

Peculiarities of using different nanostructures for surface-enhanced Raman scattering

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Abstract— Raman scattering as an effective tool for material characterization has one disadvantage which could be solved by using metallic nanostructures. As a result of this, Raman signals of the studied structures could be enhanced by different nanostructures by using surface-enhanced Raman scattering (SERS). The enhancement of the SERS process depends on the material, shape, and geometrical parameters of the nanoparticles, while at the same time on the excitation wavelength and the nature of the selected analyte. Different nanostructures (nanoislands, nanoparticles, nano trees) were created and analyzed, and their parameters were optimized to obtain a higher enhancement factor and to find out the detection limit of the selected analyte. Also, the different creation methods were compared from the point of view of the sensing application.

Keywords— Nanostructures, Raman spectroscopy, Surface-enhanced Raman spectroscopy, Metallic nanoparticles, Photonics.

I. INTRODUCTION

Raman spectroscopy is a type of investigation method, as a result of light-matter inelastic interaction, gives information about the bond structure of different materials, without destroying them. It is a non-destructive and effective analytical tool for material characterization. It uses a high-intensity monochromatic light source, with varied intensity and wavelength. As a result of inelastic light scattering, the material irradiated by this light could be detected, from which bonding structure can be determined. Raman spectroscopy as a method has a lot of fields of application such as material science (investigation of the bond structure of a material), biology (identification of cell structures, molecules), criminology (examination of textiles and other liquids), mineralogy (investigation of rocks, identification of minerals), food safety (detection of microplastics, determination of their types), pharmaceutical industry (investigation of different pills, their lateral and depth distribution), etc. Raman spectroscopy is an essential investigation tool for characterizing a material's bond structure and it has a few major disadvantages: the low intensity of Raman signals, the fluorescence, which increase the background noise and decrease the signal, and the Raman materials [1]. This technique has an important role to study surface

contamination and creating sensing devices based on this method.

One of the ways to solve this disadvantage is by enhancing the Raman signals of the studied molecules, mostly by metallic nanostructures. In case we are talking about surface-enhanced Raman scattering (SERS). This possibility allows us to analyze low-concentration of molecules, and analytes, and even detect one molecule. It became possible by using metallic nanostructures to enhance the Raman signal of the studied molecules by hundred-thousand times in magnitude [1]. This method could be essential for studies of different nanostructures, and different surface contamination or to create high-efficient sensing devices based on them. As a result, it could help to develop the production process, so the quality of the product. For example, it is getting a powerful tool in food quality and safety. Also, from the point of view of electronic technology, it could help to detect contamination, and problems in production, as a result, develop and obtain better products. In another hand, the development of electronic technology could lead to obtaining nanostructures with larger enhancement factors and lower detection limits.

As our previous research shows that thermal de-wetting of thin metallic layers, silver-gold nanostructures, or even silicon nano-trees covered by gold nanolayers could be used for SERS application [2-5]. In this research, we compare the results obtained during the examination of nanostructures created by spark ablation and vapor-liquid-solid techniques, to find the optimal creation parameters for the SERS substrate with a higher enhancement factor, which is suitable to detect the least analyte and will be suitable for further applications.

II. MATERIALS AND METHODS

A. Preparation of different nanostructures as SERS substrates

The first type of nanostructures were gold nanoislands created by thermal de-wetting of thin gold layers. Varying the creation parameters (gold thin layer thickness, time, and temperature of annealing), the parameters of the created structures (the nanoisland's geometrical parameter, and their plasmon absorbance wavelength) could be controlled. The thin gold layer thickness was 12 and 9 nm. While the annealing temperature was 450, 500, and 550 °C, the annealing time was 15, 30, 60, and 120 minutes. The process is shown in Figure 1.

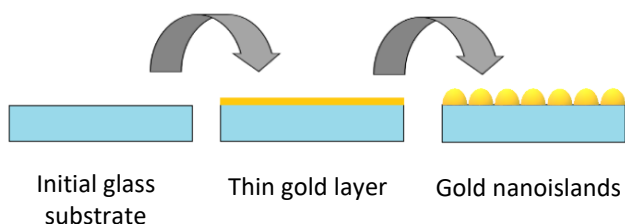


Figure 1. The schematic diagram of the creation of gold nanoislands [2,3].

