

# Low-cost SERS substrates composed of hybrid nanoskittles for a highly sensitive sensing of chemical molecules

Jean-François Bryche, Benoît Bélier, Bernard Bartenlian, Grégory Barbillon

### ▶ To cite this version:

Jean-François Bryche, Benoît Bélier, Bernard Bartenlian, Grégory Barbillon. Low-cost SERS substrates composed of hybrid nanoskittles for a highly sensitive sensing of chemical molecules. Sensors and Actuators B: Chemical, 2016, 239, pp.795-799. 10.1016/j.snb.2016.08.049 . hal-04228371

### HAL Id: hal-04228371 https://hal.science/hal-04228371

Submitted on 4 Oct 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# *Low-cost SERS substrates composed of hybrid nanoskittles for a highly sensitive sensing of chemical molecules*

Jean-François Bryche<sup>1,2</sup>, Benoît Bélier<sup>1</sup>, Bernard Bartenlian<sup>1</sup>, Grégory Barbillon<sup>1,\*</sup>

<sup>1</sup> Centre de Nanosciences et de Nanotechnologies, CNRS, Univ Paris Sud, Université Paris-Saclay, C2N-Orsay, 91405 Orsay Cedex, France <sup>2</sup> Laboratoire Charles Fabry, CNRS, Institut d'Optique Graduate School, Université Paris-Saclay, 91227 Palaiseau Cedex, France

Article accepted: August 2016



#### ABSTRACT

In this paper, we report on the low-cost and quick fabrication at the 4-in. wafer-scale of hybrid nanoskit-ties for a highly sensitive detection of chemical molecules. This quick and low-cost fabrication is achieved by using the native oxide layer as a physical etch mask coupled to an evaporation of a gold layer. The hybrid nanoskittles obtained with this technique are disordered on the 4-in. wafer of Si, and a good definition of nanoskittles and a good reproducibility of SERS signal are obtained on the whole wafer. Moreover, we studied experimentally the sensitivity of these Au/Si nanoskittles for SERS sensing. Finally, enhancement factors in the range of  $10^7 - 1.1 \times 10^8$  were found for the detection of thiophenol molecules with hybrid nanoskittles.

Keywords: SERS; Sensors; Gold; SIlicon

#### 1. Introduction

Actually, the development of Surface Enhanced Raman Scattering (SERS) substrates having high enhancement factors (EF) is the key aspect for the biological and chemical sensing. Advances in nanofabrication techniques have led to a big number of novel SERS substrates, such as colloidal metallic nanoparticles [1–3], metal-lic nanostructures on different surfaces [4–6]. These substrates have demonstrated a large Raman enhancement, however, cer-tain fabrication techniques of these substrates are technologically demanding in terms of time and expensive for a mass produc-tion destined to industrial applications, like Deep UV lithography [7], and Electron Beam Lithography (EBL) [5,8–11]. In addition, other lithographic techniques are available in order to fabricate these SERS substrates with a lower cost such as Nanoimprint Lithography (NIL) [12–14], NanoSphere Lithography (NSL) [15–19]. However, these two types of fabrication techniques can have a limit on the definition of nanostructures obtained on large surfaces. The use of silicon nanowires (SiNW) coupled to metallic nanoparticles is now very well-studied as SERS substrates for their high EFs in order to obtain a better detection limit [20–22]. In addition, Maiolo et al. have obtained a performing electrochemical biosensor from a highly disordered array of SiNWs covered by a gold film characterized by electrochemical impedance spectroscopy [23]. Another advantage of disordered SiNWs is their fabrication with large-surface techniques.

The aim of this paper is to present a simple, quick and low-cost way to realize highly sensitive SERS substrates composed of hybrid (Au/Si) nanoskittles at the 4-in. wafer-scale. To do that, the native oxide layer of a silicon wafer is used as etch mask, which is followed by an anisotropic process of Reactive Ion Etching (RIE) through this native oxide layer and the last step is a gold evaporation. These SERS substrates can be easily integrated into existing Raman spectrophotometers. The ability of Au/Si nanoskittles to be highly sensitive SERS sensors is investigated by using the interaction between gold and thiophenol molecules.

