TWO SUBSTRATES FOR SURFACE ENHANCED RAMAN SPECTROSCOPY

Magdaléna Kadlečíková[1], Ľubomír Vančo[2], Juraj Breza[1], Marian Vojs[1], Pavol Michniak[1]

[1] *Slovak University of Technology in Bratislava, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia*
[2]*Slovak University of Technology in Bratislava, University Science Park Bratislava Centre, Vazovova 5, 812 43 Bratislava, Slovakia*
E-mail: magdalena.kadlecikova@stuba.sk

1. Introduction

Surface enhanced Raman spectroscopy (SERS) is an analytical technique based on amplifying the signal of Raman scattering by simultaneous interaction of light with free-electron-like metal nanostructures and with molecules located on their surfaces. It is generally accepted that the SERS enhancement factor depends on two decisive mechanisms: electromagnetic and chemical. Electromagnetic amplification plays a dominant role. Preparation of active substrates for SERS aims at creating a structure that contains, on the surface, metallic particles or a discontinuous layer with metallic fragments with nanodimensions below 100 nm. Signal amplification is different for various metals creating the surface of the active substrate. The highest amplification is achieved when the frequency of electron oscillation in the metal is close to the frequency of the primary laser radiation. For laser radiation in the visible and near infrared regions (400 to 1000 nm) this condition is satisfied if the surface is covered by gold or silver [1].

An active surface for SERS may be prepared by several techniques such as lithography, physical vapour deposition, chemical and electrochemical methods:

- Lithographic techniques (e-beam lithography, nanosphere lithography [2]). Electron lithography is the best method for controlling the shape, position and periodicity of the patterns, though periodicity is not a necessary condition for active SERS substrates. Its drawback, however, is costly instrumentation, laboriousness and a small active area.
- Physical vapour deposition (PVD), thus vacuum evaporation or sputter deposition of metals.
- Chemical vapour deposition (CVD) techniques, see [3, 4].
- Chemical etching and patterning of metallic foils.
- Cyclic structuring of a metallic anode in an electrolyte.
- Electrochemical deposition on a substrate, electrolytic separation from electrolytes [5].
- Cathode reduction [6].
- A special family of methods includes the techniques of self-organization of nanoparticles.

2. Experiment

In this experimental work we examined the activity of two types of active substrates with a nanostructured silver layer for SERS.

2.1 Ag/NCD/Si active substrates

The activity of substrates based on nanocrystalline diamond (NCD) with silver decoration (see Fig. 1) was proved by identification of red fluorescent dyes of alizarine, purpurine and rhodamine 6G. Classical Raman spectroscopy fails to characterize any of the three substances alizarine, purpurine and rhodamine 6G because of a high fluorescent continuum. SERS on active Ag/NCD/Si substrates allowed to resolve the spectra of alizarine

and purpurine despite the similarity in their chemical compositions. The concentration of red dyes in alcohol was about 10^{-3} mol/dm^3. The surfaces of active Ag/NCD/Si substrates were covered also by blue inks and resolved the substances contained in the inks. In addition, Raman maps allowed to reveal the order of single lines made by a pen.
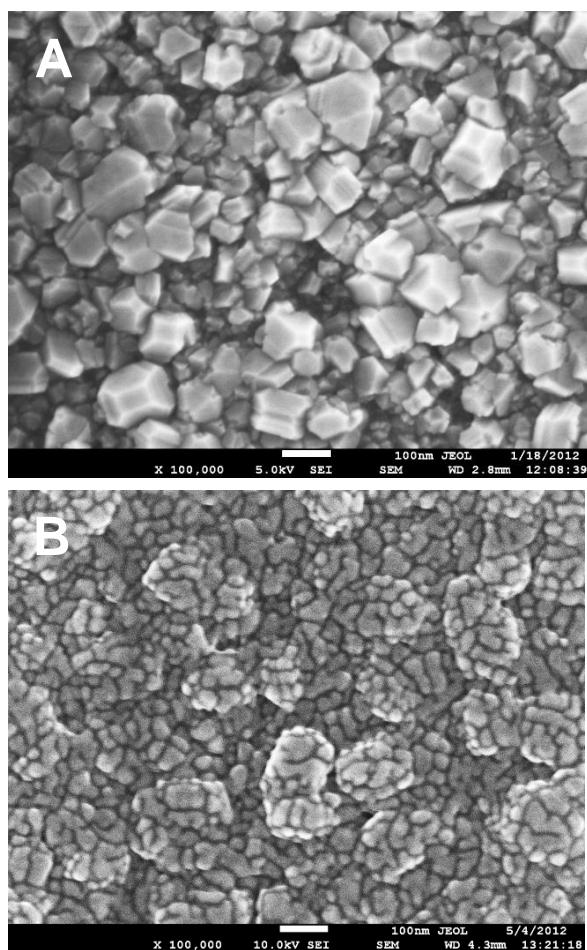

