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Application-oriented use of Laser-induced Periodic Surface Structures

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Abstract

This paper investigates the phenomenon of Laser-induced Periodic Surface Structures (LIPSS) on Si single crystals. As usual, by variation of parameters, the morphological and physical properties of the resulting surfaces can be tailored, with respect to their use in many applications. One application-oriented use of LIPSS is the preparation of SERS (Surface Enhanced Raman Spectroscopy) substrates, which can be used to detect extremely low concentrations of molecules. In this experimental work, a possible way of manufacturing of SERS substrates, followed by SERS enhancement testing has been shown.

Keywords*: LIPSS, Raman scattering, femtosecond laser, surface treatment, SERS enhancement.*

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1. Introduction

1.1. About LIPSS

The micro- and nano-meter periodic surface structures are created by laser surface treatment - LIPSS (Laser-induced Periodic Surface Structures) [1]. The LIPSS are created on metals, semiconductors and insulators. Morphological changes are formed as a result of the laser-material interaction by continuous and pulsed laser beam irradiation. The physical properties of the formed LIPSS are influenced by several parameters of the laser irradiation, such as the wavelength of the laser beam, irradiated energy density, pulse width and energy. In addition to the irradiation conditions, the properties of the created LIPSS can be significantly influenced by the free electron density, initial surface roughness and material structure of the irradiated material, as well as the physical and chemical properties of the used medium [2].

The formed LIPSS have different mechanical and optical properties according to their modified surface and material structure properties and as a result they can be used in many different industrial applications. A possible tribological application of LIPSS is the controlled modification of wear properties of different steel surfaces, which can increase the service life of micro-components [3]. Another possible application field of LIPSS is the optical grid, which can be used to modify the optical properties of the elements of equipment for the semiconductor industry [4]. A biomedical application of LIPSS is the surface structuring of titanium-based implants. The LIPSS-covered surface provides the adhesion and growth of cells, so the integration can be accelerated, and the lifespan can also be increased [5].

Another possible application field of LIPSS are the formation of SERS substrates used in surface-enhanced Raman spectroscopy. The plasmonic structured surface of the substrates results in a significant Raman signal amplification of the investigated molecules due to the localized plasmon resonance [6].

1.2. Surface-enhanced Raman spectroscopy

The SERS is a complementary measurement technique to Raman spectroscopy. During surface-enhanced Raman spectroscopic measurements, the molecule to be tested is adsorbed onto the SERS active surface followed by the examination of the Raman spectrum of the molecule. The explanation of SERS enhancement is described by a mechanism based on chemical and electromagnetic interaction. The chemical interaction only affects the amplification to a small extent, so the electromagnetic theory can be used. According to the electromagnetic mechanism, surface plasmons are excited as a result of the incoming laser light. This leads to an increase in the electric field strength between the surface particles, which significantly increases the intensity of the Raman scattering emitted by the molecules to be examined. Based on theory, the amplification of the Raman signals can be increased by optimizing the size and shape of the surface particles and the distance between them.

The SERS substrates can be fabricated by different production techniques. For instance, roughening the surface of a plasmonic material or coating of the structured base surface with a plasmonic material (gold or silver). The aim of the experimental work was to fabricate a SERS substrate using the latter technique [7].

2. Examination methods

During the experimental work polished 4-inch p-type Si (111) wafer was used as SERS substrate [7]. The laser surface treatment was performed with a Coherent Monaco Nd:YAG (1035 nm wavelength) femtosecond impulse width (277 fs) laser device equipped with a 254 mm focal length F-theta lens. The surface of the structured silicon was coated with a gold layer using an AJA Orion vacuum evaporator at a pressure of 10-9 Pa. The surface of the SERS substrates were examined with a 4th generation TESCAN VEGA scanning electron microscope. The SERS enhancement of the fabricated substrates were investigated with the commonly used aqueous solution of 4-aminothiophenol (4-ATP) as a standard probe. The measurements were performed using a Horiba LabRAM HR800 Raman microspectroscope with a 633 nm wavelength, 1 mW laser power. The Olympus BXFM microscope at magnification x50 and numerical aperture 0.6 was used to focus the laser onto the surface.