#### 2. Experimental

#### 2.1. Low-cost fabrication of SERS substrate

\* Corresponding author. E-mail address: gregory.barbillon@c2n.universite-paris-saclay.fr (G. Barbillon). The fabrication process of large area of hybrid nanoskittles (NSs) is divided into two parts: (i) etching through the mask obtained by

the native oxide layer, (ii) deposit of titanium and gold layers under vacuum by Electron Beam Evaporation (EBE).

Nanoskittle fabrication process does not require pre-patterning of the surface as it uses the native oxide layer as a physical etch mask. The samples are undergone an anisotropic RIE process with  $C_4F_8$ ,  $O_2$  and  $SF_6$  passivation and etching steps for a few tens of cycles. The process is known as switched process in which fluorine from  $SF_6$  etches the Si while  $C_4F_8$  passivates the surface. By varying the process parameters such as cycle times, number of cycles, platen and coil power and substrate temperature the formation of the nanostructured Si features on the Si substrate can have the appropriate size distribution, depth and density. Then, for the last step of fabrication, a 2 nm titanium layer used as adhesion layer, and a gold layer of 30 nm are deposited by EBE.

#### 2.2. Thiophenol functionalization on SERS substrates

Thiophenol molecules are used in order to study the sensitivity of these SERS substrates. The functionalization protocol is described as follows: (i) preparation of a 0.1 mM solution of thiophenol in ethanol, (ii) dipping the sample in the solution during 2.5 h, (iii) washing thoroughly with pure ethanol, (iv) drying with nitrogen. For SERS studies, thiophenol molecules are mainly chosen as probe molecule for their ability of grafting on metallic surface. Indeed, thiophenol molecules have a similar behavior to other alkanethiols, i.e. the formation of a self-assembled monolayer. In addition, the thiophenol concentration used for the Raman experiments in solution is 1 M.

#### 2.3. Optical characterization

A Labram spectrophotometer from Horiba Scientific is used for the Raman measurements. The excitation wavelength ( $\lambda_{exc}$  = 633 nm) was used for all experiments with a power of ~1 mW. The acquisition time was fixed to 20 s. The laser was focused on the substrate using a microscope objective (×100, N.A. = 0.9). The Raman signal from the SERS substrates is collected by the same objective in a backscattering configuration. This spectrophotometer has a spectral resolution of 1 cm<sup>-1</sup>. In addition, for classical Raman measurements in solution, a macro-objective with a focal length of 40 mm (N.A. = 0.18) and the 633 nm wavelength was also used. All obtained spectra have been normalized by the acquisition time and the laser power in order to compare them.

#### 3. Results and discussion

In the first part, we have realized Au/Si nanoskittles with the fabrication method described in the Section 2.1. The cross-sectional and top-view SEM images of these hybrid nanostructures are displayed in Fig. 1. A good definition of Au/Si nanoskittles is achieved at the 4-in. wafer-scale. The diameter and the height of the hybrid NSs are determined to be  $220 \pm 10$  nm, and 750  $\pm$  90 nm, respectively. The homogeneity of hybrid nanoskit-tles is relatively correct in terms of dimensions. However, this homogeneity can be improved by controlling better the thickness of the native oxide layer. To evaluate the NS sensitivity, thio-phenol molecules are grafted on hybrid nanoskittles by using the protocol described previously. Then, the SERS substrates are char-acterized by Raman measurements. Fig. 2(a) and (b) reveals the SERS spectrum of Au/Si nanoskittles obtained at the excitation wavelength of 633 nm. Fig. 2(c) represents the Raman spectrum of reference obtained in solution (ethanol). Thus, characteristic Raman shifts of thiophenol molecules [24] are well-observed like those at 419/1000 cm<sup>-1</sup> corresponding to the out-of-plane C-C-C stretch, 1025 cm<sup>-1</sup> corresponding to the out-of-plane C-H stretching, 1075 cm<sup>-1</sup> corresponding to the C-C-C stretch in-plane and C-S stretching, and at 1575 cm<sup>-1</sup> corresponding to the C-C stretching. Some exceptions are observed in Fig. 2(a) due to the nature of substrate (SiNW arrays), which are the multi-phonon peaks located at 520  $\rm cm^{-1}$  [25,26] and in the regions of 600–700  $\rm cm^{-1}$ and 900–980 cm<sup>-1</sup> [26,27]. For Fig. 2(c), other Raman peaks are also observed which correspond to peaks of ethanol. In order to eval-uate this sensitivity of hybrid nanoskittles and to compare it with other nanostructures, which are gold nanodisks on gold film [10], the enhancement factor is calculated for the 5 characteristic Raman peaks of the thiophenol molecule previously cited. EF is given by the following equation:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}}$$
(1)

