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Nanostructured substrate with nanoparticles fabricated by femtosecond laser for surface-enhanced Raman scattering

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Abstract A simple and fast method to fabricate nanostructured substrates with silver nanoparticles over a large area for surface-enhanced Raman scattering (SERS) is reported. The method involves two steps: (1) dip the substrate into a silver nitrate solution for a few minutes, remove the substrate from the solution, and then air dry and (2) process the silver nitrate coated substrate by femtosecond (fs) laser pulses in air. The second step can create silver nanoparticles distributed on the nanostructured surface of the substrate by the photoreduction of fs multiphoton effects. This study demonstrates that an enhancement factor (EF) greater than 5×10^5 , measured by 10^{-6} M Rhodamine 6G solution, can be achieved. The proposed technique can be used to integrate the SERS capability into a microchip for biomedical and chemical analysis.

1 Introduction

Since the 1970s, the phenomena of surface-enhanced Raman scattering (SERS) by molecules adsorbed on a roughened metal surface have been widely investigated [1, 2]. The

enhancement factor (EF) can be as high as 10^{14} – 10^{15} using Rhodamine 6G (R6G) which allows the technique to be sensitive enough to detect a single molecule on a rough noble metal (e.g., silver and gold) surface [3]. Different techniques to fabricate metallic nanoparticles on semiconductor substrates for SERS applications have been reported. For example, Kao et al. demonstrated a controllable uniform SERS substrate with metalized nanostructured poly(p-xylylene) films [4]. Qiu et al. fabricated silver-capped silicon nanowires using an electroless metal deposition method to achieve high SERS intensities [5]. Chan et al. demonstrated a porous silicon SERS substrate for small molecules by using a 6-step fabrication method [6]. Lin et al. developed a method to fabricate silicon wafer SERS substrates in the aqueous solution of silver nitrate machined by the fs laser [7]. Diebold et al. employed the fs laser pulse-train to fabricate a nanostructured silicon substrate followed by silver thermal evaporation for SERS detections [8].

In this paper, we report a simple method that can simultaneously fabricate nanostructures and generate silver nanoparticles by fs laser pulses over a large area of the silicon substrate. The SERS substrate was measured to have higher than 5×10^5 of EF using R6G as the analyte molecule at the excitation wavelength of 632.8 nm. This technique shows a possibility of integrating SERS capability to high order microdevice systems for chemical or biological detections.

2 Experiment

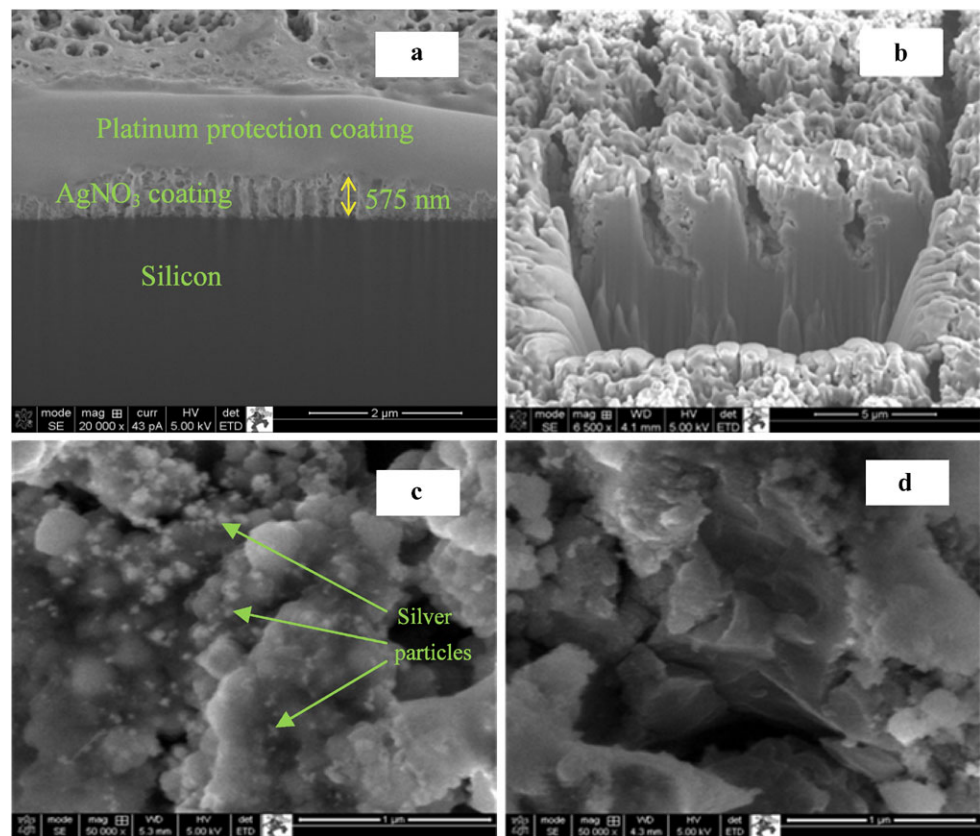
The SERS substrate is prepared in the following steps. First, a silicon wafer sample was cleaned ultrasonically in methanol and then dipped into a 1.0 M aqueous silver nitrate solution for 10 min at room temperature. Next, the sample