3. Experimental work

3.1. Preparation of SERS substrate

The SERS manufacturing process was started by laser engraving the back side of the silicon wafer in order to achieve a final substrate size of 6×4 mm (**Figure 1**).

In order to the make the subsequent chopping of the silicon wafer easier, the wobbling technique was used during laser beam irradiation, and to ensure adequate heat dissipation another silicon wafer, located below the target wafer, was used.

After the engraving of the silicon wafer, structured 2×2 mm areas were created in the centre of the polished side by femtosecond laser equipment (**Figure 2**).

The laser irradiation was carried out with 1 MHz repetition frequency, 6.6 μJ pulse energy, 10 mm/s scanning speed and threefold overlap at atmospheric pressure.

After the surface structuring, the silicon wafer was coated with 5 nm titanium adhesion layer and 80 nm gold plasmonic layer using a vacuum evaporator (**Figure 3**).

After the coating process, the silicon wafer was broken into 6×4 mm pieces using lens tissue.

3.2. Investigation of SERS enhancement

The SERS enhancement of the fabricated substrates was investigated using 4-aminothiophenol (4-ATP) solution by Raman spectrometer (**Figure 4)**.

3 μL of the solution was dropped onto the active surface of the SERS substrates, and after the solvent evaporation, analysis was carried out.

Measurements were performed by diluting the initial $0{,}5 \cdot 10^{-2}$ M stock solution to three orders of magnitude. An evaluable spectrum was obtained up to a solution with a concentration of $0{,}5 \cdot 10^{-4}$ M (**Figure 4**). The most diluted $0{,}5 \cdot 10^{-5}$ M solution no longer provided the spectrum characteristic of 4-ATP.

After the evaporation of the solvent, an approximately 100×110 μm areas was mapped using 2 μm steps on the substrate dropped with 4-ATP stock solution ($0.5 \cdot 10^{-2}$ M).

