

# Nanostructured Surface Enhanced Raman Scattering Substrates for Explosives Detection

Michael Stenbæk Schmidt, Jesper Kenneth Olsen,  
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**—Here we present a method for trace detection of explosives in the gas phase using novel surface enhanced Raman scattering (SERS) spectroscopy substrates. Novel substrates that produce an exceptionally large enhancement of the Raman effect were used to amplify the Raman signal of explosives molecules adsorbed onto the substrate. The substrates were fabricated in a cleanroom process which only requires two steps to produce well controlled nano-sized high aspect ratio metal pillars. These substrates had superior chemical sensing performance in addition to a more cost effective fabrication process compared to existing commercial substrates. Therefore it is believed that these novel substrates will be able to make SERS more applicable in mobile explosives detection systems to be deployed in for example landmine clearance actions.

## I. INTRODUCTION

The need for trace detection of explosives is larger than ever. For example, it is estimated that 5,000–20,000 people are killed or maimed each year by the 110 million landmines deployed in 75 countries [1]. Today landmine clearance in third world countries mainly relies on physical probing of the earth by hand in combination with screening with metal detectors. This method is extremely labor intensive and time consuming. In developed countries mobile trace detection of explosives is primarily carried out by trained dogs. However, dogs require a skilled handler and are expensive to train and maintain. Hence, a cheap method enabling trace detection of explosives molecules commonly found in landmines could introduce a paradigm shift in the way minefields are cleared.

## II. SURFACE ENHANCED RAMAN SCATTERING

In conventional Raman spectroscopy a laser is directed onto a bulk amount of analyte. A small fraction of photons (~1 in 10,000,000) are inelastically scattered by the analyte molecules. The energy of the inelastic scattered photons is a function of the chemical bonds in the analyte. Since each molecule will give rise to a unique photon scattering profile individual chemical species can be identified from the resulting Raman spectra [2]. Discovered in 1974, surface

enhanced Raman scattering (SERS) spectroscopy is a technique that allows for the generation of a much stronger Raman signal from trace amounts of analyte molecules when these are adsorbed onto an activated metal surface or structure: a so called SERS substrate. In SERS, the electromagnetic field induced by laser excitation is greatly enhanced by localized surface plasmons at the surface of noble metal nanoparticles. Particularly large enhancements of the electromagnetic field, also called “hot spots”, are found in between adjacent metal nanoparticles [3].

If an analyte molecule is located in this hot spot it will result in an enormous Raman signal from the analyte [4]. Hence the focus of substrate fabrication is on increasing the number of hot spots in order to increase the sensitivity of a SERS based sensor.

As it is vibrations in the chemical bonds of the analyte that result in the Raman spectrum, any chemical species can in theory be analyzed. 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. As such, SERS has been named as a very promising method for explosives sensing with fast analysis speed and high sensitivity being the main advantages [5-6]. Currently, the inability to mass produce cost effective nanostructured SERS-substrates with suitable enhancement is impeding the use of SERS sensors in both laboratories and mobile applications.

## III. SERS SUBSTRATES

Numerous SERS-active structures have been employed and described in literature [7]. The two most popular approaches are colloid solutions of noble metal nanoparticles and roughened noble metal substrates.

One challenge with colloid solutions is bringing the metal nanoparticles close enough together in order to form hot spots, while at the same time preventing large conglomerations of nanoparticles from forming before the analyte is introduced.

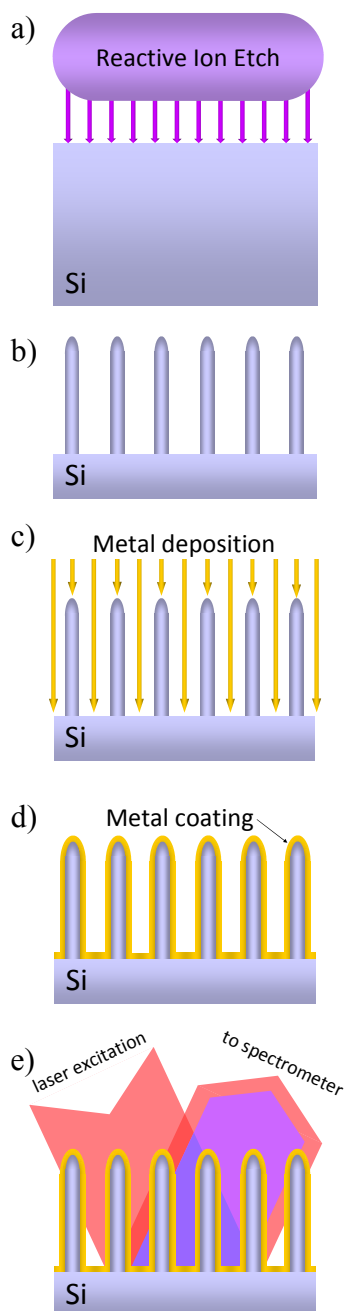


Figure 1. Schematic of the fabrication process. a)→b) A blank silicon wafer is structured by maskless reactive ion etching to form free standing nano-pillars. c) The pillars are coated with metal by electron beam evaporation or magnetron sputtering. d) The resulting structures are free standing metal coated nano-pillars. e) The substrate enhances the Raman effect enabling trace detection of explosives adsorbed to the surface.

