

Technical University of Denmark



Towards easily reproducible nano-structured SERS substrates

Schmidt, Michael Stenbæk; Boisen, Anja; Hübner, Jörg

Published in:
Sensors, 2009 IEEE

Link to article, DOI:
[10.1109/ICSENS.2009.5398468](https://doi.org/10.1109/ICSENS.2009.5398468)

Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Schmidt, M. S., Boisen, A., & Hübner, J. (2009). Towards easily reproducible nano-structured SERS substrates. In Sensors, 2009 IEEE (pp. 1763-1767). IEEE. DOI: 10.1109/ICSENS.2009.5398468

DTU Library

Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Towards Easily Reproducible Nano-structured SERS Substrates

Michael Stenbæk Schmidt, Anja Boisen

DTU Nanotech, Department of Micro- and Nanotechnology
Technical University of Denmark
Kongens Lyngby, Denmark
michael.schmidt@nanotech.dtu.dk

Jörg Hübner

DTU Danchip
Technical University of Denmark
Kongens Lyngby, Denmark

Abstract— In this paper we present a quick and easy method for producing relatively large areas of substrate that enhance the Raman effect, using standard semiconductor processing techniques such as reactive ion etching of silicon and electron beam metal deposition. As standard cleanroom processes are used, it is possible to narrowly control the parameters of the fabrication process to create silicon nano-pillars with controlled heights and spacing. The silicon nano-pillars are coated by thin films of silver and/or gold to create surfaces that greatly enhance the Raman effect. Surface enhanced Raman scattering (SERS) has numerous applications in chemical sensing, with high sensitivity and fast analysis speed seen as the main advantages, and these novel substrates are believed to be able to make SERS more applicable.

I. INTRODUCTION

When incident photons hit molecules, most of these are elastically scattered. However a tiny fraction of the impacting photons undergo inelastic scattering and thus experience a change in frequency, which can be measured by spectrometers. This is the basis for Raman spectroscopy [1]. Each molecule will give rise to a unique photon scattering profile and hence individual chemical species can be identified from the resulting Raman spectra. Three decades ago [2-3] it was discovered that the surface on which the molecule is located, has a profound influence on the number of inelastically scattered photons. Thus, by choosing suitable surfaces the Raman signal could be enhanced by many orders of magnitude. In surface enhanced Raman scattering (SERS) the local electromagnetic field is greatly enhanced at the surface of nanoparticles. Particularly large enhancements of the electromagnetic field are found in between adjacent nanoparticles, also called “hot spots” [4]. For this reason SERS has shown great potential of becoming a versatile analytical tool for both chemical and biochemical sensors in liquid and gas phases. In fact, single molecule detection with SERS has been demonstrated [5].

Numerous approaches to create SERS substrates have been reported in literature including electrochemically roughened

gold electrodes, silver colloidal nanoparticles deposited on roughened silver surfaces or AgO films deposited on glass slides by chemical deposition [6]. However, electrochemically roughened metallic substrates generally exhibit large variations in nanostructure with subsequent large variations in enhancement effects across the substrate. In addition to the uniformity being difficult to control, dispersions or solutions of metallic nanoparticles often have the disadvantage of requiring organic barrier layers to prevent agglomeration [7] which could influence the SERS signals. Processes where a nanostructure is defined, by for example electron beam lithography [8], and covered by thin films of metal (gold or silver) have also gained in popularity. Electron beam fabrication techniques are more controlled and ordered but have the major disadvantage of being very time consuming with subsequent very high production costs. Therefore, substrates which produce a high signal enhancement while at the same time being easily reproducible on the nanoscale are desirable.

Using standard cleanroom silicon processing techniques, SERS substrates have previously been developed at DTU Nanotech [9]. This class of substrates demonstrated enhancement factors of 7.6×10^7 . In this paper we present a completely new protocol for creating substrates which greatly improve Raman enhancement and which enable chemical detection that is more than a factor 100 more sensitive than previously published surfaces [9] and compared to commercially available SERS substrates [10].