The second type of investigated nanostructures was nanoparticle agglomerated films fabricated by depositing spark-generated gold, silver, and gold-silver nanoparticles onto quartz microscope substrates. The schematic illustration of the process is shown in Figure 2. The spark discharge generator chamber, in which the nanoparticle creation is going on (1), the heater (2), and the impactor (3) are utilized for the creation of metallic nanoparticles on the glass silica sample holder. The arrows are showing the direction of gas and aerosol flowing. As a result of this method, the created nanostructures differed in their composition: pure gold (S1) and silver (S5), $\text{Ag}_{25}\text{Au}_{75}$ (S2), $\text{Ag}_{44}\text{Au}_{56}$ (S3), and $\text{Ag}_{50}\text{Au}_{50}$ (S4).

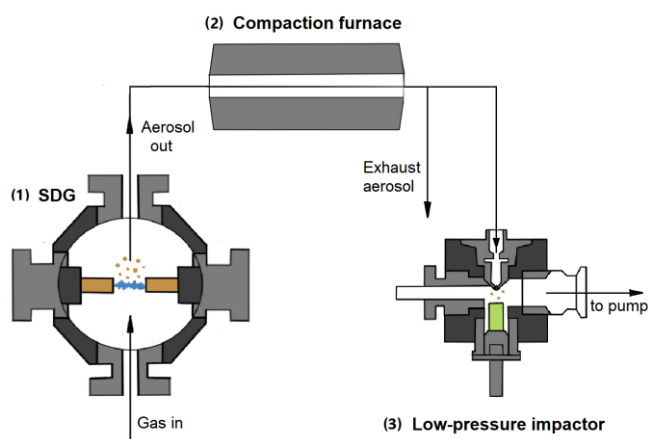


Figure 2. Illustration of the metallic nanostructures creation. [4].

The third investigated nanostructures were gold nanolayered silicon nano trees which were created by the low-pressure chemical vapor deposition (LP CVD) method. Geometrical parameters of the created nanostructures could be varied by the number of cycles. Figure 3 shows a scheme

of gold nanolayered silicon nano trees synthesis. We used for our investigation the four cycles with one silane shot per cycle. As a result, we created 5 different samples: 0, 1, 2, 3, and 4 cycles.

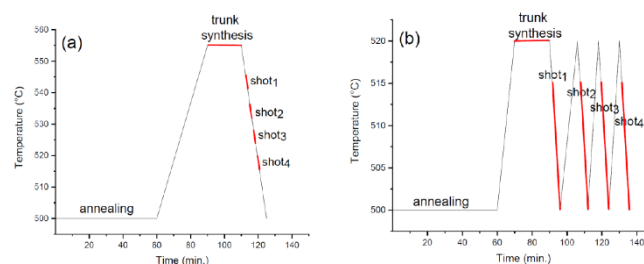


Figure 3. Scheme of silicon nano trees synthesis steps synthesized by LP-CVD [5].

B. Investigation of the created nanostructures

Freshly prepared metallic nanostructures were investigated by scanning electron microscopy (SEM). The SEM pictures were taken with a ThermoFisher Scientific Scios 2 at low voltage (1-2 kV) and short working distance (~4 mm). All the investigated samples were studied in different locations and magnifications

Figure 4 shows the Scanning electron microscope images of different nanostructures for the SERS application.

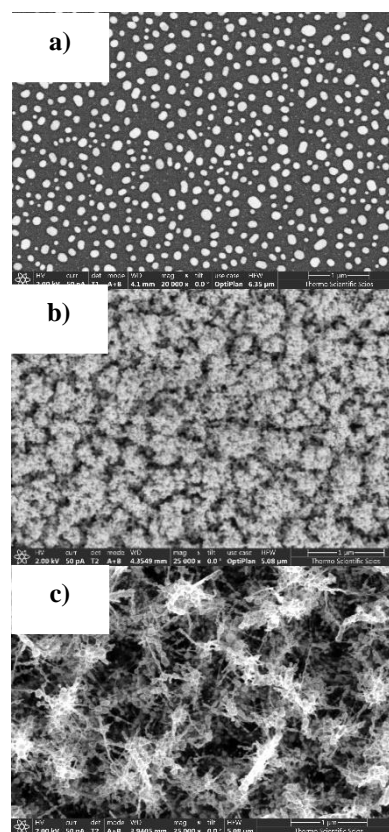


Figure 4. SEM images of the created and investigated nanostructures: a) Thermal de-wetted gold nanostructures, b) Ag-Au gold nanostructures created by arc-discharge method, c) Silicon nano trees covered by gold layer.

