Surface-enhanced Raman scattering in femtosecond laser-nanostructured Ag substrate

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Abstract. We demonstrate that a surface-enhanced Raman scattering (SERS) substrate could be directly fabricated on the surface of Ag film by femtosecond laser micromachining. According to the morphology observation by SEM, an amount of nanoparticles, nanoprotrusions, and nanospikes were found to form in the ablation region and the density and size distribution of these Ag nanoparticles depended possibly on the incident laser intensity. Additionally, a large area of nanostructured region was produced by fast line scanning, and an enhancement factor of ~105 was obtained in this region after the sample was soaked in the rhodamine 6G solution for 30 min.

1. Introduction

In the past few decades, femtosecond laser micromachining, based on its ultrashort interaction time and ultrahigh power density, has demonstrated unique advantages in the field of micror or nanostructuring on various material surfaces [1~3]. In the case of metals, the femtosecond laser micromachined areas have already ranged from surface ablation, drilling and cutting [4] to manufacture functional microstructures for microfluidics, biological sensor or chemical catalysts [5~8]. Recent research results show that some induced nanostructures on the metal surface could significantly enhance the resonant excitation of localized surface plasmons [9~11]. For example, Guo et al. reported a new technique to control surface reflectivity of metal from UV to terahertz band by femtosecond laser direct patterning [9]. In that process, femtosecond laser irradiation could produce periodic metal species in form of nanoparticle, nanosphere, nanoprotrusion, and nanocavity on the surface. As a result, these novel phenomena greatly richen the optical properties of metal. In addition, it is well known that some noble metal nanoparticles absorbed by individual molecules could be active sites for surface enhanced Raman scattering (SERS), so we try to use femtosecond laser to fabricate an SERS substrate on the surface of Ag film.

Since SERS has very high sensitivity in individual molecular detection, it has been extensively studied since its discovery in 1977 [12, 13]. Up to date, the fundamental mechanism of SERS is still far to understand, but most of the SERS results include a resonant scattering process in the rhodamine (R6G)/Ag system. In this paper, we used rhodamine solution to overlay a femtosecond laser-nanostructured Ag film, and an SERS enhancement factor (EF) of ~105 at a 514nm excitation wavelength was obtained. We think that this is an easy femtosecond laser writing technique to pattern large areas Ag substrate for SERS.
2. Experimental
The Ag films used in this experiment were coated by magnetron sputtering method (JGP-450a made by SKY Technology Development Co., Ltd), and the film substrates were borosilicate glass. The target material was Ag with purity of 99.99%. The sputtering time was 20 minutes.

A regenerative amplified Ti: Sapphire mode-locked pulse laser (Spitfire, Spectra-Physics Co.) emitted a train pulse of 1 kHz, 120 fs and 800 nm. A Gaussian profile laser beam was guided onto the Ag film by a 20× objective lens (N.A. = 0.3), and the diameter of the focused point was about 10 µm in the focal point. By using a computer controlled 5-axis motion stage with minimum resolution of 1µm, we could select the irradiated region through moving the laser focal point. The average power of incident laser could be controlled by adjusting a neutral density filter.

Two kinds of rhodamine aqueous solution with respective concentrations of 10⁻⁷M and 10⁻³M were prepared for SERS measurement. Firstly, the rhodamine powders were dissolved in distilled water, and then an amount of NaCl was added into the solution so that the Cl⁻ ion can stabilize the rhodamine’s absorption on Ag nanoparticles. After the two solutions were stirred by magnetic stirrer for 1 hour respectively, the femtosecond laser-nanostructured Ag film sample was soaked in the 10⁻⁷M rhodamine solution for 30 minutes. And a referenced Ag film sample without femtosecond laser irradiation was soaked in 10⁻³M rhodamine solution for 30 minutes as well. The Micro-Raman spectrometer (Renishaw Invia) was used for SERS measurement with 514 nm excitation wavelength.

3. Results and discussion

![SEM images of surface morphology of the nanostructured Ag film after one pulse irradiation at fluence of 1.27 J/cm².](image1)

Figure 1. (a) SEM images of surface morphology of the nanostructured Ag film after one pulse irradiation at fluence of 1.27 J/cm². (b) ~ (d) The nanoscale structures in the respective regions in (a).