where  $I_{SERS}$ ,  $I_{Raman}$  represent the SERS and Raman intensities, respectively.  $N_{SERS}$ ,  $N_{Raman}$  are the number of excited molecules in SERS and Raman experiments, respectively.  $N_{SERS}$  is given by this expression:

$$N_{SERS} = N_A \times S_{illuminated} \times \sigma_{Surf}$$
(2)

where  $N_A$  is the Avogadro's number (mol<sup>-1</sup>),  $S_{illuminated}$  is equal to the sum of the lateral and top surfaces of one nanoskittle (NS surface:  $S = 5.6 \times 10^5$  nm<sup>2</sup>) multiplied by the number of nanoskittles determinated in the zone illuminated by the laser (~1  $\mu$ m<sup>2</sup>). The number of nanoskittles is around 2. Indeed, the average nanoskittle density, which is calculated on several different zones of the substrate, is 2 *NS*/ $\mu$ m<sup>2</sup>. Finally,  $\sigma_{Surf}$  is the surface coverage of thiophenol, which is around 0.544 nmol/cm<sup>2</sup> [28,29]. Thus, thiophenol molecules, which are taken into account, are adsorbed on both lateral and top sides of the nanoskittles, and the number of excited molecules  $N_{SERS}$  is  $3.67 \times 10^6$ . Indeed, no SERS signal is



**Fig. 1.** SEM images: (a) large area of hybrid nanoskittles obtained with our fabrication technique, and the inset of (a) is a zoom of one nanoskittle (scale bar = 250 nm). (b) Zoom of Au/Si nanoskittle:  $D \sim 220$  nm and  $h \sim 750$  nm.





**Fig. 2.** (a) SERS spectrum obtained with hybrid NSs at  $\lambda_{exc}$  = 633 nm, and the red rectangle of (a) is the zoom of the zone from 975 cm<sup>-1</sup> to 1650 cm<sup>-1</sup>, which is displayed in (b). (c) Raman spectrum of reference obtained in solution (ethanol). Characteristic Raman shifts are observed at 419/1000/1025/1075 and 1575 cm<sup>-1</sup> for thiophenol molecules. All spectra have been normalized by the laser power and the acquisition time.

observed from the smooth gold layer (not represented in Fig. 2, and as observed in Refs. [9,10]).

In addition, for the Raman experiments in solution, the number of excited molecules  $N_{Raman}$  is  $9.45 \times 10^{11}$  obtained by the following formula [14]:

$$N_{Raman} = N_A \times C \times V_{sca} \tag{3}$$

Table 1

For the five Raman peaks studied here, enhancement factors (EF) at the excitation wavelength of 633 nm for the two types of nanostructures: (a) Au/Si nanoskittles and (b) Au nanodisks on gold film from our Ref. [10] (nanodisk diameter  $\sim$ 210 nm and periodicity of 400 nm).