II. EXPERIMENTAL

The fabrication process is based on a reactive ion plasma etch (RIE) of undoped 4 inch diameter polished single crystal silicon wafers which forms aperiodic arrays of silicon nano-pillars [11]. The silicon nano-pillars are subsequently coated by a layer of gold and/or silver, Fig. 1 The etching process is self-masking, hence

Funding: Danish Agency for Science and Technology's, Program Commission on Nanoscience Biotechnology and IT (NABIIT).

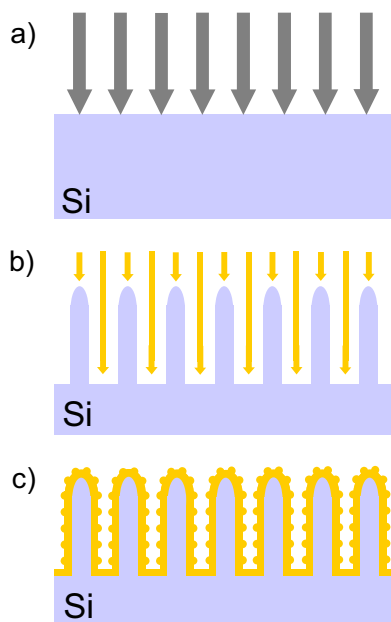


Figure 1. Schematic of the fabrication process. a) A blank silicon wafer is structured by maskless reactive ion etching to form free standing nano-pillars. b) The pillars are coated with metal by electron beam evaporation. c) The resulting structure are free standing metal coated nano-pillars with rough surfaces.

eliminating the need for a time consuming photolithographic patterning step. An Advanced Silicon Etcher (Surface Technology Systems MESC Multiplex ICP) was operated at a $\text{SF}_6:\text{O}_2$ ratio of 1 to 1.12, a platen power of 110 – 130 W and a chamber pressure of 8 to 56 mTorr to form nanostructured silicon peaks at a rate of approximately 2 nm/s. Since the etch time defines the height of the peaks the height can be tailored.

Metallization was performed by electron beam evaporation (Alcatel SCM 600) at deposition rates of 10 Å/s at pressures of 2×10^{-6} mbar. The metal layer thickness could be varied with an accuracy of ± 5 nm and metallization thicknesses of 50 to 400 nm in 50 nm intervals were applied. Gold and silver layers and mixtures of both were tested.

The excitation source for Raman spectroscopy was a near-infrared external cavity stabilized diode laser with a wavelength of 785 nm (Torsana Laser Technology) and a power of approximately 150 mW at the sample surface with a probe spot diameter of 160 μm (InPhotonics). Spectra were obtained using both 100 μM Rhodamine 6G and self assembling monolayers of thiophenol deposited on the sample surfaces.

III. RESULTS

Due to the close control of process parameters in the two machines used, the silicon nanostructures could be fine-tuned to create suitable surfaces for Raman enhancement. Both the height and concentration of pillars could be controlled in the RIE process.