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Fig. 1 (a) SEM image showing the thickness of AgNO_3 coating (tilted 45 degrees), (b) SEM image showing the surface substructure after fs laser micromachining, (c) high magnification of the SEM image showing silver nanoparticles on laser machined substrate with AgNO_3 coating, (d) high magnification of the SEM image showing no silver nanoparticles on laser machined substrate without AgNO_3 coating



was removed from the silver nitrate solution and air dried [9]. A thin layer of silver nitrate was formed on the sample surface. Finally, the silicon sample was processed by the fs laser micromachining system. The repetition rate, center wavelength and pulse width of the fs laser (Legend-F, Coherent, Inc.) are, respectively, 1 kHz, 800 nm and 120 fs. The laser fluence can be adjusted by a combination of a half-wave plate and a linear polarizer and the laser light was directed into an objective lens (Olympus UMPLFL 20 \times , NA = 0.46) and focused onto the upper surface of the silicon sample. The silicon sample was moved by a computer-controlled stage at the desired speed. Upon finishing a line scan, the silicon sample was stepped transversely by 2 μm to start another line scan. It took about 2 min to complete a 200 μm \times 60 μm area. After fs laser micromachining, the silicon sample was rinsed with acetone to remove extra silver nitrate. The sample was dried by N_2 flow and was immediately used for SERS measurements to avoid surface oxidation in air.

Characterization of the silicon SERS substrate was carried out on a 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 600 line/mm grating with an integration time of 2 s.

3 Results and discussion

Figure 1 shows the field emission scanning electron microscope (SEM) images of the fs laser nanostructured silicon substrate. The thickness of the silver nitrate coating is about 700 nm, Fig. 1(a). The laser machining direction is from left to right, and the periodic structures can be clearly seen on the machined silicon substrate, Fig. 1(b), which has been reported [10, 11]. From the high magnification SEM image, Fig. 1(c), many nanoparticles in the size of 20–100 nm were found on the laser ablated silicon substrate. Those silver nanoparticles were confirmed and proved by EDS (Energy-dispersive X-ray spectroscopy) results, which are not shown here. And for comparison purposes, a silicon substrate without coating with a silver nitrate solution was machined under the same conditions, and there are no nanoparticles on the nanostructures, Fig. 1(d).