Raman shift (cm <sup>-1</sup> )	EF(a)	EF(b)
419	$1.1  imes 10^8$	$1.5 imes10^{6}$
1000	$3.1  imes 10^7$	$1.4  imes 10^6$
1025	$5.6  imes 10^7$	$9.5  imes 10^5$
1075	$3.6  imes 10^7$	$2.8  imes 10^6$
1575	$7.0  imes 10^7$	$2.4\times10^{6}$

where *C* is the concentration used for thiophenol molecules (1 M), and  $V_{sca}$  is the scattering volume. This volume is given the following equation:  $V_{sca} = A \times H$ , where *A* = scattering area (=disk area of which the diameter is 5 µm) and *H* is approximately 80 µm (scattering height), thus  $V_{sca} = 1570 \ \mu\text{m}^3 \sim 1.57 \ \text{pL}$ .

From the results of Table 1, the largest EF value, which was found for the hybrid nanoskittles, is  $1.1 \times 10^8$  with the Raman shift of 419 cm<sup>-1</sup>. We also observed that our Au/Si nanoskittles are more sensitive than our gold nanodisks on a gold film. Indeed, EFs with Au/Si nanoskittles are improved by a factor 73.3, 22.1, 58.9, 12.9 and 29.2 for the Raman peaks at 419, 1000, 1025, 1075 and 1575 cm<sup>-1</sup> respectively. This improvement of the SERS signal is attributed to high-efficient "hot spots" from two aspects: (i) the plasmonic coupling between gold balls and the semiconducting silicon sub-strate [20,30], and (ii) the shape (or morphology) of the nanoskittle [20,21,31,32]. Moreover, the reflectivity of substrate can be also a supplementary explanation of the enhancement of SERS signal. Indeed, several groups have demonstrated that the SERS intensity increased with the reflectivity [15,33]. In our experiments, we have a gold layer of 30 nm at the bottom of nanoskitlles, which has a better reflectivity (around 74%, see Ref. [15]) than silicon (around 40% or less, see Ref. [33]) at the excitation wavelength of 633 nm. Thus, this gold layer could increase the SERS signal. In addition, Akin et al. have obtained EFs of  $\sim 10^6$  with Ag nanoparticles on sil-icon nanowires [32]. By comparison, our hybrid nanoskittles are more simple, quick and low-cost to fabricate and also have a better sensitivity (EF =  $10^7$  – 1.1 Qn **Osher** hand, the low reproducibility of SERS signals is the major constraint that should be considered in order to realize a good SERS substrate. To assess the reproducibility of our hybrid nanoskittles, SERS spectra of thiophenol molecules were collected from several randomly selected zones on the whole wafer under same experimental conditions. Fig. 3 displays an example of SERS spectra obtained from two different zones, which are opposite compared to the center of the wafer. We have observed a good reproducibility for all spectra obtained on the whole wafer.

To quantify the reproducibility, the relative standard deviation (RSD) is calculated for all the five peaks studied here. Table 2 reveals the RSD values concerning to the SERS intensity of five Raman peaks. According to these RSD values, we can conclude that a good reproducibility (RSD <7%) is achieved across the 4-in. wafer of the hybrid nanoskittles.

Та	bl	е	2	

RSD values for the five peaks of thiophenol molecules studied with our hybrid nanoskittles.

Raman shift (cm <sup>-1</sup> )	RSD (%)
419	6.6
1000	2.8
1025	2.5
1075	1.3
1575	4.9



Fig. 3. Example of SERS spectra obtained with hybrid NSs at  $\lambda_{exc}$  = 633 nm for two different zones, which are opposite compared to the center of the wafer.