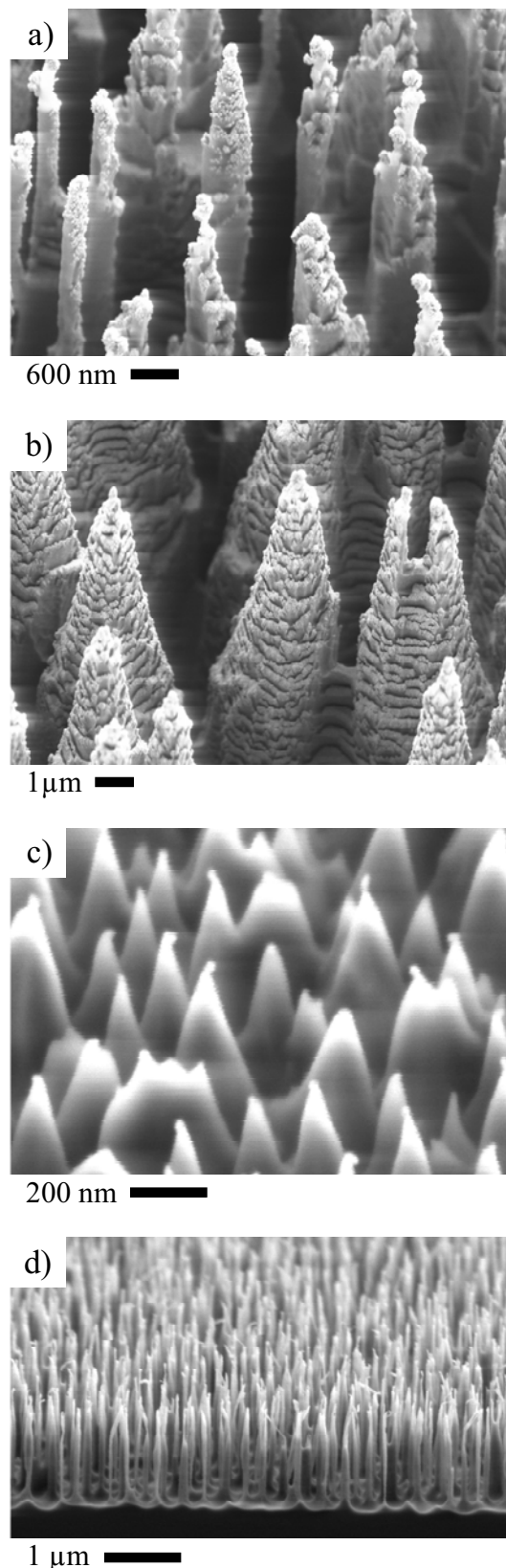


Figure 2. SEM images of various silicon micro- and nanostructures achievable with maskless reactive ion etching. a) and b) have been metalized. Note the different scale bars.

Fig. 2 shows examples of four different silicon nanostructures obtainable using maskless RIE. The nanostructure which is shown in Fig. 2a) is a reproduction of the samples that have previously been demonstrated at DTU Nanotech [9]. The side wall angle or taper of the nano-pillars could be controlled by adjusting the SF₆:O₂ ratio in the plasma to give more conical shaped peaks as illustrated by Fig. 2b). Furthermore, the peak concentration could be controlled by adjusting the chamber pressure as illustrated by the resulting nanostructures shown in Fig. 2c). For SERS applications we found that both the shape and the density of the pillars are key variables.

As seen by comparing Fig. 2d) with Fig. 3a) the height of the pillars (1.6 μm and 670 nm respectively) is a function of etching time. The side wall angles, inter peak distances and shape of the pillars appeared unaffected by prolonging the etch time.

Greatest Raman enhancement was achieved with vertical pillars with a peak density of 2 x 10⁹ peaks/cm², Fig. 3a). This is two orders of magnitude more peaks per unit area than for the pillars shown in Fig. 2a) (4 x 10⁷ peaks/cm²). The Raman enhancement using the new protocol was approximately 110 times larger than the less dense peak arrays shown in Fig. 2a). Based on measurements on polished

silver substrates the enhancement factor of the silver coated nano-pillars was on the order of 10⁹. Hence one of the reasons for the large increases in Raman enhancement is thus to be found in the larger number of peaks in the excitation spot. Furthermore, the nature of peak metallization is critical in order to obtain a large enhancement. The best enhancement was measured when the peaks were completely coated with metal. This was difficult to obtain for the larger pillars shown in Fig. 2a)-b) which could be an additional reason for the less than optimal Raman enhancement. Smaller pillars, which were 20 - 100 nm wide before coating, could grow to more than the double in size after metallization. An issue is the risk of burying the pillars by depositing too much metal. Hence the metallization process had to be tailored to the silicon nanostructures. Pillars with a height of ~500 nm were used for metallization optimizations where a 250 nm layer of silver was found to give the largest Raman enhancement.

