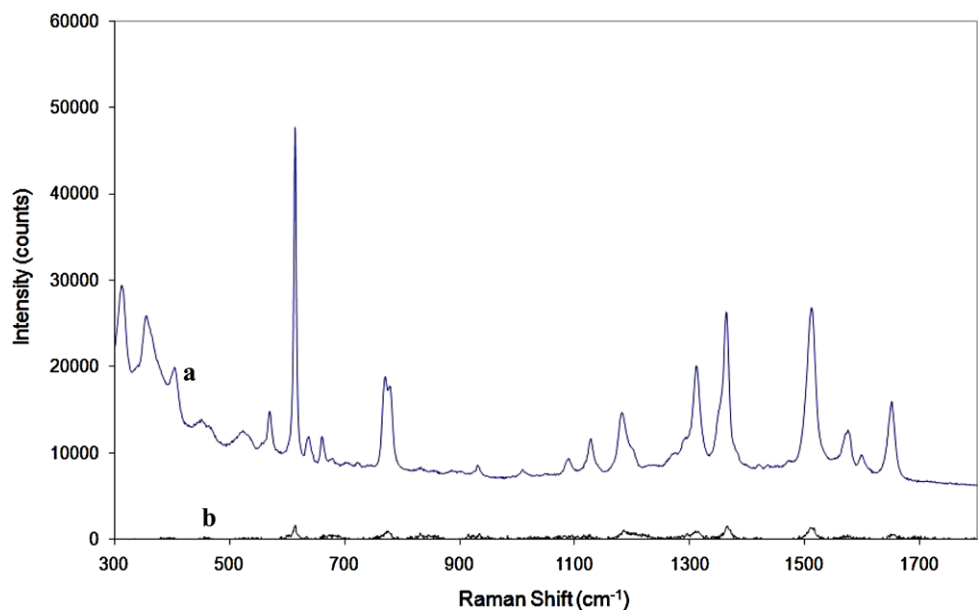
## 3 Results and discussion

**Microscopic characterizations** A single laser pulse ablated an area about 1.5  $\mu\text{m}$  in diameter on the glass substrate as observed under scanning electron microscope (SEM). Figure 1a shows the field emission SEM image of the fs-laser-nanostructured silica glass substrate. Figures 1b and c show

**Fig. 2** UV–Vis absorption spectrum of a silver-coated fs-laser-ablated SERS glass substrate



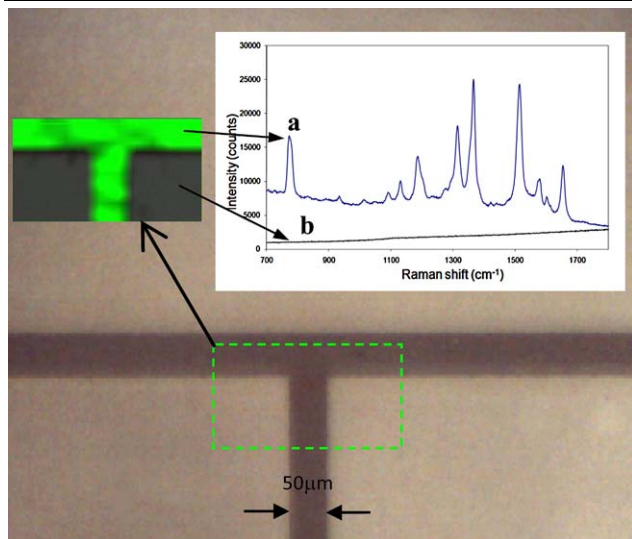
**Fig. 3** Raman spectra of R6G. (a) Raman spectrum of R6G  $10^{-7}$  M solution dispersed on the silver-coated laser-ablated SERS substrate with an excitation laser power of 1.7 mW and integrated time of 5 s, and (b) Raman spectrum of R6G  $10^{-3}$  M solution on the laser ablated but non-silver-coated glass substrate with an excitation power of 17 mW and integrated time of 5 s



the top and side view SEM images of a laser ablated glass substrate after 5-min silver deposition. The laser-scanned silica surface exhibited a highly porous structure with hollow holes of a size of several 100 nanometers. The depth of the hole is about 700 nm estimated from the side view SEM image. We believe that the overlapping between two adjacent exposures created the nanometer scale roughness. The UV–Vis absorption spectrum of the silver-coated laser-ablated substrate was measured by a spectrometer (Cary 5 UV–Vis). As shown in Fig. 2, the absorption maximum was found at 390 nm. The fs-laser-sculptured pores well accommodated chemically deposited silver particles on the order of 50–100 nm, which, we believe, created an appropriate metallic surface that accounted for the strong SERS signal.

