ROMANIAN JOURNAL OF INFORMATION SCIENCE AND TECHNOLOGY
Volume **12**, Number 4, 2009, 496–503

SERS-Active Substrate Based on Macroporous Silicon

Teodora IGNAT[1], Roberto MUNOZ[2], Irina KLEPS[1],
Mihaela MIU[1], Isabel OBIETA[2], Monica SIMION[1]

[1]IMT-Bucharest, Romania
[2]Inasmet Foundation, Department of Biomaterials and Nanotechnologies,
San Sebastián, Spain

E-mail: `teodora.ignat@imt.ro`

Abstract. Novel architectures with nanometric are very promising as building blocks for future nanotechnological applications. Metallic substrates with ordered morphology have been shown to be very effective for surface-enhanced Raman scattering (SERS). The sensitivity of detection is increased by several orders of magnitude by using this technique. In this paper we investigate SERS on thermal evaporated gold layer / porous silicon substrate comparatively to a PVD-gold layer/flat silicon substrate.

Key words: gold nanoparticles, SERS, porous silicon, SAMs.

1. Introduction

Thin films of nanostructured materials are of great interest due to their potential applications in chemical sensing [1], nanoelectronics [2], optical devices [3, 4].

Among these systems, metal films with controlled nanostructure and composition are intensely investigated due to their interesting physical and chemical properties. One of their most important applications is surface enhanced Raman scattering (SERS).

The discovery of Raman signal enhancement on the order of 10^{14} in the presence of nanometre-sized metal structures allows the applying of the Raman scattering technique for single-molecule investigation.

Particular attention has been aimed at the modifying noble metals by coating them with thin, oriented molecular films. Among them, self-assembled monolayers (SAMs) of thiols on silver and gold surfaces are of considerable interest due to simplicity of preparation and flexibility in designing required.

Thiols chemically react with many metals (e.g. Ag, Au, Cu) and bond themselves to the metal surfaces via very strong and stable metal–sulphur bonds [5, 6]. On metal surfaces modified with thiolates monolayers the electrostatic [7], hydrophobic [8], or covalent [9, 10] attachment of bio-molecules is usually possible without the loss of their essential properties.

More than 30 years the activity was concentrated in a complete understanding of the enhancement mechanism of SERS and in the realization of reproducible substrates.

Contrary to claims most substrates are not reproducible. Also, in most of techniques there is no control over the formation of the metallic structures. [11–13].

In this paper, we report a method for the fabrication of a SERS substrate based on nanostructured gold on macro-porous silicon (Au/PS) capped with 11-mercapto-undecanoique acids (11-MUA).

Ultrasensitive detection properties achieved in Raman characterization of the organic monolayer comparatively with their adsorption on PVD-Au/Si has been observed.

2. Experimental condition

2.1. Substrates preparation

Mesoporous silicon with average pore diameter of 1.5 μm was fabricated by electrochemical etching of p-Si wafers (5–10 Ωcm) in a 4 % HF in DMF electrolyte, by applying a current density of 7.7 mA/cm^2. Ohmic contact was formed on the backside of the Si wafer and anodization was done in a single-tank cell (AMMT GBH).

2.2. Gold deposition

A gold layer of 100 nm thickness was deposited by cathodic sputtering on PS substrate, using a Cr layer of 10nm for it adhesion.

2.3. 11-MUA immobilization

The monolayers were formed by immersion of gold substrates in 2mM aqueous thiol solutions for 24 h. All the electrochemical samples were modified shortly after preparation. High quality, clean gold substrates are needed to produce high quality SAMs. So, for obtaining consistent results the PVD-gold on silicon samples were cleaned in piranha solution.

2.4. Characterization

Scanning electron microscopy

Scanning Electron Microscopy (SEM) characterization was realized with a TESCAN VEGA 5136 LM, resolution 3 nm @ 30 kV, accelerating voltage 200 V–30 kV, electron gun source: tungsten filament, magnification: 13× – 1.000.000×, detectors: SE, BSE, LVSTD.