Scanning electron microscopy (SEM) investigations showed that the metal coatings formed rough layers with what appeared to be lumps embedded in the metal layers

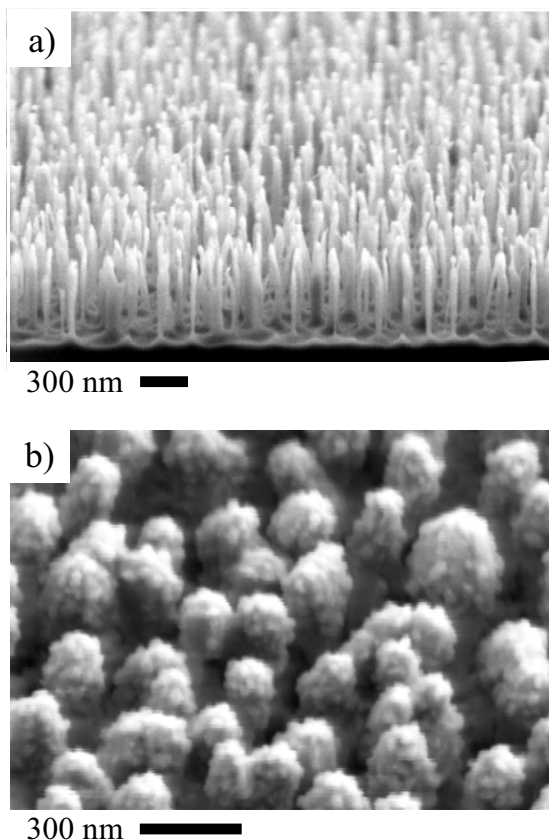


Figure 3. SEM images of silicon nano-pillars a) before (tilted 70 °) and b) after metallization with 250 nm silver (tilted 45 °).

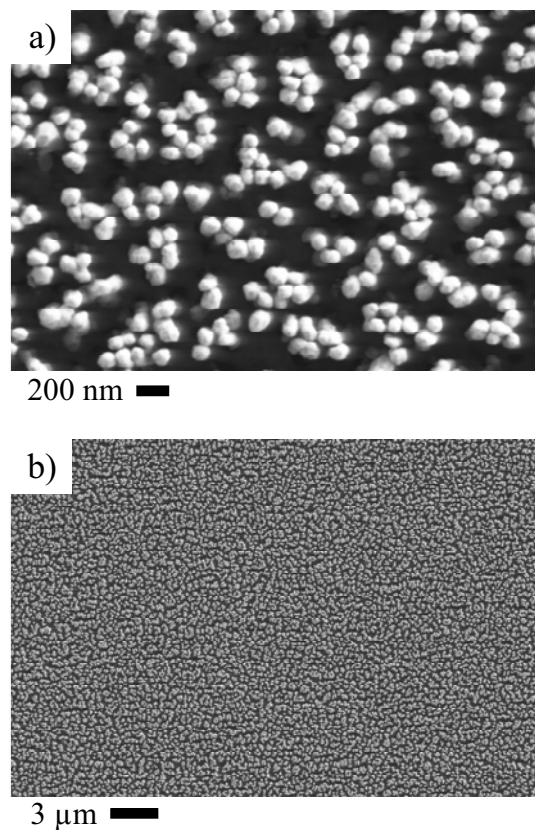


Figure 4. SEM images using secondary electrons taken at a right angle to the surface. a) High magnification image of the nano-pillars. A large number of hot spots are believed to form in the spaces between the pillars lying closest together thus accounting for the large enhancement of the Raman signal. b) A uniform distribution of metal covered nano-pillars are seen over a large area. This nanostructure is repeated over an area of 28 cm³ on a 4 inch silicon wafer.

coating the silicon pillars, Fig. 3b). The large enhancement effects measured on these substrates is hypothesized to be partially due to hot spots forming between these nanosized particles in the rough metal layer.