The spectra of the laser ablated silicon substrates were measured as shown in Fig. 2. Trace (a) is the SERS spectrum of the R6G solution (10^{-6} M) on a randomly selected spot in the laser ablated area with the excitation laser power of 1.7 mW and integration time of 2 s. Trace (b) is the Raman spectrum of the R6G solution of 10^{-3} M concentration measured on the ablated silicon substrate without AgNO_3 coating using the excitation laser power of 8.5 mW and integration time of 2 s. Trace (c) is the Raman spec-

Fig. 2 (a) SERS spectrum of R6G 10^{-6} M solution on the laser ablated SERS silicon substrate with an excitation laser power of 1.7 mW and integration time of 2 s, (b) Raman spectrum of R6G 10^{-3} M solution on the laser ablated silicon substrate without AgNO_3 coating with an excitation power of 8.5 mW and integration time of 2 s, (c) Raman spectrum of R6G 10^{-3} M solution on the unblasted silicon substrate with AgNO_3 coating with an excitation power of 8.5 mW and integration time of 2 s

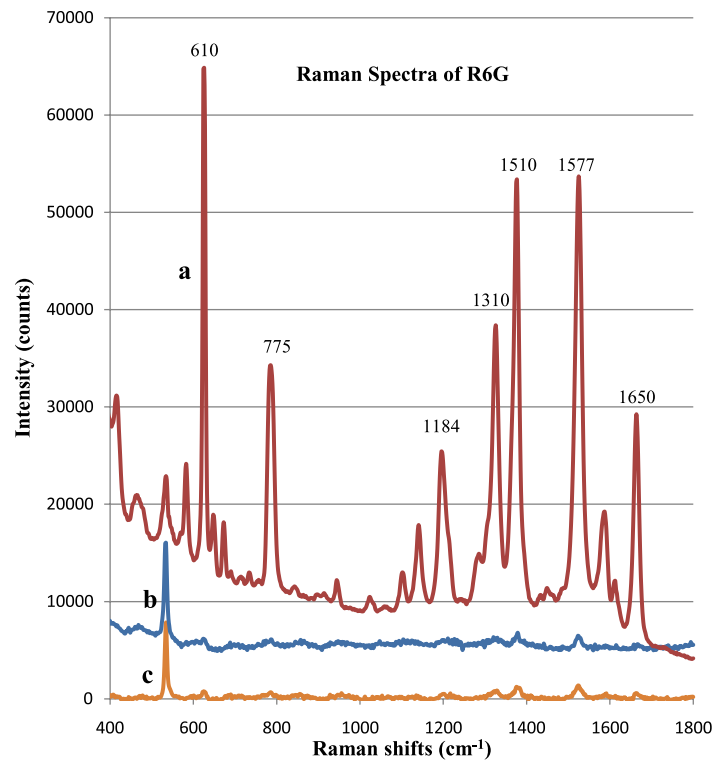


Table 1 Peak positions of R6G on the silicon SERS substrate

Assignment	Raman shifts (cm^{-1})
Xanthenes ring deformations	610
C–H bend	775
Xanthenes ring deformations, C–H bend, N–H bend	1184
Xanthenes ring deformations, N–H bend, CH_2 wag	1310
Xanthenes ring deformations, C–H bend	1360
Xanthenes ring deformations, C–N stretch, C–H bend, N–H bend	1510
Xanthenes ring deformations, N–H bend	1577
Xanthenes ring deformations, C–H bend	1650

trum of the R6G solution of 10^{-3} M concentration measured on the unblasted silicon substrate with AgNO_3 coating using the excitation laser power of 8.5 mW and integration time of 2 s. The trace (a) peak positions are listed in Table 1. By comparing traces (a) and (b), it clearly indicates the strong SERS spectrum in trace (a) is caused by the existence of silver nanoparticles due to the photoreduction of AgNO_3 , and the nanostructures alone caused by fs laser micromachining have no effect on SERS. Without fs laser micromachining, there is no SERS signal for a substrate coated with a silver nitrate layer. The Raman scattering cross-section EF can be estimated by the following equation [12, 13]:

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

where I_{nR} and I_{SERS} are, respectively, the normal Raman and SERS intensities in the unit of $\text{mW}^{-1}\text{sec}^{-1}$ [14]. N_{nR} and N_{SERS} represent, respectively, the number of molecules probed on the reference sample and on the SERS substrate. Using the Raman peak at 610 cm^{-1} as the basis of calculation [15], the EF was estimated to be 5.4×10^5 .