Atomic Force Microscopy

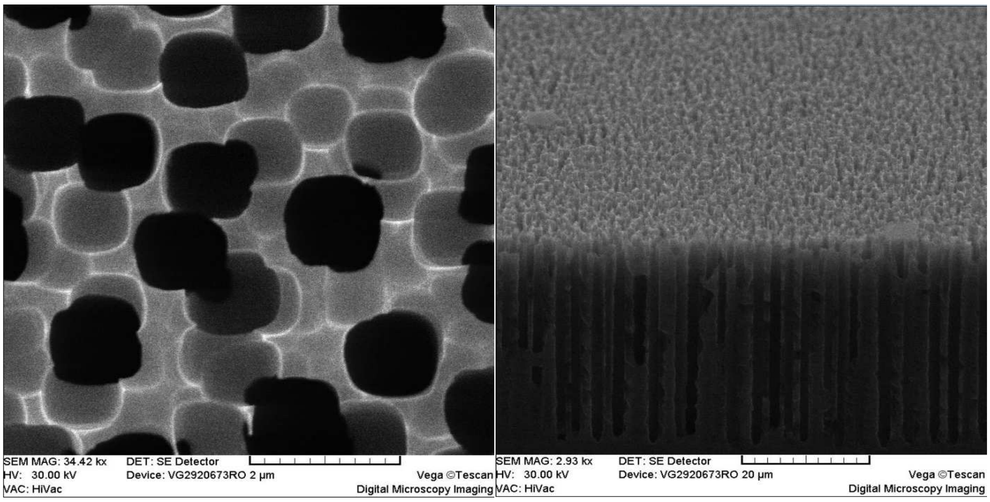
A MultiMode$^{\text{TM}}$Atomic Force Microscope from Digital Instruments with a “J” type scanner on a contact mode was used in Inasmet-Tecnalia San Sebastian to measure the topography of the samples at the nano-scale.

Raman measurements were carried out on Renishau InVia Raman spectroscope attached to a Leica microscope. A 50× objective was used to focus the laser on the sample surface and to collect the scattered light from the sample surface. A 785 nm and 514 nm wavelength laser excitations were used to irradiate the surface.

3. Results and discussion

3.1. Sample morphology

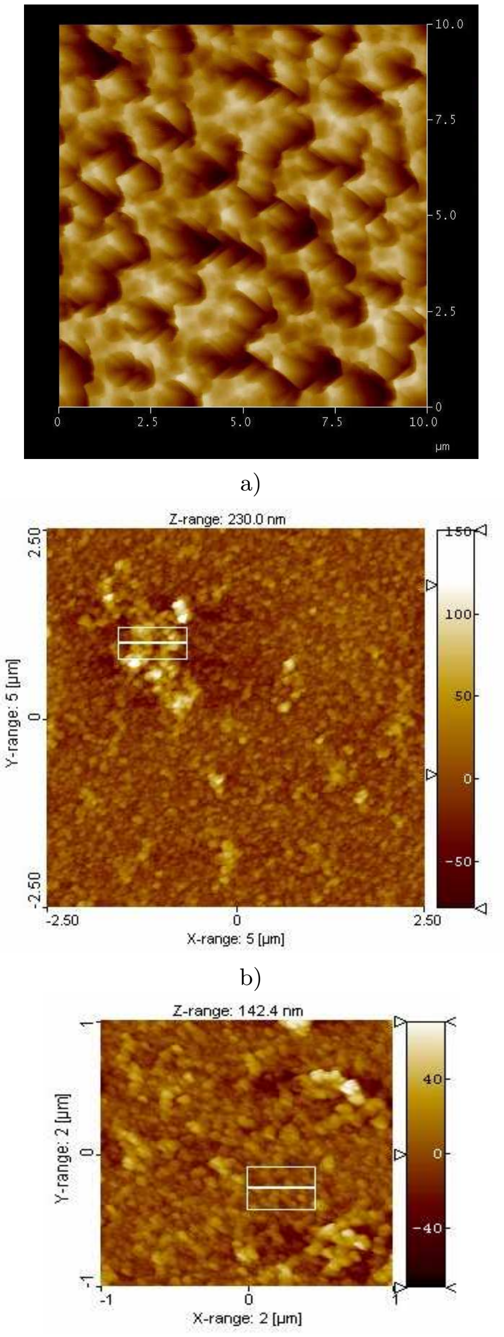
PS substrate morphology was investigated by scanning electron microscopy which revealed 1.5–1.7 μm pore size.