#### 4. Conclusion

In this paper, we demonstrated the low-cost and quick fabrication of highly sensitive SERS substrates for chemical sensing. Indeed, the important point of this fabrication technique is the use of a native oxide layer as a physical etch mask in order to realize the nanoskittles. Then, we have studied the sensitivity of these SERS substrates and compared these results to those obtained for gold nanodisks on a gold film, and also for Ag nanoparticles on silicon nanowires. The highest EF values have been achieved with the Au/Si nanoskittles (EF =  $10^7 - 1.1 \times 10^8$ ) fabricated with our lowcost and quick technique. To finish, highly defined nanoskittles realized by this technique were obtained at the 4-in, wafer-scale, as well as reproducibility of SERS signal (RSD <7%), which are important points for industrial applications. Despite these achievements demonstrated here, several important challenges in this research domain are to solve: the tunable fabrication of hybrid nanoskitlles with desirable dimensions (e.g. height, size distribution), as well as the exploration of the SERS sensing based on these hybrid nanoskittles for practical applications in a reproducible way. Next, hybrid nanoskittle-based SERS sensors could serve as a reliable and analytical tool for a great number of applications in a close future.

### Acknowledgements

The authors acknowledge ANR P2N (ANR-12-NANO-0016), and this work was partly supported by the French RENATECH network.

#### References

- [1] S. Nie, S.R. Emory, Probing single molecules and single nanoparticles by
- surface-enhanced Raman scattering, Science 275 (1997) 1102–1106.
- [2] D. Rodriguez-Fernandez, J. Langer, M. Henriksen-Lacey, L.M. Liz-Marzan, Hybrid Au-SiO<sub>2</sub> core-satellite colloids as switchable SERS tags, Chem. Mater. 27 (2015) 2540–2545.
- [3] A. La Porta, A. Sanchez-Iglesias, T. Altantzis, S. Bals, M. Grzelczak, L.M. Liz-Marzan, Multifunctional self-assembled composite colloids and their application to SERS detection, Nanoscale 7 (2015) 10377–10381.
- [4] R. Gillibert, M. Sarkar, J.F. Bryche, R. Yasukuni, J. Moreau, M. Besbes, et al., Directional surface enhanced Raman scattering on gold nano-gratings, Nanotechnology 27 (2016) 115202.

