THESES OF DOCTORAL (PhD) DISSERTATION

Plasmonic gold surfaces and nanostructures for surface-enhanced Raman scattering

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1. INTRODUCTION

Raman scattering and infrared absorption are two well-known phenomena used in vibrational spectroscopy to investigate specific material properties. The Raman effect is based on the inelastic scattering of light on vibrations of molecules, crystals and other substances. Raman spectroscopy can be used to investigate a variety of organic and inorganic, solid, liquid and gaseous, ordered and disordered materials and their allotropic modifications.

SERS is a technique that can significantly increase the Raman scattering cross-section, by up to 4 to 10 orders of magnitude, compared to normal Raman. The major part of this amplification is based on the enhancement of the electromagnetic field of excited and / or scattered light through an interaction with surface plasmons of metal nanostructures. The gain depends on the type of metal used as well as on the size and morphology of the nanostructures.

According to the Web of Science search engine, more than 1,000 publications were published in 2010, that were closely related to surface-enhanced Raman spectroscopy. This number was doubled by 2016, reaching 2,000 publications a year. The growth trend has continued in recent years. This is not surprising, since under well-chosen measurement conditions the method allows the detection of even a single molecule. SERS has applications in biology, medical diagnostics, chemistry and physics. There are several papers dealing with the SERS analysis of DNA, and the technique is also capable of analyzing complex fluids such as human blood. More research is

focused on comparing biomarkers in the body fluids of sick and healthy people. It is no exaggeration to say that it is only a matter of time before devices and equipment using SERS technology becomes part of the everyday diagnostics. This requires efficient, high quality and reproducible SERS substrates.

2. OBJECTIVES

Surface enhanced Raman scatting is intensively studied nowadays. After the detailed explanation of the phenomenon, research focuses on the preparation of efficient SERS substrates, on the increase of selectivity and the combination of SERS with other methods. The aim of my PhD work was the development of efficient SERS surfaces capable of recording Raman signals of functional groups on the surface of micro-objects such as aerosols, cells or bacteria, and their study by using experimental and numerical methods.

I dealt with the following specific tasks during my work:

— Comparative characterization of SERS substrates of periodic arrays of cavities having different morphology and size using experimental and numerical methods.

— Application of the obtained results for the preparation of perforated, liquid-permeable SERS substrates suitable for trapping micro-objects, and characterization of the obtained surfaces.

— Preparation and characterization of substrates capable for trapping and study of red blood cells.

— Characterization of SERS structures formed by entrapping 50-250 nanometer sized gold nanospheres in quadrilateral pyramidal cavities having two-micrometer base.

3. MATERIALS AND METHODS

3.1. Technologies used for production of Surfaces

The SERS surfaces were manufactured using micromechanical technologies. This widely used method allows precise control of size, shape and arrangement of microscopic surface structures, and even 3D structures. The purpose of photolithography is to create a lateral protective layer with a pattern corresponding to the intended surface structures, which isolates certain parts of the surface while making others accessible for chemical etching. The sample was prepared in the MEMS laboratory of the Institute of Technical Physics and Materials Science, Centre for Energy Research, Hungarian Academy of Sciences. The lithographic mask was made using a Heidelberg DWL66 mask generator. As a masking layer, a 100-500 nm thick SiO_2 layer was deposited on the Si substrate using APCVD (atmospheric pressure chemical vapour deposition) technology. A properly structured photoresist layer was formed using a Karl Süss MA 6 mask fitting instrument. The silicon oxide was removed from the desired areas with an HF-containing caustic/etchant.

Silicon etching plays an important role in shaping the 3D morphology of SERS surfaces. In the present case, special wet chemical etching techniques were used to create SERS substrates, utilizing the differences between isotropic and anisotropic etching. A silicon single crystal substrate allows a highly effective anisotropic etching using alkaline etch systems because of the difference in energies between Si-Si bonds in different crystal planes. To form SERS substrates, SiO_2 was etched in a buffered HF solution, and an HF / HNO_3 system was used for Si isotropic etching. The technology also provides the possibility of combining the above-mentioned methods, which allows the production of rounded-edge cavities. Perforated SERS structures were also produced by anisotropic etching, but the starting material was a 1 μm thick epitaxial silicon on insulator (SOI) wafer. The substrates produced by 3D micromechanical technologies were covered first with a 5 nm titanium adhesive layer, on top of which a 100-150 nm gold layer vas deposited by electron beam vacuum evaporation in an AJA Orion vacuum atomizer / vaporizer (AJA International Inc.).

3.2. Methods used for morphological characterization

The morphology of SERS substrates was analyzed by scanning electron microscopy (SEM) and white-light interferometry. SEM measurements, with resolution up to 2 nanometers, were performed by using a Zeiss LEO 1540 XB Crossbeam and a Jeol JSM-25 device.

Since the SERS substrates tested had a gold layer on their surface, no additional measures were taken to prevent electrostatic charge buildup. The SEM measurements were made in the Institute of Technical Physics and Materials Science of the Centre for Energy Research, Hungarian Academy of Sciences.

The white-light interferometric surface analyzer used to characterize the SERS substrates is a multifunctional device which can determine the microstructure and topography of a surface by means of vertical scanning measurements and represent them in three dimensions, which enables the analysis of the examined surface from different aspects.