Fig. 1:

(A) Layer of nanocrystalline diamond (NCD) before evaporation of silver.

(B) Silver layer with a thickness of approx. 15 nm evaporated on NCD. NCD was deposited on single-crystalline (100)-oriented silicon (ON Semiconductor Czech Republic, s.r.o., Rožnov pod Radhoštěm) by hot filament chemical vapour deposition (HF CVD). The silicon substrate was nucleated by a suspension of nanocrystalline diamond powder (<10 nm). In the HF CVD process, precursors of methane and hydrogen were used in ratio 1.5:300 sccm. Subsequently, silver layers were deposited on NCD by vacuum evaporation (Sigma-Aldrich, 99.99% purity [7]) from an electrically heated molybdenum boat.
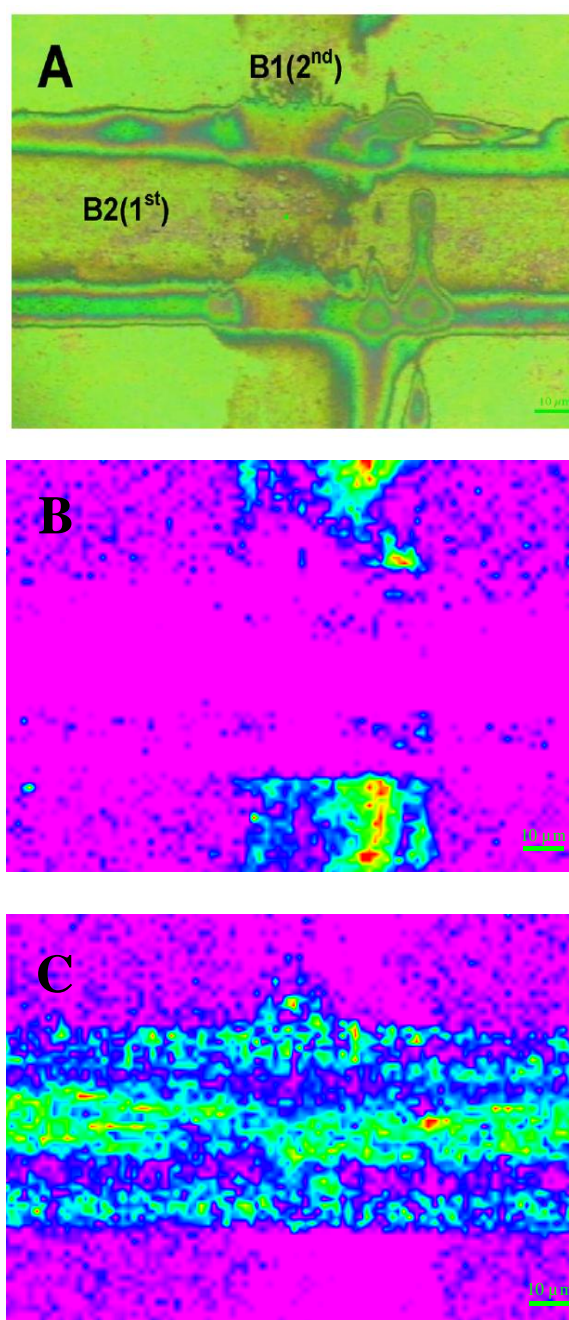

Fig. 2:

(A) Optical micrograph of the cross of two lines written by two different inks B1 and B2 on a Ag/NCD/Si active surface with indicating the order of writing.