- [5] Q. Yu, P. Guan, D. Qin, G. Golden, P.M. Wallace, Inverted size-dependence of surface-enhanced Raman scattering on gold nanohole and nanodisk arrays, Nano Lett. 8 (2008) 1923–1928.
- [6] L. Pérez-Mayen, J. Olivat, A. Torres-Castro, E. De la Rosa, SERS substrates fabricated with star-like gold nanoparticles for zeptomole detection of analytes, Nanoscale 7 (2015) 10249–10258.
- [7] T. Vo-Dinh, A. Dhawan, S.J. Norton, C.G. Khoury, H.N. Wang, V. Misra, et al., Plasmonic nanoparticles and nanowires: design, fabrication and application in sensing, J. Phys. Chem. C 114 (2010) 7480–7488.
- [8] A.C. Faure, G. Barbillon, M. Ou, G. Ledoux, O. Tillement, S. Roux, et al., Core/shell nanoparticles for multiple biological detection with enhanced sensitivity and kinetics, Nanotechnology 19 (2008) 485103.
- [9] J.F. Bryche, R. Gillibert, G. Barbillon, M. Sarkar, A.L. Coutrot, F. Hamouda, et al., Density effect of gold nanodisks on the SERS intensity for a highly sensitive detection of chemical molecules, J. Mater. Sci. 50 (2015) 6601–6607.
- [10] J.F. Bryche, R. Gillibert, G. Barbillon, P. Gogol, J. Moreau, M. Lamy de la Chapelle, et al., Plasmonic enhancement by a continuous gold underlayer: application to SERS sensing, Plasmonics 11 (2016) 601–608.
- [11] C. David, N. Guillot, H. Shen, T. Toury, M. Lamy de la Chapelle, SERS detection of biomolecules using lithographed nanoparticles towards a reproducible SERS biosensor, Nanotechnology 21 (2010) 475501.
- [12] G. Barbillon, F. Hamouda, S. Held, P. Gogol, B. Bartenlian, Gold nanoparticles by soft UV nanoimprint lithography coupled to a lift-off process for plasmonic sensing of antibodies, Microelectron. Eng. 87 (2010) 1001–1004.
- [13] G. Barbillon, Plasmonic nanostructures prepared by soft UV nanoimprint lithography and their application in biological sensing, Micromachines 3 (2012) 21–27.
- [14] M. Cottat, N. Lidgi-Guigui, I. Tijunelyte, G. Barbillon, F. Hamouda, P. Gogol, et al., Soft UV nanoimprint lithography-designed highly sensitive substrates for SERS detection, Nanoscale Res. Lett. 9 (2014) 623.
- [15] J.F. Bryche, A. Tsigara, B. Bélier, M. Lamy de la Chapelle, M. Canva, B. Bartenlian, et al., Surface enhanced Raman scattering improvement of gold triangular nanoprisms by a gold reflective underlayer for chemical sensing, Sens. Actuators B: Chem. 228 (2016) 31–35.
- [16] S.Y. Lee, H.C. Jeon, S.M. Yang, Robust plasmonic sensors based on hybrid nanostructures with facile tunability, J. Mater. Chem. 22 (2012) 13903–13907.
- [17] J.F. Masson, K.F. Gibson, A. Provencher-Girard, Surface-enhanced Raman spectroscopy amplification with film over etched nanospheres, J. Phys. Chem. C 114 (2010) 22406–22412.
- [18] J.P. Camden, J.A. Dieringer, J. Zhao, R.P. Van Duyne, Controlled plasmonic nanostructures for surface-enhanced spectroscopy and sensing, Acc. Chem. Res. 41 (2008) 1653–1661.
- [19] M. Baia, L. Baia, S. Astilean, J. Popp, Surface-enhanced Raman scattering efficiency of truncated tetrahedral Ag nanoparticle arrays mediated by electromagnetic couplings, Appl. Phys. Lett. 88 (2006) 143121.
- [20] E. Galopin, J. Barbillat, Y. Coffinier, S. Szunerits, G. Patriarche, R. Boukherroub, Silicon nanowires coated with silver nanostructures as ultrasensitive interfaces for Surface-Enhanced Raman Spectroscopy, ACS Appl. Mater. Interfaces 1 (2010) 1396–1403.
- [21] M.L. Zhang, X. Fan, H.W. Zhou, M.W. Shao, J. Antonio Zapien, N.B. Wong, et al., A high-efficiency surface-enhanced Raman scattering substrate based on

silicon nanowires array decorated with silver nanoparticles, J. Phys. Chem. C 114 (2010) 1969–1975.