a) b)

Fig. 1. Scanning electron microscopy image of porous silicon substrate: a) top-view; b) cross-section view.

AFM has demonstrated to be a powerful and very descriptive tool on characterization of different gold samples. Areas in different locations were scanned in order to perform roughness analysis and quantification of the samples. The 3D AFM image of the Au/macro PS (Fig. 1) emphasized substrate morphology with gold nanoparticles of around 70 nm.



a)

b)

c)

Fig. 2. AFM images of PVD-evaporated gold on a) macroporous silicon substrate; b-c)flat silicon substrate.

3.2. Raman characterization

Analysis of the SERS spectra of alkanethiols can be very helpful in determination of conformation of adsorbed molecules.

785 nm near-infrared laser excitation

PVD-gold on macroporous silicon substrate Raman spectrum is presented in Fig. 3. At lower wavenumbers 658.38cm^{-1} can be seen the stretching vibration of adsorbed molecules. From the literature [14] this vibration is attributed to the gauche (G) conformer of the S-C-C chain, whereas the band at 737 cm^{-1} is typical of the trans (T) conformer. The intensity of C-S gauche conformer is bigger than the trans conformer.

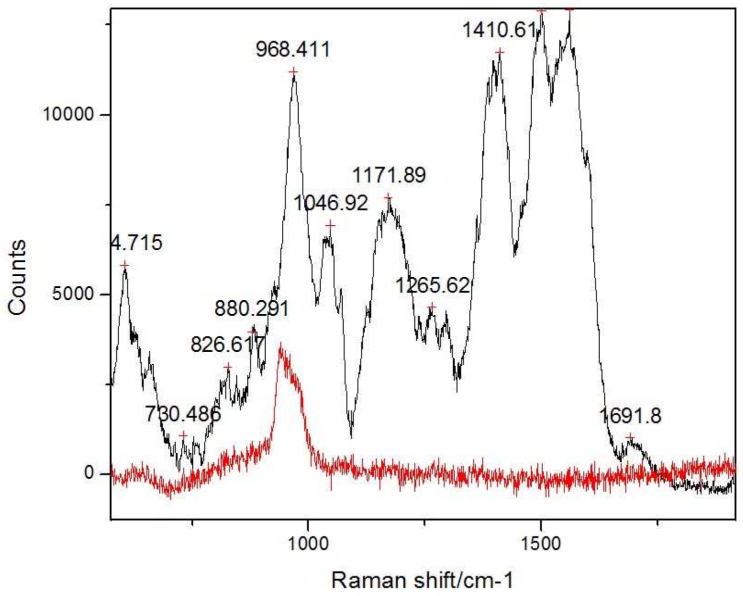


Fig. 3. SERS spectrum - 785 nm - of 11-MUA on PVD-gold substrate/ porous silicon (black) and PVD- gold substrate/silicon (red) obtained by immersion of the gold substrates in 2mM 11-MUA aqueous solution for 24h.

The surface selection rule of SERS state that adsorbate vibrations connected to molecular scattering components perpendicular to the metal surface are more strongly enhanced. This means that the MUA monolayer in this region of the substrate is more or less perpendicular to the surface.