(B) Raman map of ink B1 in the spectral window from 1531 to 1551 cm^{-1}.

(C) Raman map of ink B2 in the spectral window from 1517 to 1531 cm^{-1} [8, 9].

Figure 2 shows an example of discriminating two different blue inks in crossed lines. The cross was written directly on the active Ag/NCD/Si substrate by two commercially available pens. In this case, the advantage of the active substrate was also its roughness due to which the deposited silver layer was sufficiently adherent and was not wiped off during writing. Figure 2A shows the optical micrograph of the cross lines with indicating the order of writing. Figures 2B and 2C are SERS maps allowing to unambiguously resolve the two inks used and the order of writing. For more detail see [8-10]. Discrimination of the two blue inks was possible on the basis of subtle spectral differences and suppression of fluorescence.
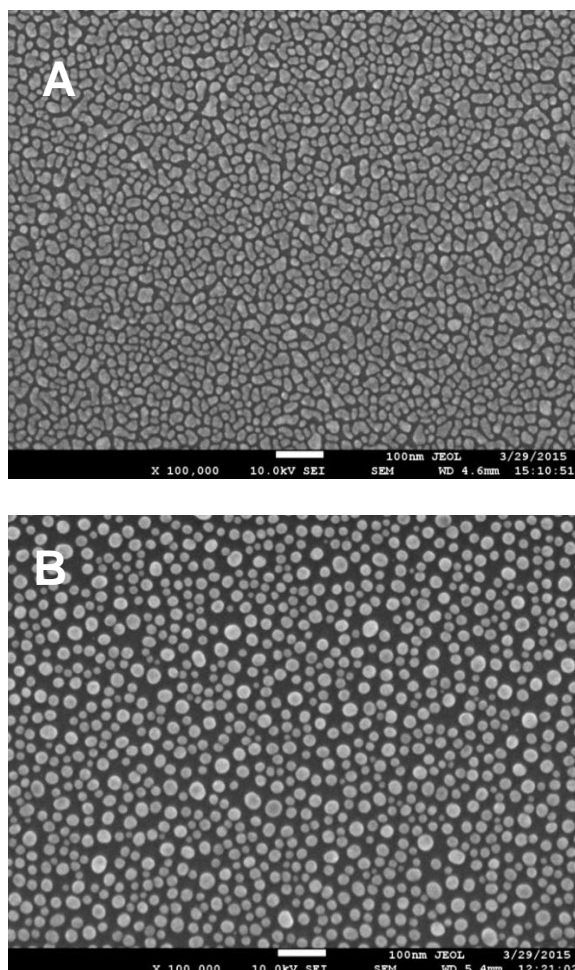

Fig. 3:

(A) Silicon dioxide layers were deposited onto (111)-oriented monocrystalline silicon substrates from MEMC, St. Peter, USA, by plasma enhanced chemical vapour deposition (PE CVD) in apparatus Oxford PlasmaLab 80 using silane and N_2O vapours with gas flows 85:710 sccm, working pressure 133 Pa and substrate temperature 300°C±10%. Subsequently, discontinuous metallic films were deposited by vacuum vapour deposition of silver on SiO_2/Si structures. During evaporation, the thickness of the deposited Ag film was monitored by an oscillating quartz crystal and reached 5 nm.