- [22] M.S. Schmidt, J. Hübner, A. Boisen, Large area fabrication of leaning silicon nanopillars for surface enhanced Raman spectroscopy, Adv. Mater. 24 (2012) OP11–OP18.
- [23] L. Maiolo, D. Polese, A. Pecora, G. Fortunato, Y. Shacham-Diamand, A. Convertino, Highly disordered array of silicon nanowires: an effective and scalable approach for performing and flexible electrochemical biosensors, Adv. Healthc. Mater. 5 (2016) 575–583.
- [24] K.T. Carron, L. Gayle Hurley, Axial and azimuthal angle determination with surface-enhanced Raman spectroscopy: thiophenol on copper, silver, and gold metal surfaces, J. Phys. Chem. 95 (1991) 9979–9984.
- [25] S. Piscanec, M. Čantoro, A. Ferrari, J. Zapien, Y. Lifshitz, S. Lee, et al., Raman spectroscopy of silicon nanowires, Phys. Rev. B 68 (2003), 241312(R).
- [26] P.A. Temple, C.E. Hathaway, Multiphonon Raman spectrum of silicon, Phys. Rev. B 7 (1973) 3685–3697.
- [27] M. Khorasaninejad, J. Walia, S.S. Saini, Enhanced first-order Raman scattering from arrays of vertical silicon nanowires, Nanotechnology 23 (2012) 275706.
- [28] J.D. Caldwell, O. Glembocki, F.J. Bezares, N.D. Bassim, R.W. Rendell, M. Feygelson, et al., Plasmonic nanopillar arrays for large-area, high-enhancement surface-enhanced Raman scattering sensors, ACS Nano 5 (2011) 4046-4055.
- [29] D.A. Stern, E. Wellner, N. Salaik, L. Laguren-Davidson, F. Lu, N. Batina, et al., Adsorbed thiophenol and related-compounds studied at Pt(111) electrodes by EELS, auger spectroscopy and cyclic voltammetry, J. Am. Chem. Soc. 110 (1988) 4887–4893.
- [30] H. Wang, X. Jiang, S.T. Lee, Y. He, Silicon nanohybrid-based surface-enhanced Raman scattering sensors, Small 10 (2014) 4455–4468.
- [31] R. Chen, D. Li, H. Hu, Y. Zhao, Y. Wang, N. Wong, et al., Tailoring optical properties of silicon nanowires by Au nanostructure decorations: enhanced Raman scattering and photodetection, J. Phys. Chem. C 116 (2012) 4416–4422.
- [32] M.S. Akin, M. Yilmaz, E. Babur, B. Ozdemir, H. Erdogan, U. Tamer, et al., Large area uniform deposition of silver nanoparticles through bio-inspired polydopamine coating on silicon nanowire arrays for practical SERS applications, J. Mater. Chem. B 2 (2014) 4894–4900.
- [33] Q. Zhou, Y. Liu, Y. He, Z. Zhang, Y. Zhao, The effect of underlayer thin films on the surface-enhanced Raman scattering response of Ag nanorod substrates, Appl. Phys. Lett. 97 (2010) 121902.

#### Biographies

Jean-François Bryche, 26 years old, he received his Master degree in applied physics at University of Paris-Sud in 2013. Currently, he is a PhD student at the Centre for Nanoscience and Nanotechnology (Orsay, France) and at the Charles Fabry Laboratory from the Institute d'Optique Graduate School (Palaiseau, France). He works on the development of SPR and SERS sensors by nanostructuring the surface with several lithography techniques.

**Benoit Bélier** received his Master degree in applied physics at the University of Limoges in 1994. Then, he earned a fifth year diploma (DEA) from the University of Montpellier II in microelectronics and optoelectronics in 1996. He received his PhD in electronics and optoelectronics from the University of Montpellier II in 1999. In 2000, he was post-doctoral fellow at the Laboratory for Analysis and Architecture of Systems (Toulouse, France). His research involves development and microfabrication of MEMS for biological applications. Currently, he is a CNRS research engineer at the Centre for Nanoscience and Nanotechnology (Orsay, France).

**Bernard Bartenlian** is a CNRS researcher, physicist, at the centre for Nanoscience and Nanotechnology of Université Paris-Sud/Université Paris-Saclay. In 1991, he obtained his PhD in Materials Science for the MBE growth and characterization of Ga(Al)As on silicon. From 1992 to the mid.2000 years, he worked on the study of magnetic nanostructure properties for the storage of ultra-high density recording, using top-down and bottom-up approaches. Since, he works to the adaptation of non-conventional lithographies to biological applications. He also collaborates with jurist researchers on the nanotechnologies regulation. He is involved in the teaching of his research in Master degree.

**Grégory Barbillon** completed his PhD in Physics (2007) at the University of Technology of Troyes (France). Then, he obtained his Habilitation (HDR) in Physics (2013) at the University of Paris Sud (Orsay, France). Actually, he is contractual researcher at the Centre for Nanoscience and Nanotechnology (Orsay, France) in the group of Nanobiophotonics. His research interests were focused on Plasmonics, Nanophotonics, Nanophotonics, Nanotechnology and Fluorescence.