The XPS (X-ray Photoelectron Spectroscopy, KRATOS AXIS 165) measurements were conducted to verify the existence of silver particles. The sputter etching technique was performed to remove possible contaminations on the substrate. The full graph XPS spectra of the silicon SERS substrate are shown in Fig. 3(a). The C_{1s} peak at the binding energy of 284.5 eV (NIST X-ray Photoelectron Spectroscopy Database) was used as an energy reference. As seen in Fig. 3(b), the peak value of C_{1s} is 285.0 eV, which implies

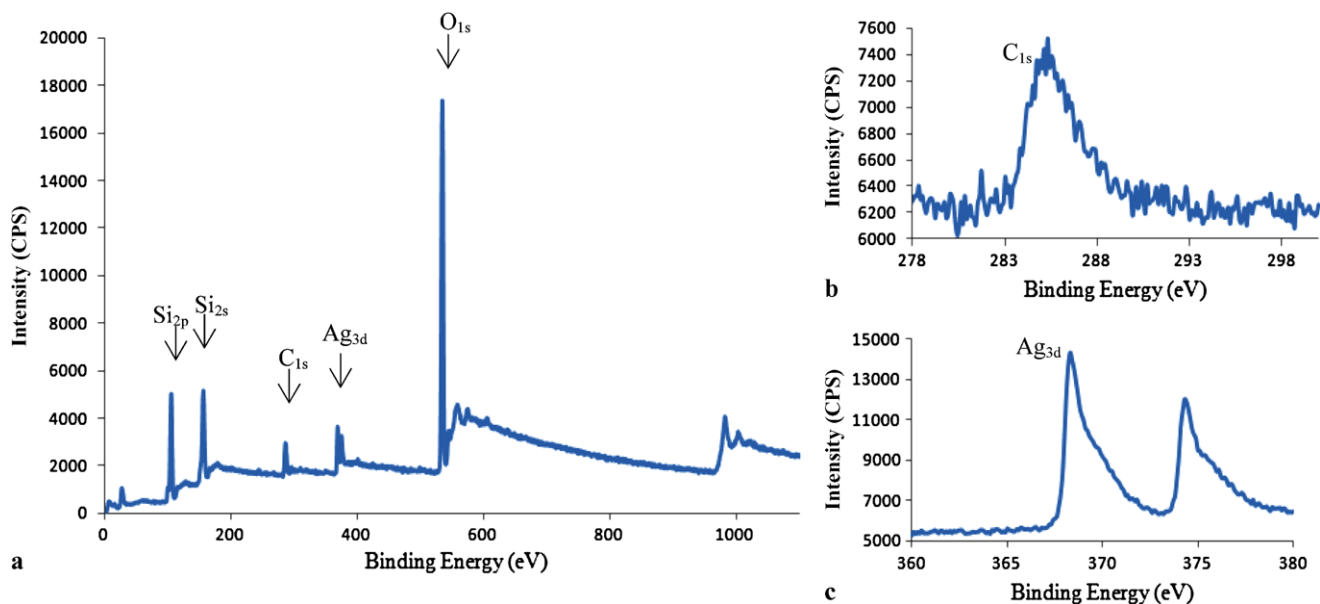


Fig. 3 XPS graph of the silicon SERS substrate. (a) Full graph (1000 ms per 1 eV); (b) graph of C_{1s} (500 ms per 0.1 eV); (c) graph of Ag_{3d} (500 ms per 0.1 eV)