It was also seen that after metallization the pillars leaned towards each other to form clusters as shown in Fig. 4a). The inter distances between the tips of the pillars are on the order of 0-10 nm. This agglomeration is hypothesized to lead to further formation of surface plasmon resonance hot spots. Furthermore, it has been suggested that aperiodic arrays have larger Raman enhancing properties than regular periodic arrays [12]. As it is clearly seen in Fig. 4a) the surfaces are aperiodic on the nanoscale.

The silicon nanostructures could be produced uniformly over relatively large areas, Fig. 4b). Neglecting edge effects, most of a 4 inch wafer ($\sim 28 \text{ cm}^2$) contains Raman enhancing area. Upscaling the process to larger wafers is believed achievable facilitating large scale fabrication of SERS surfaces.

Examples of Raman spectra of Rhodamine 6G and thiophenol obtained on the nanostructured silicon surfaces

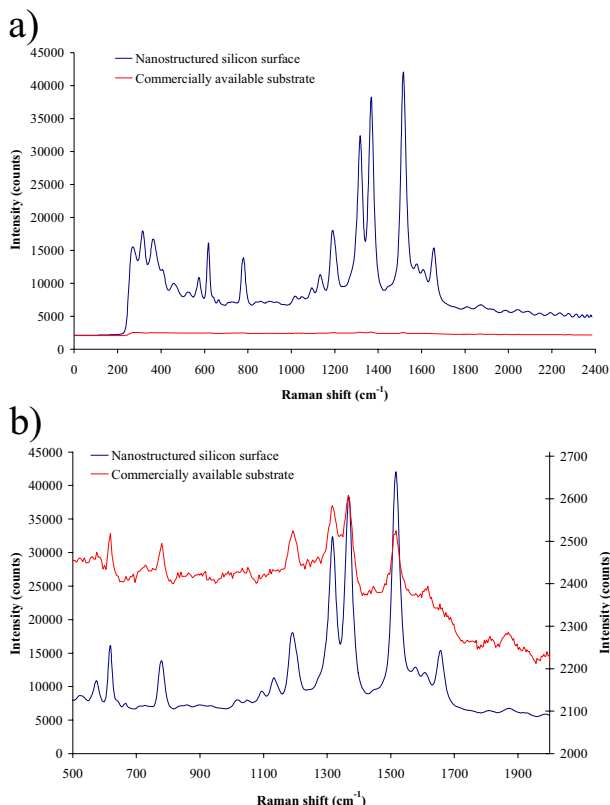


Figure 5. a) The Raman spectrum of a $1 \mu\text{L}$ of $100 \mu\text{M}$ rhodamine 6G dropped onto the silver coated nanostructured surface shown in Fig. 3b) and on a commercially available substrate [10] (gold coated) using the same y-axis. b) For clarity the gold coated commercial substrate is plotted on a second y-axis. The spectra were obtained using 785 nm excitation with an integration time of 1 second.