The integrated intensity of the main band of Si

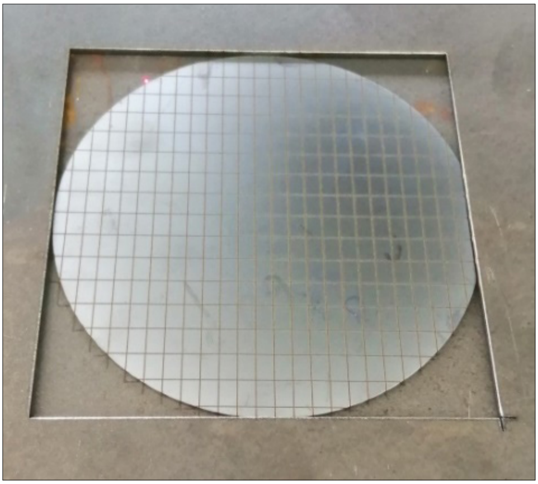

Figure 1. *The back side of the silicon wafer after laser engraving*

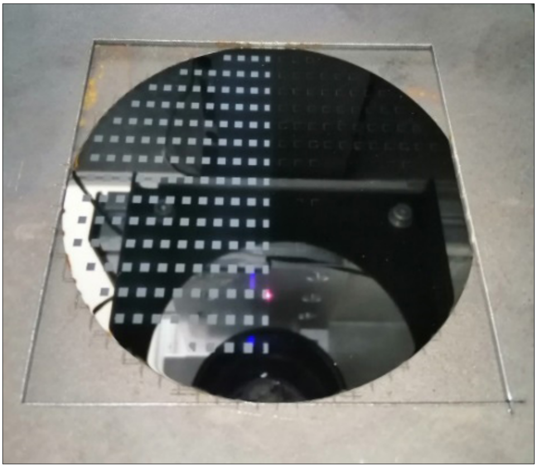

Figure 2. *The surface of the silicon wafer during laser surface treatment.*

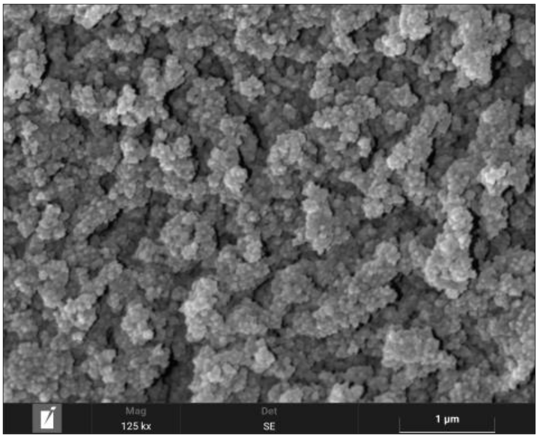

Figure 3. *The structured surface of SERS substrate coated with gold.*

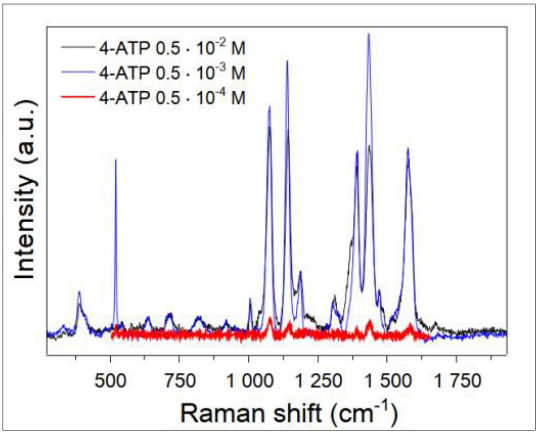

Figure 4. *Raman spectra of 4-ATP solutions with different concentrations on the fabricated SERS substrate.*

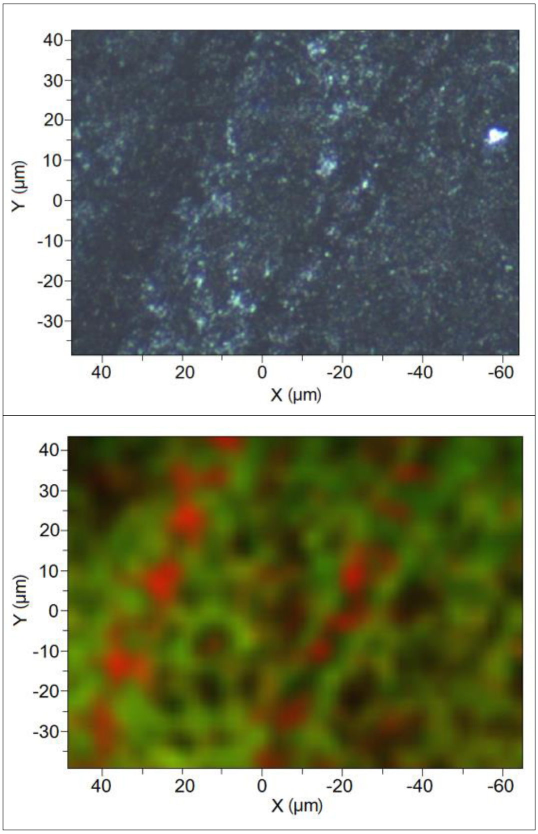

Figure 5. *Raman mapping of the SERS substrate measured with 4-ATP stock solution: optical microscopic image of the examined area (figure above), map illustrating the Raman intensities of Si (red) and 4-ATP (green) signals (figure below).*

(measured at 521 cm^{-1}) is marked in red, and the integrated intensity of the most intense bands of 4-ATP (between 1050–1600 cm^{-1}) is marked in green is on the map shown in **Figure 5.** There are two intensive diagonal lanes belonging to the band of Si. The amplifications of 4-ATP are appeared on the edge of ring-like spots with a diameter of 10 µm which can referred to the morphological units repeating by laser beam overlapping.