C. SERS measurements.

The studied dye molecule was Rhodamine 6G (R6G). The 10^{-5} M of it was used for the measurements. For this purpose, a 50 μ l amount of it was put onto the created nanostructures and dried in air. The investigations were carried out with a Horiba LabRam Raman microscope setup, with an excitation laser with wavelengths of 473, 532, and 633 nm. The Raman spectra of the studied R6G were taken at several points on the studied samples, and averages were calculated. To analyze the enhancement of the metallic nanostructures, the Raman spectra of higher concentration R6G solution (10 mM) were taken on a normal silica glass or a silicon substrate, depending on the substrate of the metallic nanostructures. The intensity is optimized for different lasers. During the investigation, the measurement time is 30 s, the accumulation is 5. For all investigated samples, the excitation laser beam was focused on the surface of the studied metallic nanostructures using an x50 lens.

To calculate the enhancement of the Raman signal of the studied R6G analyte solution, the enhancement factor was calculated based on the Raman signal of the C-C aromatic ring vibration at 1650 cm^{-1} . Raman signal of the analyte at the normal substrate - I_{Raman} , while at the metallic nanostructure, where enhancement takes place - I_{SERS} . In another hand, the concentration of analyte for normal substrate was 10^{-3} M, while for the metallic nanostructures was 10^{-5} M. Based on this data the enhancement factor (EF) was found.

In this research, the EF was estimated by the following equation [7]:

$$EF = \frac{I_{\text{SERS}}/10^{-5}}{I_{\text{NR}}/10^{-3}} \quad (1)$$

III. RESULTS AND DISCUSSION

The created metallic nanostructures were investigated as SERS substrates and their enhancement factor was calculated for different excitation sources. Figures 5-7 show the Raman spectrum of R6G recorded on reference substrate and the different nanostructures: figure 5 – gold nanoislands, figure 6- gold, silver, and gold-silver nanoparticles, figure 7 – silicon nanotrees with gold layers,

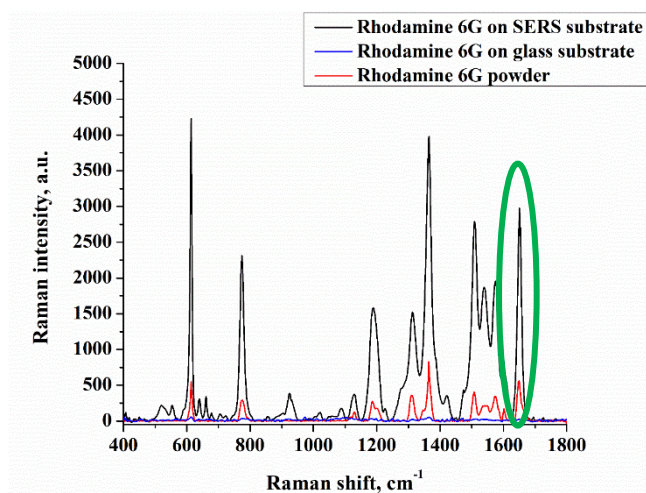


Figure 5. Raman spectra of R6G measured on gold nanoisland SERS and pure glass substrates, and in solid form.

In Figure 5, analyzing the measured Raman spectra of the studied R6G analyte could be obtained in all cases, while for the created metallic nanoislands samples it appeared with a higher Raman signal intensity. A higher degree of EF was obtained by using the excitation source with 532 nm.

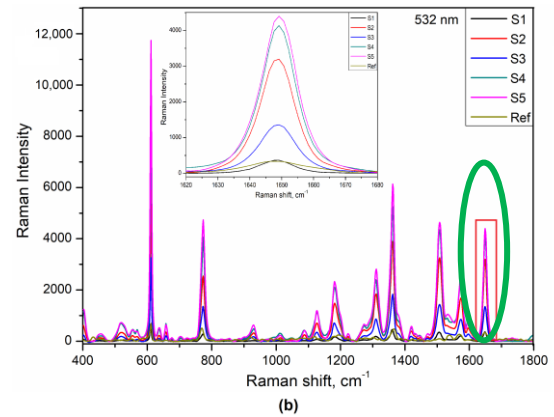


Figure 6. Raman spectra of R6G on S1-S5 and the reference sample.

Raman spectra of the studied R6G analyte were recorded at 532 nm on the reference and the metallic nanostructured substrates as well (see Figure 6). It could be seen, that all nanostructured samples show a higher Raman signal of the investigated R6G in comparison to the reference sample. The EF value depends on the parameters of the studied samples and the excitation wavelength.