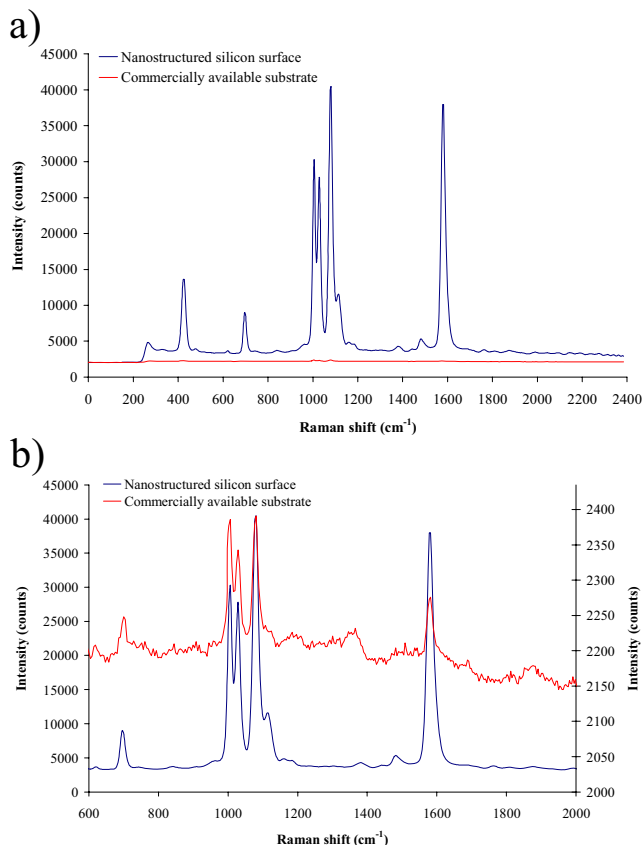


Figure 6. a) The Raman spectrum of a self assembling monolayer of thiophenol on the silver coated nanostructured surface shown in Fig. 3b) and on a commercially available substrate [10] (gold coated) using the same y-axis. b) For clarity the commercial substrate is plotted on a second y-axis. The spectra were obtained using 785 nm excitation with an integration time of 0.5 seconds.

with silver coatings are shown in Fig. 5 and Fig. 6 respectively, with the results obtained on a commercially available SERS substrate overlain for comparison. It is seen that the signal to noise ratio measured on the silver coated silicon nano-pillars shown in Fig. 4 is an improvement compared to the commercial substrate. In all fairness it should be mentioned that the commercial substrate is a gold structure which is known to have a weaker Raman enhancement than silver. However, gold covered silicon nano-pillars are still two orders of magnitude better Raman enhancers (not shown here) than the commercial substrate.

IV. DISCUSSION

Relatively large areas ($\sim 28 \text{ cm}^2$) of uniform Raman enhancing surfaces can be routinely produced in a two-step process which takes no more than 20 minutes from start to finish of where most of this time is spent pumping to vacuum. The RIE process is narrowly controlled by the processing equipment hence enabling the tailoring of diverse silicon nanostructures as demonstrated in Fig. 2. We find that this technique is superior to current electron beam lithography defined surfaces in terms of cost and time and it is more

reproducible than chemically deposited rough metal layers and metallic nanoparticle arrays.

Some examples of producing SERS substrates using self-masking silicon processes followed by electron beam metal evaporation have been reported in literature [13-14]. In the case of [13] an enhancement factor on the order of 10^7 is reported on silver coated silicon nanostructures. The difference in enhancement reported here compared to the enhancement factor reported in [13] possibly lies in the inter peak distance. We observed an increase in enhancement factor with decreasing inter peak distance. Therefore, we believe that Raman enhancement can be improved by finding the optimal inter peak distance and this is now the subject of our current studies. Furthermore, the amount of metal deposited must be adjusted to this inter peak distance in order to avoid forming a continuous metal layer lying on top of the peaks.

Hu et al. [14] report an enhancement factor of 6×10^7 on silver coated silicon nanostructures very similar to those shown in Fig. 2c). Reference [14] also suggests that metal nanoparticles on the sides of the peaks are responsible for the observed Raman enhancement effect and is thus in agreement with the observations presented here. It should be noted that the conical peaks in [14] and Fig. 2c) do not appear to be uniform in height. It is hypothesized that the increase in enhancement factor reported here compared to [14] can be attributed to the clustering enabled by the mechanical movement of the high aspect ratio vertical silicon nano-pillars shown in Fig. 4a).

It is believed that the type of structures presented in this paper can be directly used in SERS equipment already in use today for a wide spectrum of chemical and biochemical applications including hand held devices [15] as both reproducibility and enhancement have been improved significantly compared to existing substrates. Due to the simple and quick nature of the fabrication process this production method should be up-scalable thus ultimately enabling a significant reduction in the cost per unit.

ACKNOWLEDGMENT

This work was funded by the Danish Agency for Science and Technology's, Program Commission on Nanoscience Biotechnology and IT (NABIIT).