Approximately 3.5–5 times (depending on the band) difference can be observed between the minimum and maximum intensities on the amplified bands of 4-ATP in **Figure 6.** The difference may be caused by the morphology of the substrate since the measurements were made in same focal plane during the mapping.

4. Product development

To further investigation of SERS enhancement of the substrate measurements were made with a 10^{-5} M Rhodamine 6G solution. During the same measurement conditions, the SERS enhancement of the fabricated substrate sensitivity was compared with commercially available SERS products [8].

The SERS enhancement of the fabricated substrate is within an order of magnitude comparable to the gold and silver-based SERS substrates of market leading companies (**Figure 7**).

Based on the promising results obtained during the investigation of the SERS enhancement product development was started.

The SERS substrates were put in a labelled PCR tube (**Figure 8**). The wrapped SERS substrates were placed in a vacuumed plastic bag and packed in a paper box with instructions for use (**Figure 9**).

5. Conclusions

There are many application-oriented uses of LIPPS. During the experimental work, we aimed to produce a SERS substrate applying surface-enhanced Raman spectroscopy with femtosecond pulse laser equipment.

The SERS enhancement investigation of the fabricated substrate was examined with 4-ATP and Rhodamine 6G molecule. During the Raman measurements, the amplification of the SERS substrate was compared with products available on the market. Based on the obtained results, the enhancement

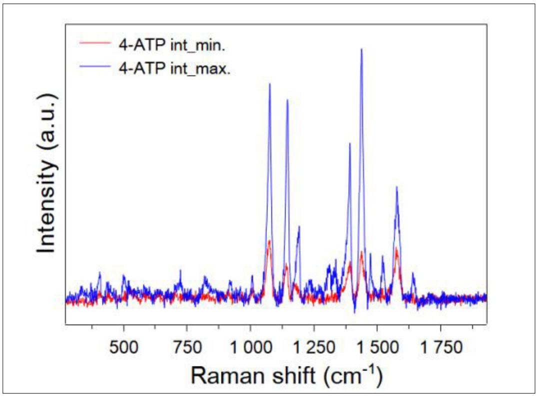

Figure 6. *The minimum and maximum integrated spectra of the enhanced bands of 4-ATP in the Raman map are presented in Figure 5*

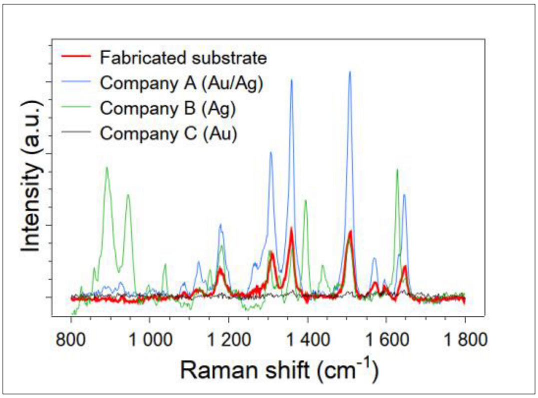

Figure 7. *Comparison of the SERS enhancement of commercially available substrates.*

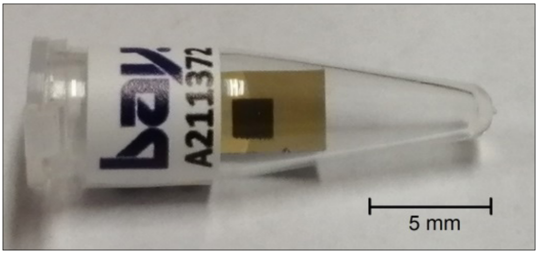

Figure 8. *The fabricated SERS substrate.*

Figure 9. *The packed SERS substrates.*

of the prepared SERS substrate approaches the sensitivity of market-leading products.

Based on the results, the SERS substrate product development has been started.

Acknowledgment

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