After the as-deposited Ag film was cleaned by de-ionized water, a femtosecond laser pulse with 4 µJ energy was irradiated to the surface through 20X objective lens. To avoid the optical breakdown of Ag film, the focused plane was set to be 100 µm above the sample surface. Figure 1 shows the SEM images of surface features of the nanostructured Ag film after femtosecond laser irradiated at fluence
of 1.27 J/cm$^2$. In the laser irradiated region, an obvious nano-scale web structure like a coral could be observed. Besides that, a few of nanoparticles, nanoprotrusions and nanospikes formed at the end of each branch of this structure, and they looked rather random and sparse. As the Gaussian distribution of the laser profile, the size and density of the formed Ag nanoparticles showed a little discrepancy [Figure 1. (b)~(d)]. The Ag nanoparticles (∼150nm) in the center region was slightly larger than the ones (∼50nm) in the surroundings, but their densities were contrast to their sizes. The proposal mechanism was that these larger structures were associated with surface defects or laser beam intensity inhomogeneities [10].

Since the Ag nanoparticles could be formed by femtosecond laser ablating, a large area of nanostructured region was produced by line-scanning the Ag film surface. The stage moving speed was about 50 µm/s. As shown in figure 2 (a), a series of parallel lines with uniform nanostructures occurred after femtosecond laser ablation. Under the magnified observation [Figure 2 (b) and (c)], we could found some microgrooves formed in the ablated region. In addition, many nanoparticles and nanoprotrusions resided on these concave-convex structures. In this condition, these generated Ag nanoparticles constituted an electric-coupling system in which the giant electromagnetic enhancements could be achieved through interacting their electric fields between any two adjacent ones under the resonance excitation [11]. By this means, these nanoparticles became the so-call “hot spots” to support the SERS.

Figure 3. shows the SERS spectra of a femtosecond laser nanostructured Ag film with 10$^{-7}$M R6G solution (red line) and the normal spectra of the as-deposited Ag film with 10$^{-3}$M R6G solution (black line). For the two spectra, the 514 nm excitation powers are 10mw and 1mw, respectively. The accumulation times is 10s for both ones. The apparent enhancement factor was experimentally measured by direct comparison using the following relation:

\[
EF = \left( \frac{RS^{ENH}}{RS^{REF}} \right) \times \left( \frac{C^{REF}}{C^{ENH}} \right),
\]

where \(RS^{ENH}\) and \(RS^{REF}\) are the measured Raman intensities,
and $C^{\text{REF}}$ and $C^{\text{ENH}}$ are the solution’s concentrations for normal and enhanced samples [14]. According to this equation, we calculated that their EFs at different Raman peaks $610$ cm$^{-1}$, $770$ cm$^{-1}$, $1358$ cm$^{-1}$, $1507$ cm$^{-1}$, and $1647$ cm$^{-1}$ were $5.4 \times 10^5$, $5.3 \times 10^5$, $7.3 \times 10^5$, $6.2 \times 10^5$, and $9.3 \times 10^5$, respectively. These EFs proved substantially that the femtosecond laser-nanostructured Ag film could be used to enhance signal sensitivity for the SERS measurement. Generally, there existed two enhancement processes derived from physical and chemical mechanisms in the SERS [15, 16]. In this experiment, the formed Ag nanoparticles ($<200$nm) created an electromagnetic enhancement because they could support surface plasmon resonance at visible wavelengths, which is in term of a physical enhancement process. Simultaneously, most of the Ag nanoparticles combined with the rhodamine molecules also yielded a resonance Raman enhancement due to a metal-to-molecule or molecule-to-metal charge-transfer electronic transition, which is a chemical enhancement process. Due to the working together of these two enhancement processes, the rhodamine Raman scattering signals on the surface of the nanostructured Ag film exhibited a very large cross-section enhancement factor of $\sim 10^5$.

![Figure 3](image)

Figure 3. (a) The SERS spectrum of the nanostructured Ag film in $10^{-7}$ M R6G solution (red line) and (b) the Raman spectrum of the as-deposited Ag film in $10^{-3}$ M R6G solution (black line: $\times 10$).

4. Conclusions
We fabricated a kind of SERS substrate by using femtosecond laser ablation on the surface of Ag film. After femtosecond laser irradiation, a textured nanostructure surface with an amount of Ag nanoparticles could be obtained. Due to the laser intensity varying, the density and size of these formed Ag nanoparticles showed a little discrepancy in the different parts of the ablation region. However, by means of a femtosecond laser line-scanning technique, a uniform nanostructure in large-scale could be produced, which was used to the substrate for the SERS measurement. In the current
rhodamine/Ag system, the enhancement factor of the Raman signal is found to be as high as $\sim10^5$. We suggest that this SERS substrate on the surface of Ag film can be applied for detecting micro quantity analyte in chemistry and biomedicine fields.

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