Hybrid micro/nano-structure formation by angular laser texturing of Si surface for surface enhanced Raman scattering

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Abstract: Surface enhanced Raman spectroscopy (SERS) has drawn much research interest in the past decades as an efficient technique to detect low-concentration molecules. Among many technologies, which can be used to fabricate SERS substrates, laser ablation is a simple and high-speed method to produce large-area SERS substrates. This work investigates the angular texturing effect by dynamic laser ablation and its influence on SERS signals. By tuning the angle between the Si surface and laser irradiation, the distributions and sizes of laser induced hybrid micro/nano-structures are studied. By decorating with a silver film, plenty of hot spots can be created among these structures for SERS. It is found that when the incident laser angle is 15° at the laser fluence of 16.0 J/cm², the SERS performance is well optimized. This work realizes antisymmetric distribution of nanoparticles deposited on Si surface, which provides a flexible tuning of the hybrid micro/nano-structures’ fabrication with high controllability for practical applications.

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1. Introduction
Since its discovery in 1977, the technique of surface enhanced Raman scattering (SERS) has drawn much research interest due to its fascinating uses in low-concentration biomolecules' detection and analysis [1, 2]. Two main mechanisms, chemical and electromagnetic enhancement can explain the SERS enhancement [3]. In particular, the latter mechanism is widely accepted as the dominated effect. Due to electromagnetic field enhancement from localized surface plasmon resonances (LSPR), Raman signals can be improved by boosting the intensity of incident photons and Raman scattered photons [4]. Based on this principle, many SERS-active substrates with strong and robust enhancement factors (EFs) have been investigated, such as metallic nanospheres, nanowires, nanocavities and nanorods via chemical syntheses, surface nano-patterning as well as self-assembly [5–7]. Although great successes have been achieved in higher EFs for ultra-sensitive detection [8], poor reproducibility and low reliability of substrates with low throughput as well as complicated fabrication processes have limited its extensive applications [9–11]. Therefore, to address these issues, a simple and fast-speed approach to develop SERS substrates is required.

Laser ablation has initiated a facile route for the fast fabrication of nanostructures over a large area on solid substrates [12, 13]. In the past decade, femtosecond laser microfabrication attracted wide research attention due to its unique properties of high peak power within very short pulse duration and the phenomenon of multiphoton absorption [14]. An one-step femtosecond laser processing was demonstrated to generate grating-like nanostructures as well as the formation of Ag nanoparticles in the aqueous solutions simultaneously [15]. Feng et al. proposed a simple method to fabricate large-area and uniform femtosecond laser induced surface structures on Au coated Si substrates [16]. Furthermore, Yang et al.
developed an efficient approach to fabricate nanopillars decorated with Ag nanoparticles on Si surface by controlling femtosecond laser double-pulse delay [17]. However, the femtosecond laser processing of SERS substrates is time-consuming attributing to its short laser pulse duration and small spot size, which is expected to pattern the surface structures in the nanoscale [18]. Lin et al. reported a rapid and simple method to achieve the SERS substrates by annealing a gold film into gold nanoparticles with nanosecond laser pulses [19]. Meanwhile, Cu nanoparticles with stable properties were obtained in aqueous solutions by nanosecond laser ablation [20]. Recently, Yang et al. investigated an effective approach to employ the nanosecond laser to directly create different sizes of nanoparticles on Si surfaces in air followed by Ag film coating for SERS detection. Via optimizing laser fluence and thickness of Ag film, sensitive and uniform SERS substrates were obtained [21]. Although these one or two step nanosecond laser ablation have shown its good reliability for SERS applications by improving the processing parameters, the effect of angular laser irradiation has not been studied.

In this paper, the behavior of angular laser micro/nano-texturing is investigated by tuning the incident laser angle with respect to Si substrate. Different from the conventional laser processing that the symmetrical distributions of hybrid nanostructures are created on Si surface with nanoparticles decorated along the microgrooves, the non-normal incidence of the laser irradiation on the Si surface is advantageous to aggregate the nanoparticles on one side of the Si surface. The distributions and sizes of nanoparticles can be well optimized by effectively tuning the incident laser angle. After coating a layer of Ag film, SERS intensity is investigated in different regions at various incident laser angles. It is found that the SERS performance is the highest when the incident laser angle is 15° at the laser fluence of 16.0 J/cm². This work initiates a new way to flexibly tune micro/nano-structure distributions for SERS applications.