(B) One of the silicon substrates with an Ag film was annealed (RTA) at 500°C for 120 seconds in vacuum (2×10^{-3} Pa). The scanning electron micrograph shows silver nanoparticles created by annealing of a discontinuous silver layer.
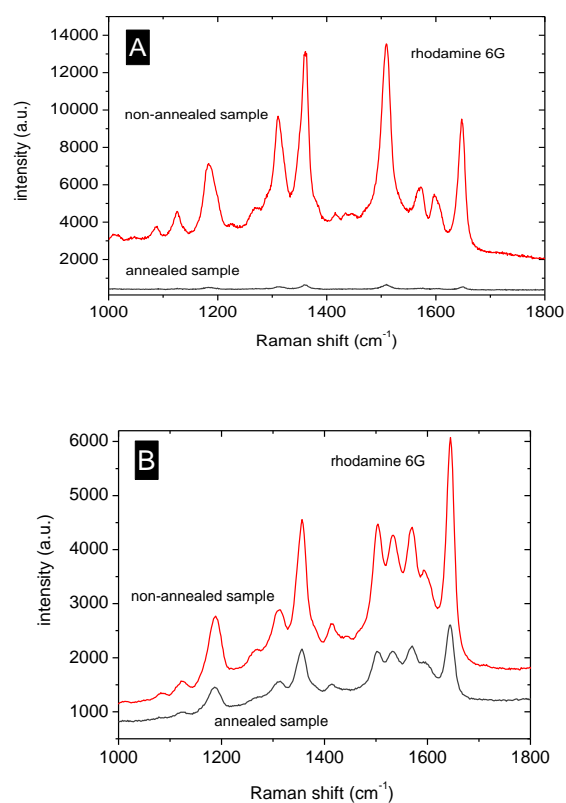
Fig. 4:

(A) Raman spectra of R6G deposited on non-annealed and annealed structures. The spectra were obtained with 632.8 nm He-Ne laser excitation. An objective with a magnification of 100× was used, the laser power was 4.25 mW and the data collection time 1 second.

(B) Raman spectra of R6G deposited on non-annealed and annealed structures excited by laser radiation with a wavelength of 473 nm. Objective magnification 100× LWD, laser power approx. 13 mW, integration time 2 seconds.

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2.2 Ag/SiO$_2$/Si active substrates

The second type of active substrates consisted of a silicon substrate with deposited layers of SiO$_2$ and Ag, see Fig. 3. We studied the effect of annealing, thus of the shape, arrangement and distance of Ag particles upon SERS of rhodamine 6G.

Figure 3A is a SEM micrograph of the deposited silver layer with a thickness of 5 nm. The layer of Ag is discontinuous, the Ag islands having nano-dimensions and various shapes. The SiO$_2$ layer is in this particular case a 2 nm thick native oxide continually covering the whole Si substrate. Figure 3B is a SEM micrograph of the silver layer after its annealing an a RTA furnace. After annealing, the islands of the discontinuous Ag layer created semi-spherical formations. The change in the shapes of the silver nanoparticles resulted in a change of the activity of the substrate for SERS as demonstrated in Fig. 4. When excited by a wavelength of 633 nm, the Raman spectrum of rhodamine 6G (see Fig. 4A) was better developed and approximately 40 times amplified in the case of a non-annealed sample in comparison with an annealed structure.

The observed phenomenon proves that optical resonance conditions in small metallic objects are not purely intrinsic of the material properties but they are strongly linked to the geometry. Two objects made with the same metal but with different geometries will have different resonance conditions [1, 11]. For comparison, Fig. 4B shows Raman spectra of rhodamine 6G on annealed and non-annealed structures excited by laser radiation with a wavelength of 473 nm.

3. Conclusion

In summary, we demonstrated the activity of two substrates with nanostructured silver layers for SERS. The silver nanoparticles can induce a strong localized electromagnetic field and help to suppress undesired photoluminescence, which was verified by identifying red fluorescent organic alizarine, purpurine and rhodamine 6G on both types of substrates. The surfaces of active substrates Ag/NCD/Si were covered also by blue inks and subtle spectral differences allowed to resolve the substances contained in the inks and, in addition, Raman maps allowed to reveal the order of single lines made by different pens. Annealing of the Ag/SiO$_2$/Si substrate changes the shape, arrangement and distance of Ag particles hereby affecting SERS of rhodamine 6G. In the case of a non-annealed sample excited by a wavelength of 633 nm the Raman spectrum of rhodamine 6G was better developed and approximately 40 times amplified in comparison with an annealed structure. The observed phenomenon confirms the fact that optical resonance conditions in small metallic objects are not purely intrinsic of the material properties but they are strongly linked to the geometry.

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