3.3. Numerical methods

The Finite Difference Time Domain method (FDTD) is widely used to solve the Maxwell equations on complex geometries in electromagnetism and photonics. The method is based on solving equations on discrete spatial and temporal lattice cells (so-called Yee cells), where the electrical component is positioned at the edges of the cell and the magnetic component is located at the sides of the cell. In addition, FDTD is a time-domain technique, so it gives time-dependent electric $\vec{E}$(t) and $\vec{H}$(t) magnetic fields. During FDTD calculations, the obtained results are automatically interpolated to each grid point. I have modelled the distribution of electric field strength by interaction with a plane wave for various SERS surfaces, including structures containing perforated and trapped gold nanospheres using the Lumerical FDTD

Solutions v.8.15.736 software. Since the SERS surfaces studied represent arrays of cavities, I used periodic boundary conditions for modeling them in the directions parallel to the surface. In perpendicular direction perfectly matched layer (PML) boundary conditions were applied. While modelling, I used the size data obtained from the morphological characterization of the SERS surface. Based on these, I created the inverse geometry, adjusting silicon as the substrate material, and then added a gold top layer, the thickness of which was set at 150 nm. In order to determine the field distribution, I placed three monitor planes in the simulation cell: two along the axes of symmetry of the cell and one parallel to the surface. Another 2 monitors were used to record reflected and transmitted field strength. The parameters used in the model were validated in several aspects.

3.4. Raman studies

Two Raman spectrometers were used for Raman and SERS measurements: a Renishaw 1000 Raman system integrated with a Leica DM/LM microscope and a Renishaw inVia Raman instrument integrated with a Leica DM2700 microscope. Although several excitation light sources are available for these devices, the Raman measurements were performed at 785 nm excitation. The spectra were displayed using appropriate versions of the Renishaw WIRE software running on the PCs connected to the spectrometers, where the exposure time, laser power, integration, measurement range was set.

3.5. Method for the determination of enhancement

The enhancement factor (EF) was determined using 1 mM solution of benzophenone in ethanol. For spectroscopic measurements, the solution was dripped to the SERS surface and, after drying, the spectra were recorded. As a reference, I always used the spectrum measured on a solution dripped onto a flat gold surface (out of the cavities). In practice, this meant that in addition to the structured portion of the SERS substrates, I dripped solution on the gold-plated silicon surface and used its spectrum as a reference for determining the SERS EF. The drops were deposited using an Eppendorf pipette so that the amount applied to the surfaces was always the same. The diameter of the excitation spot on the sample was approx. 1 μm when using a 100× magnification microscope objective (NA 0.9) at 785 nm excitation. With the help of the Raman spectrometer it was possible to combine the optical microscopy image of the structures and the location of the laser spot, so I could always set the excitation beam in the middle of the inverse structure. The laser power was reduced with the help of the built-in neutral density filters in order to avoid saturation of the detector during the recording of SERS spectra. The power delivered to the sample was the same for normal Raman and SERS measurements as were the integration time and accumulation. During experiments I found that the benzophenone solution on the gold surface evaporates according to a constant moistening angle mechanism, and the solution eventually dries in a smaller area. Although SERS enhancement occurs only in a very thin layer on the gold surface, the rest of the

benzophenone inside the cavity contributes to the measured SERS (or more accurately SERS + Raman) intensity through normal Raman scattering. Therefore, the SERS enhancement factor (SE) was calculated as follows:

$$SE = \frac{I_{SERS} + I_{RSC}}{I_{RSS}} \quad (1)$$

where I_{SERS} is the SERS intensity, I_{RSC} is normal Raman scattering from the cavity, while I_{RSS} is the normal Raman intensity measured on the flat gold surface. Since I_{RSC} reduces the SERS enhancement factor and its value is unknown and difficult to determine, I used the SE value given above as a relative SERS enhancement factor for comparative characterization of the samples.

4. NEW SCIENTIFIC RESULTS

The new scientific results achieved in my research work are summarized in the following Thesis:

1.1. *By comparing Raman spectroscopic signals recorded on periodic arrays of cavities of a quadrilateral pyramid, rounded quadrilateral pyramid, and hemispherical shape of different sizes created in silicon wafers, I showed that the quadrilateral pyramidal pattern with two-micrometer base size has the largest SERS enhancement factor.* *[I,II]*

1.2. By performing finite-difference time-domain model calculations, I determined the local distribution of the electric field and

the maximum enhancement factor of the investigated structures. I found the field enhancement to be the largest in quadrilateral pyramids, where the maximum is localized at the bottom part of the cavity. Also, the intensity of the hotspots of the electric field decreases when the shape is going from structures with definite edges (quadrilateral pyramids) to surfaces of constant curvature (hemispheres). [I,II]

2.1. By using optical microscopy, scanning electron microscopy and Raman spectroscopy, I demonstrated that a flow-through periodic array of inverse, truncated quadrilateral pyramidal cavities, formed by photolithography on a silicon substrate with a two-micrometer base and covered with a layer of gold, is suitable for entrapment of two micrometer-sized particles, and for surface enhancement Raman amplification of characteristic Raman bands of functional groups residing on the particle surface. [III,IV]

2.2. By performing finite-difference time-domain model calculations I showed that the maximum of electric field enhancement is concentrated at the bottom surface of the two-micrometer sized polymer microsphere entrapped in a gold-coated truncated quadrilateral pyramidal cavity. [III,IV]

3. Several orders of magnitude increase of the Raman scattering and fluorescence intensity was observed in structures formed by entrapping 50-250 nanometer-sized gold nanospheres at the bottom of a gold-plated quadrilateral pyramidal cavity with two-micrometer base. I found that the overall amplification of the intensity of Raman scattering

and fluorescence increases with the size of the gold nanosphere. By performing finite-difference time-domain model calculations on these structures, I showed that in structures with 200 nm sized and larger gold nanospheres the maximum of electric field enhancement is localized in the surrounding of gold nanospheres, and the high plasmonic enhancement is concentrated in closed gaps between the curved and planar surfaces of the nanosphere and the inverse pyramid, respectively. [V,VI]

4. PUBLICATIONS RELATED TO THESIS

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