**SERS characterizations** An aliquot of 3  $\mu\text{L}$  R6G ( $10^{-7}$  M in distilled water) was dropped on the substrate. The dropped solution was spread evenly onto an area of about 3 mm in diameter. The estimated R6G molecular coverage on the substrate surface was  $2.6 \times 10^{12}$  molecules/ $\text{cm}^2$ . This was equal to about one molecule per 39  $\text{nm}^2$ . In a densely packed R6G monolayer, a single molecule is supposed to take no more than 4  $\text{nm}^2$  in area [13, 14]. In our experiment, the R6G molecular coverage was low enough to exclude the formation of multilayers. In other words, each dye molecule should directly interact with the substrate surface.

Using the bench-top Raman spectrometer, the Raman spectrum of a 5-min silver-coated substrate was measured as given in Fig. 3. Trace (a) is the Raman spectrum of the



**Fig. 4** Raman mapping of a T-shaped SERS area fabricated by fs-laser ablation followed by 5-min silver chemical plating, (a) Raman spectrum of R6G solution in the laser-structured area, and (b) Raman spectrum of R6G solution in the nonstructured area

R6G solution on a randomly chosen spot in the laser ablated area with the excitation laser power of 1.7 mW and integration time of 5 s. Trace (b) is the Raman signal of R6G solution of  $10^{-3}$  M concentration measured on a laser ablated but uncoated glass substrate using the excitation laser power of 17 mW and integration time of 5 s. Comparison between these two traces indicates a strong Raman signal enhanced by the silver coated laser ablated glass substrate. According to References [14, 15], Raman scattering cross-section EF for the substrate can be estimated by the following equation

$$EF = \frac{I_{\text{SERS}} N_{\text{nR}}}{I_{\text{nR}} N_{\text{SERS}}} \quad (1)$$

where  $I_{\text{nR}}$  and  $I_{\text{SERS}}$  are the normal Raman and SERS intensities in the unit of  $\text{mW}^{-1} \text{s}^{-1}$  [16], respectively.  $N_{\text{nR}}$  and  $N_{\text{SERS}}$  represent the number of molecules probed in the reference sample and on the SERS substrate, respectively. Using the Raman peak at  $610 \text{ cm}^{-1}$  as the basis of calculations [17], the signal enhancement was estimated to be  $2.5 \times 10^6$ .

**Raman mapping** The uniformity of laser ablated SERS substrate was investigated by Raman mapping. Figure 4 shows the microscopic optical image and Raman mapping of a T-shape SERS activated region ( $250 \mu\text{m} \times 150 \mu\text{m}$ ). The mapping was taken as the Raman intensity integrated in the range from  $700$  to  $1800 \text{ cm}^{-1}$ . The excitation laser power was 1.7 mW; the integration time was 2 s; the microscopic lens was a  $10\times$  objective ( $\text{NA} = 0.25$ ); the spatial scanning step was  $10 \mu\text{m}$ . The inset of Fig. 4 shows the optical microscopic image of the T shape area, where the width of the laser structured area was  $50 \mu\text{m}$ . The Raman signal distribution shows a good homogeneity over the laser ablated area, while the nonstructured area has no observable

Raman signal. It is worth noting that the intact region was also deposited by silver particles during the same chemical plating process. However, the coated silver layer alone did not have a significant contribution to the SERS enhancement compared to the laser-ablated area. We believe it is the combination of porous surface fabricated by fs laser and silver coating that accounts for the strong SERS signal.

## 4 Conclusion

To summarize, a SERS substrate fabricated by femtosecond-laser (fs-laser) ablation on a silica glass, followed by chemical plating of silver, was demonstrated. An EF of  $2.5 \times 10^6$  was measured using a  $10^{-7}$  M R6G solution. Besides the high EF, the fs-laser-structured area has shown a good uniformity characterized by Raman mapping. Fs-laser technique could be potentially used to fabricate SERS regions with a controlled dimension and arbitrary pattern by fast and convenient laser 2D scanning enabling integration of SERS into high-order optical system on a single glass chip.

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