2. Experimental methods

The hybrid micro/nano-particles are fabricated by a nanosecond pulsed laser ablation system on the n-type Si (100) surface. The laser wavelength is 1064 nm with the pulse duration (τ) of 10 ns, pulse repetition rate (PRR) of 100 kHz, laser spot size of ~20 μm and laser scanning speed of 100 mm/s. Figure 1(a) shows the schematic diagram of the experimental setup. The effective laser fluence on the Si surface is fixed as a constant (16.0 J/cm²) by changing pulsed energy while the angle changes the laser spot area irradiated on the Si surface. The nanosecond pulsed laser ablation creates microgrooves along the ablation path and different sizes of nanoparticles are produced and deposited on the Si surface. Via tuning the laser incident angle, nanoparticles can be aggregated on different regions of the Si surface. Figure 1(b) shows the microscope image of a single line formed by laser beam on the Si substrate at an incident laser angle of 15°. Four different geometry regions are illustrated. The bandwidth of each region is 15 μm. Ag thin film with the thickness of 25 nm is then deposited on the ablated Si surface by a thermal evaporator.

To characterize the fabricated hybrid micro/nano-structures, a JEOL JSM – 5600 field emission scanning electron microscope (FESEM) is used to exam the morphology of the samples. Hybrid SERS substrates are functionalized with a self-assembled monolayer of 4-methylbenzenethiol (4-MBT). The substrates are submerged inside a 10 mM 4-MBT solution made with ethanol for 8h to allow the formation of self-assembled monolayer and then rinsed in an ethanol solution for 30s, followed by nitrogen drying. To characterize the SERS properties of the substrates, a Renishaw 2000 Raman Imaging Microscope is applied with a laser excitation wavelength at 532 nm. The employed laser power is 11 mW with the accumulation time of 2 s. The Raman signals are obtained through a 50 × (NA = 0.8) microscope objective lens and detected by a thermoelectrically CCD array.
3. Results and discussion

Figure 2 shows the SEM images of the four geometrical regions marked in Fig. 1(b) at different incident laser angles. Via controlling the incident laser angle, more nanoparticles can be antisymmetrically aggregated in side B, while less nanoparticle in side A. In each region, the size distribution is gradually changed with the distance away from the microgroove. The Si surface of region I illustrates the microgroove with hybrid micro/nano-structures. As can be seen from the graphs, despite of tuning the incident laser angle, limited nanoparticles can be observed in region I. This is due to the anisotropic ejection of Si atoms from the microgroove at a high laser fluence. Region II is near the microgroove and contains nanoparticles with the size ranging from 50 nm to 200 nm. In region III, smaller Si nanoparticles with the size less than 50 nm can be observed. Furthermore, laser ablation angle affects the size of nanoparticles. To be specific, the size of nanoparticles becomes larger by
increasing the incident laser angle as shown in regions II and III. Furthermore, nanoparticles distribution can also be tuned by the incident laser angle. Region IV indicates the area (60-80 μm) far away from the microgroove. There is almost no particle deposited on this region at the incident laser angle of 90°. By increasing the incident laser angle, due to the larger transport path of the laser induced nanoparticles, a greater number of nanoparticles are able to aggregate in region IV, which implies that laser texturing angle plays an important role in optimizing nanoparticles’ distribution.