REFERENCES

- [1] R. Aroca, "Surface-enhanced vibrational spectroscopy," John Wiley & Sons Ltd, 2006.
- [2] M. G. Albrecht and J. A. Creighton, "Anomalous intense Raman spectra of pyridine at a silver electrode," *J. Am. Chem. Soc.*, 99 (15), 1977, pp. 5215-5217.
- [3] D. L. Jeanmaire and R. P. Van Duyne, "Surface Raman spectroelectrochemistry .1. heterocyclic, aromatic, and aliphatic-amines adsorbed on anodized silver electrode," *J. Electroanal. Chem.*, vol. 84 (1), 1977, pp. 1-20.
- [4] F. Le, D.W. Brandl, Y.A. Urzhumov, H. Wang, J. Kundu, N.J. Halas, J. Aizpurua and Peter Nordlander, "Metallic nanoparticle arrays: a common substrate for both surface-enhanced Raman scattering and surface-enhanced infrared absorption," *Am. Chem. Soc. Nano*, vol. 2 (4), 2008, pp. 707-718.
- [5] K. Kneipp, Y. Wang, H. Kneipp, L.T. Perelman, I. Itzkan, R. Dasari and M.S. Feld, "Single molecule detection using surface-enhanced Raman scattering (SERS)," *Phys. Rev. Lett.*, vol. 78 (9), 1997, pp. 1667-1670.
- [6] F. Yan, M.B. Wabuyele, G.D. Griffin, A.A. Vass and T. Vo-Dinh, "Surface-enhanced Raman scattering detection of chemical and biological agent simulants," *IEEE Sensors Journal*, vol. 5 (4), 2005, p. 665-670.
- [7] H. Wang, C.S. Levin and N. J. Halas, "Nanosphere arrays with controlled sub-10-nm gaps as surface-enhanced Raman spectroscopy substrates," *J. Am. Chem. Soc.*, vol. 127 (43), 2005, pp. 14992-14993.
- [8] E.C. Le Ru, P.G. Etchegoin, J. Grand, N. Féridj, J. Aubard, G. Lévi, A. Hohenau and J.R. Krenn, "Surface enhanced Raman spectroscopy on nanolithography-prepared substrates", *Current Applied Physics* 8, 2008, pp. 467-470.
- [9] I. Talian, K.B. Mogensen, A. Oriňák, D. Kaniansky and J. Hübner, "Surface-enhanced Raman spectroscopy on novel black silicon-based nanostructured surfaces", *Journal of Raman Spectroscopy*, 2009, DOI 10.1002/jrs.2213.
- [10] Klarite™: <http://www.d3technologies.co.uk>
- [11] M.S. Schmidt, T. Nielsen, D.N. Madsen, A. Kristensen and P. Bøggild, "Nanoscale silicon structures by using carbon nanotubes as reactive ion etch masks", *Nanotechnology*, vol. 16, 2005, pp. 750-753.
- [12] A. Gopinath, S.V. Boriskina, B.M. Reinhard and L.D. Negro, "Deterministic aperiodic arrays of metal nanoparticles for surface-enhanced Raman scattering (SERS)," *Optics Express*, vol. 17 (5), 2009, pp. 3741-3753
- [13] E. D. Diebold, N. H. Mack, S. K. Doorn and E. Mazur, "Femtosecond laser-nanostructured substrates for surface enhanced Raman scattering," *Langmuir*, vol. 25 (3), 2009, pp. 1790-1794.
- [14] M. Hu, J. Tang, F.S. Ou, H.P. Kuo, S.-Y. Wang, Z. Li and R.S. Williams, "Metal coated Si nanoglass as highly sensitive SERS sensors," *Proceedings of the SPIE*, vol. 7312 (1), 2009, pp. 73120I-6 .
- [15] J. Hubner, T. Anhøj, S. Pedersen, D.A.Zauner, A.M. Jørgensen, G. Blagoi, I. Talian and O. Hansen, "Surface enhanced Raman spectroscopy on chip," *Proceedings of the SPIE - Integrated Optics: Devices, Materials, and Technologies XII*, vol. 6896, 2008, pp. 689614-1-10.