The bands from 826 cm^{-1} can be associated with the deformation vibration of dissociated carboxylic group or with the deformation of OCO groups from the thiol molecule. The intense, sharp band observed at 968.41 cm^{-1} in the Raman spectrum come from the C-COO vibration which can be bonded to the gold substrate [9] whereas the well defined band from 1046.92 cm^{-1} come from the υ(C-C) of internal chain [15]. This gives also the information that the molecule is perpendicular to the gold surface and not parallel. The shoulder observed at 1265.62 cm^{-1} may come from the associated vibration of υ (CO) and δ (OH). Among this, the signals observed at 1295.26 cm^{-1} are attributed to the CH bending vibration. The vibrations from 1500.34 cm^{-1} and 1561.22 cm^{-1} can be associated with the symmetrical (υs) COO$^-$ or υas (OCO) and respectively antisymmetrical (υas) vibration of COO$^-$. Moreover, the small pick from 1691 cm^{-1} could be assigned to a υ(C=O) vibration. This decay in vibration may be due to the formation of hydrogen bond between COOH groups.

The 514 nm laser line was also used to excite 11-MUA on the surface. However, no SERS spectrum was observed (Fig. 4).

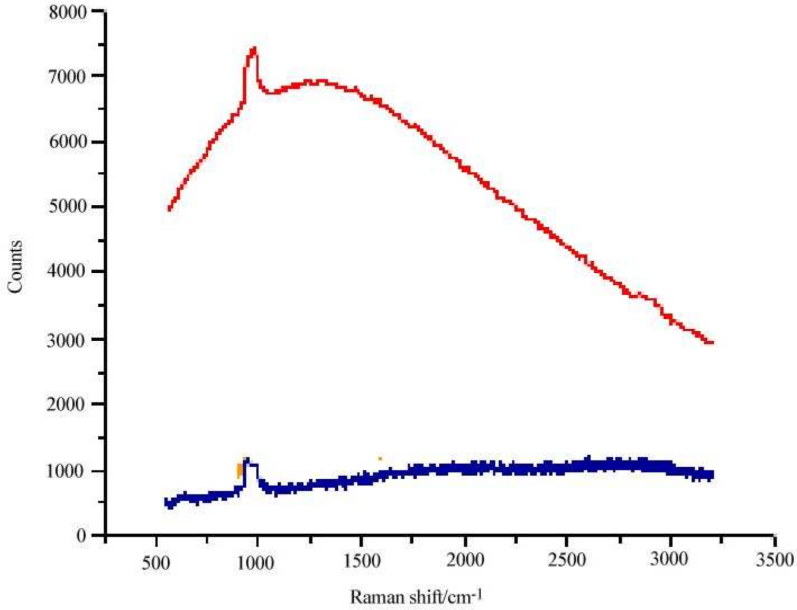


Fig. 4. Comparison of SERS spectrum -514 nm- of 11- MUA adsorbed on PVD-gold/porous silicon and PVD-gold.flat silicon substrate.

In Table 1 can be seen the correspondence bond vibration- band assignments for PVD-gold/macroPS in comparison with those of Klarite substrate.

SERS signals such as those responsible for single-molecule, are presenting a sensitive dependence for the system's nanogeometry.

4. Conclusions

PVD- evaporated gold on macroporous silicon in comparison with p-type silicon (100) substrate has been investigated as SERS for 11-MUA detection. Raman measurements emphasised higher sensitivity of the organic molecule adsorbed on PVD-gold deposited on microstructured porous silicon substrate in comparison with the PVD gold deposited on flat silicon substrate. This macroporous substrate is suitable for (bio) sensors, the characterization of organic molecule conformation on the solid surface being effectively achieved.