To characterize the size distribution precisely, selected nanoparticles within the area of 1μm × 1μm at an incident laser angle of 30° in regions II, III and IV are calculated as shown in Fig. 3(a). In each region, the nanoparticles are below 200 nm. The diameters of the nanoparticles get smaller as the region is far away from the microgroove. More specifically, there are around 87% nanoparticles with the size of 100-150 nm in region II near the microgroove. Then, 68% nanoparticles in the range of 50 to 100 nm dominate region III. Region IV, which is about 50 μm away from the microgroove, has the smallest nanoparticles with size less than 50 nm. The mechanisms will be discussed in the following part. For other incident laser angles, there is a similar trend of nanoparticles distribution in each region compared to that at 30°. Figure 3(b) illustrates the nanoparticles distribution with the size of 100-200 nm in region II at incident laser angles of 0°, 15°, 30°, 45° and 60°, respectively. Likewise, by increasing incident laser angles, larger nanoparticles are able to reach region II. Via tuning the incident laser angle, it is efficient to flexibly control the Si nanoparticles size distribution, which is available for many applications, such as superhydrophobic surfaces [22], photoluminescence (PL) [23] and SERS [21].
The experimental results can be explained by the dynamics of pulsed laser ablation as shown in Fig. 4. It is mainly attributed to the nucleation of laser induced plasma species, dynamic interaction with air molecules and particles, then deposition on Si surface [24]. At high laser fluences, the ablated Si atoms are anisotropically ejected into the air with the plasma plume formation, which consists of high kinetic energy of the species [25]. Then, the plasma species interact intensively with air molecules, resulting in the nucleation of plasma species and the nanoparticles can be formed and aggregated [26, 27]. With further expansion, the kinetic energy of the Si atoms is not high enough to support the nucleation of nanoparticles and there is a transport procedure before the nanoparticles deposit on the Si surface due to the gravity force and air resistance acting on them [24]. With the angle \( \theta \) of the Si surface increasing, the diffusion path is relatively longer in comparison to that when the laser irradiation is perpendicular to the Si surface. Therefore, the nanoparticles are able to reach the further region. This mechanism can affect the nanoparticles distribution.

![Graphs showing SERS spectra and Raman band intensity](image)

Fig. 5. (a–e) SERS spectra of 4-MBT molecules adsorbed on micro/nano-structures ablated at different incident laser angles in regions I, II, III and IV. (f) Average Raman band intensity of 1578 cm\(^{-1}\) at different incident laser angles for regions I, II, III and IV.

The nanoparticles formation and deposition at different incident laser angles can lead to various SERS performances. After 25 nm Ag film deposition on textured Si surfaces with monolayer 4-MBT adsorption, the SERS signals are measured by the Raman imaging microscope as shown in Figs. 5(a)-5(e) and the average Raman band intensity of 1578 cm\(^{-1}\) at different incident laser angles for each region is demonstrated in Fig. 5(f). It can be seen that the Raman signals in region I are very weak (~36 counts) even by changing the incident laser
angle. This is due to a small quantity of nanoparticles in this region, resulting in limited hot spots for SERS detection. The depth of the microgroove is tens of microns, which confines the Raman signals inside the microgroove, making low SERS signals be detected [21]. The intensity of Raman signals in regions II and III can be strongly enhanced and tuned by controlling the incident laser angle. In these regions, nanoparticles formed by pulsed laser ablation create high density of nanogaps and nanocavities, leading to a plenty of hotspots. Since the size of nanoparticles decreases with the distance away from the microgroove, the SERS performance in region III is better than region II at each incident laser angle. Particularly, at the incident laser angle of 15°, the SERS intensity can reach the highest. However, when incident laser angle is larger than 15°, the SERS intensities in regions II and III decrease gradually. This phenomenon is attributed to more nanoparticles being able to reach the regions far away from the microgroove, resulting in the reducing quantity of nanoparticles in regions II and III. In region IV, the SERS performance is very weak when the laser irradiation is perpendicular to the Si surface since there are few nanoparticles arriving this region. With the increasing incident laser angle, more nanoparticles can reach region IV. The SERS intensity increases to ~160 counts when the laser texturing angle is up to 60°. Therefore, via the angular laser texturing, the distributions and sizes of nanoparticles can be well tuned, which provides a flexible means to fabricate micro/nano-structures for practical SERS applications.

4. Conclusions

In summary, the distribution of nanoparticles at various incident laser angles is studied. The single line laser ablation configures the Si surface into four regions and nanoparticles’ distribution for each region is investigated. After a layer of Ag film coating followed by adsorbing the molecules over the laser ablated Si surface, higher density of nanogaps or nanocavities can be created, leading to the electromagnetic field enhancement for SERS measurement. It is found that by flexibly tuning the incident laser angle to 15° at the laser fluence of 16.0 J/cm², the SERS performance in region III is the highest with the particles less than 100 nm. This tunable angular laser texturing approach paves a new way to effectively control the distributions and sizes of nanoparticles for practical applications of Si based SERS substrates.

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