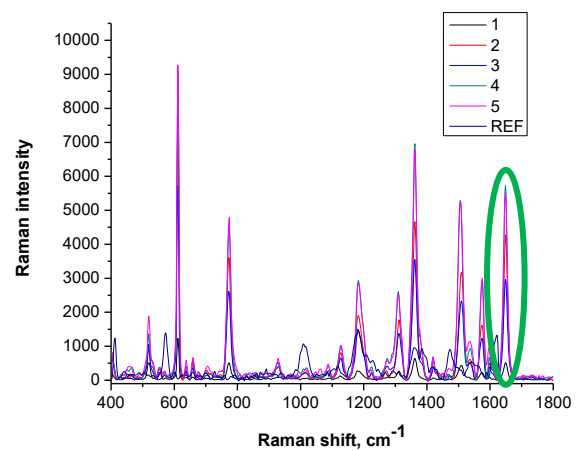


Figure 7. Raman spectra of R6G on five different nanostructured samples and the reference sample.

The Raman spectra of the investigated Rhodamine 6G were taken on the created five different nanostructured samples and on the reference one as well (see Figure 7) at 532 nm excitation wavelength. It could be seen, that the created and studied samples are enhancing the Raman signal of the studied molecule.

As a summary of the results, it was shown, that in all three cases, the metallic nanostructures increase the intensity of the Raman signal of the investigated Rhodamine 6G molecule, so the SERS effect took place. However, the enhancement factor depends on the nanostructures parameters, and also, on the laser excitation wavelength. Table 1 summarizes the enhancement factor of the gold nanostructure substrates for

different excitation sources. The error of these values was 5-10 %.

Table 1. Enhancement factor values of different samples were estimated by using Equation 1.

Sample type	SERS Enhancement Factor for Different Excitations		
	473 nm	532 nm	633 nm
Gold layer dewetting	-	56-259	2-54
Spark discharge deposition	819-197155	8904-132208	24153-195305
Low-pressure chemical vapor deposition	-	84748-539245	44202-1028550

It could be seen from Table 1, that for different sample types, we obtained different enhancement factors, which value depends on the type of creation, excitation source, and parameters of the SERS substrate.

For the gold nanoislands, which were prepared by thermal dewetting, the optimal excitation source was 532 nm, while the best performance was obtained for the sample, which initial thickness was 12 nm, and annealed at 550 °C, and for 15 minutes. This method could be optimized in the future, by adding silver to the composition, and carefully checking the influence on the temperature and on the time of the annealing of the creation process.

For the metallic nanostructures created by spark discharge deposition, larger enhancement factors were obtained as for the previous cases, which could be explained by the larger surface/volume ratio of this structure. The optimal sample and excitation source was sample 5, so for pure silver and 473 nm excitation source. However, silver is not perfect for SERS application, as its stability is worse than that of gold, and the oxidation process is much easier on its surface. The next optimal samples were sample 2, Ag₂₅Au₇₅, and 633 nm excitation source, and sample 4, Ag₅₀Au₅₀, and 532 nm excitation source. The optimization way, as the next step of studies of these nanostructures, is to investigate more, different compositions to find out a stable, but structure with high enhancement.

For the silicon nano trees, obtained with low-pressure chemical vapor deposition, the enhancement factor was even higher, which also could be explained by the higher surface/volume ratio. The better excitation source was 633 nm, while the optical structure was the sample with 3 shots. In this step, the creation parameters could be changed, and optimized, to find out the best substrate, which could be used for a higher enhancement of Raman spectra or to detect a

lower amount of the studied molecules. Also, it could help to develop an investigation method for food safety, and environmental protection, and to develop the technology.

In this paper, nanostructures created via three different methods were compared. It was shown that for all of them, the Raman spectra of the studied molecule in enhanced. The enhancement depends on the excitation source and the parameters of the created nanostructures. There are several ways to optimize the structures and obtain higher enhancement factors. However, nowadays more important became to use these nanostructures allows to study low amounts of molecules, which helps to decrease the detection limit of the studied structures.

ACKNOWLEDGMENT

The support from the ÚNKP-22-3-II-DE-53 and ÚNKP-22-5-DE-407 of the New National Excellence Program of the Ministry for Culture and Innovation from the source of the National Research, Development, and Innovation Fund is mentioned. Istvan Csarnovics is grateful for the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (BO/348/20). This research was supported by Project No. TKP2020-NKA-04 which has been implemented with the support provided by the National Research, Development and Innovation Fund of Hungary, financed under the 2020-4.1.1-TKP2020 funding scheme, project led by Prof. Dr. Géza Husi.

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