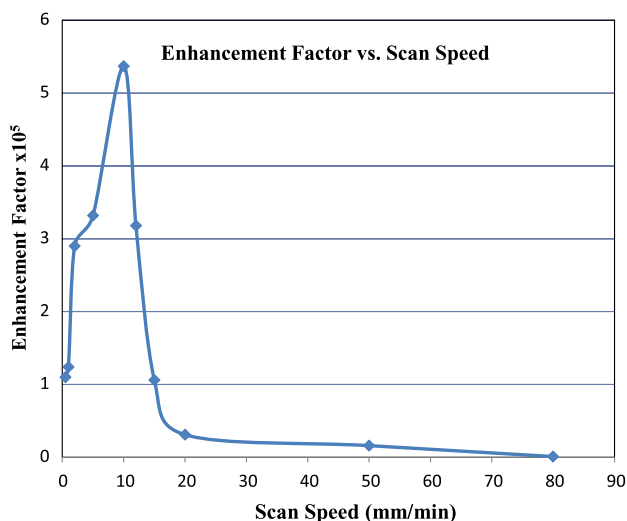


Fig. 4 SERS enhancement factor vs. laser scan speed; laser fluence is 3.56 J/cm²

the standard correction factor of C_{1s} is 0.5 eV (charge-shift value). Hence, the true value of Ag_{3d} should be 368.1 eV (i.e., 368.6 – 0.5), Fig. 3(c), which is consistent with the standard value of 368.2 eV for Ag⁰. Hence, we can conclude that the Ag⁺ ions have been reduced to Ag⁰ atoms.

Parametric studies were also conducted to study the effect of two major process parameters on the intensity of SERS. Figure 4 shows the effect of laser scan speed on the SERS enhancement factor at the laser fluence of 3.56 J/cm². It is clearly seen that there is a peak and the EF rapidly decreases to very low values when the scan speed is higher than about 18 mm/min. At a high laser scan speed, for a given laser

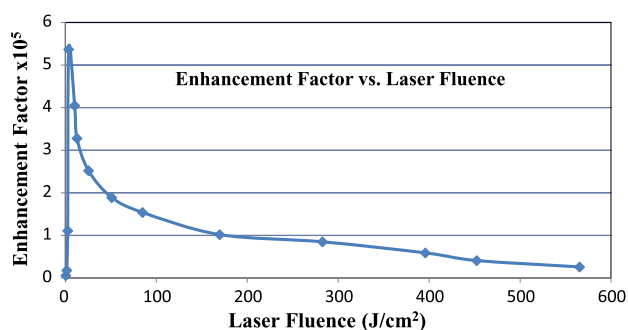


Fig. 5 SERS enhancement factor vs. laser fluence; laser scan speed is 10 mm/min

fluence, the substrate cannot be ablated to form nanostructures, and there is no time for photoreduction to produce silver nanoparticles. On the other hand, at a very low laser scan speed, most of the silver nitrate coating is ablated and removed and very few silver nanoparticles remain. Figure 5 shows the EF increases as the laser fluence increases at the scan speed of 10 mm/min. The EF reaches the maximum at the laser fluence of about 3.56 J/cm² and then it decreases as laser fluence increases. It is interesting to note that even at very high laser fluences, the EF is low but not zero. This indicates that even at a very high laser fluence, not all silver nitrate coating is ablated away by laser pulses. This is in contrast to the results shown in Fig. 4 in which when the laser scan speed is too high, there is no SERS spectrum because the silver nitrite cannot be photoreduced to become silver nanoparticles.

Due to the multiphoton effect of the fs laser pulses, silver nitrate is ionized to become silver ions which are then re-

duced to silver nanoparticles through the following process: $2\text{AgNO}_3 \rightarrow 2\text{Ag} + 2\text{NO}_2 \uparrow + \text{O}_2 \uparrow$. However, the photoreduction can occur only when laser energy exceeds a threshold value and lasts a certain period of time, which allows the photoreduction to act. In this study, as the silver nitrate is pre-coated on the substrate, a high laser intensity may remove the coating leading to no or very few silver nanoparticles. Hence, in order to achieve the maximum SERS spectra, several competing factors need to be considered in the laser micromachining process. After ultrasonical methanol bathing of the SERS substrate, the SERS spectra, although a little weaker, still exist. Hence, the fs laser pulses not only can reduce the silver ions, but can also fuse the silver particles onto the silicon substrate [10], which may enhance the stability and reliability of the SERS substrate.

4 Conclusion

In summary, we present a simple method to simultaneously obtain nanostructures and silver nanoparticles on the surface of the silicon substrate by using fs laser pulses for SERS applications. An EF of 5.4×10^5 was achieved. The proposed fast fabrication method for SERS has potential applications for biological or chemical detections.

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