Table 1

Band assignment	PS – SERS active substrate, cm^{-1}
C-S_G	658.38
C-S_T	730.48
COO- def	810.59
	826.61
OCO def	882.69
C-COO- as	968.41
	1046
υC-C	1070.15
Si-O-Si + C-H def	1159.07
C-O	1265.62
CH2 bending	1295.26
υs COO-	1410.61
	1500.34
	1541.19
υas COO-	1561.22
υCO	1691

Acknowledgements. The authors thank to PhD Adrian Dinescu for helping SEM experiments. This work was supported by the Ministry of Education and Research, ID884/2007 and TD437/2007 projects.

References

[1] RASHID M.H., BHATTACHARJEE R.R., KOTAL A., MANDAL T.K., *Synthesis of spongy gold nanocrystals with pronounced catalytic activities*, Langmuir, **22**, 2006, p. 7141.

[2] SEUNG J., GUAN Z., XU H., MOSKOVITS M., *Surface-enhanced Raman spectroscopy and nanogeometry: The plasmonic origin of SERS*, Journal of physical chemistry C, **111**, pp. 17985–17988, 2007.

[3] STOLYAROVA S., CHERIAN S., RAITERI R. *et al.*, *Composite porous silicon-crystalline silicon cantilevers for enhanced biosensing*, Sensors and Actuators B-Chemical, **131**, 2, pp. 509–515, 2008.

[4] CHANIOTAKIS N., SOFIKITI N., *Novel semiconductor materials for the development of chemical sensors and biosensors: A review*, Anal. Chim. Acta, **615**, 1, pp. 1-9, 2008.

[5] RONG G., NAJMAIE A., SIPE J.E. *et al.*, *Nanoscale porous silicon waveguide for label-free DNA sensing Source*, Biosens. & Bioel., **23**, 10, pp. 1572–1576, 2008.

[6] WIECZERZAK E., HAMEL R., CHABOT V. *et al.*, *Monitoring of native chemical ligation on solid substrate by surface plasmon resonance*, Biopolymers, **90**, 3, pp. 415–420, 2008.

[7] THOMSEN M.S., NIDETZKY B., *Microfluidic Reactor for Continuous Flow Biotransformations with Immobilized Enzymes: the Example of Lactose Hydrolysis by a Hyperthermophilic β cont;-Glycoside Hydrolase*, Eng. Life Science, **8**, 1, pp. 40–48, 2008.

[8] KUDELSKI A., *Characterization of thiolate-based mono- and bilayers by vibrational spectroscopy: A review*, Vibrational Spectroscopy, **39**, pp. 200–213, 2005.

[9] OSTUNI E., YAN L., WHITESIDES G. M., *The interaction of proteins and cells with self-assembled monolayers of alkanethiolates on gold and silver*, Colloids and Surfaces B: Biointerfaces, **15**, pp. 3–30, 1999.

[10] MICHOTA-KAMINSKA A., WRZOSEK B., BUKOWSKA J., *Resonance Raman evidence of immobilization of laccase on self-assembled monolayers of thiols on Ag and Au surfaces*, Applied Spectroscop., **60**, 7, pp. 752–757, 2006.

[11] NIKIN P., MARTYN C. D., MARK H., *Immobilization of Protein Molecules onto Homogeneous and Mixed Carboxylate-Terminated Self-Assembled Monolayers*, Langmuir, **13**, 24, pp. 6485–6490, 1997.

[12] LI L., CHEN S., JIANG S., *Protein Adsorption on Alkanethiolate Self-Assembled Monolayers: Nanoscale Surface Structural and Chemical Effects*, Langmuir, **19**, 7, pp. 2974–2982, 2003.

[13] KUDELSKI A., *Raman studies on the coverage integrity of monolayers formed on silver from various v-functionalised alkanethiols*, Vibrational Spectroscopy, **41**, pp. 83–89, 2006.

[14] SEUNG C., KEITH R., CALUM M., *Disposable tyrosinase-peroxidase bi-enzyme sensor for amperometric detection of phenols*, Biosensors and Bioelectronics, **17**, pp. 1015–1023, 2002.