One recent approach is to tie gold nanoparticles together with DNA strands to create dimers between which hot spots can form and enhance the Raman signal of any analyte located there [8]. A disadvantage of colloid solutions is that when detecting an analyte in the gas phase the detection speed is limited by diffusion through the solvent liquid.

Rough silver and gold surfaces can be fabricated by any number of methods including chemical etching, mechanical deformation, electroplating and oblique angle deposition [9-16]. However, roughened bulk metallic substrates generally exhibit large variations in nanostructure with subsequent large variations in Raman enhancement effects across the substrate. Lately, two-step processes where a well defined silicon nanostructure is created, by for example electron beam lithography, and hereafter covered by thin films of gold or silver have also gained in popularity. Electron beam fabrication techniques are more controlled and ordered but have the major disadvantage of having very high production costs and they are unfeasible over large areas.

#### IV. FABRICATION METHOD

The fabrication process employed here is based on a reactive ion etch (RIE) of undoped 4 inch diameter polished single crystal silicon wafers which forms aperiodic arrays of silicon nano-pillars [17]. The etching process is self-masking, hence 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 0.8 to 1.5, a platen power of 80 – 160 W and a chamber pressure of 6 to 72 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 heights can be tailored. To prevent contamination in the subsequent SERS spectra, the nanopillars were manufactured without the fluorocarbon passivation cycles normally used in deep reactive ion etching (the Bosch process).

By narrow control of process parameters the shape of the pillars could be controlled. The side wall angle or taper of the nano-pillars could be controlled by adjusting the  $\text{SF}_6:\text{O}_2$  ratio in the plasma. Conical pillars with various dimensions could also be produced as previously shown in [17]. Furthermore, the peak concentration could be controlled by adjusting the chamber pressure. For SERS applications we found that both the shape and the density of the pillars were key variables.

To facilitate Raman enhancement the silicon nano-pillars were subsequently coated by a layer of gold and/or silver, Fig. 1c). The nanopillars were coated with silver by electron beam evaporation (Alcatel SCM 600) and by magnetron sputtering (Kurt J. Lesker CMS 18). The finished substrate thus had metal coated nanopillars with uniform heights, Fig. 2a).

#### V. CHARACTERISATION

Approximately 80% of deployed landmines contain trinitrotoluene (TNT). However, since the military grade TNT used is not chemically pure, contaminants of 2,4-dinitrotoluene (DNT), 2,6-dinitrotoluene, 1,3-dinitrobenzene and 1,3,5-trinitrobenzene can often be detected in the headspace above a buried landmine [18]. DNT has a 40 – 100 times higher vapor pressure than TNT hence despite accounting for less than 1% of the explosive mass, DNT has been seen to have a headspace concentration above the landmine 20 times stronger than TNT [18]. For this reason DNT was selected as the test molecule.

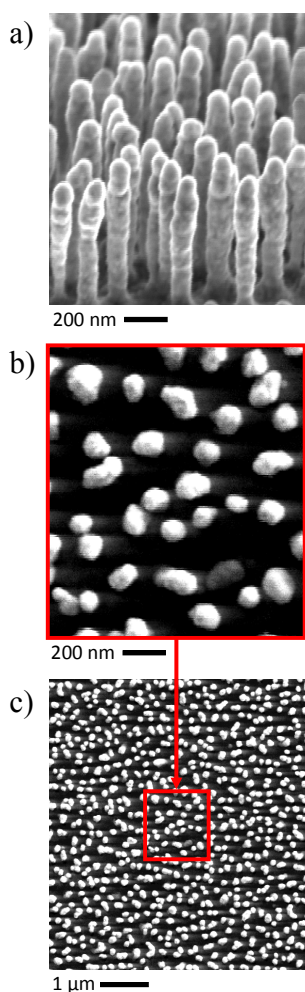


Figure 2. Electron microscope images of a SERS substrate. a) Note the complete metallization of the pillars. b)→c) SEM image perpendicular to the surface. The metalized nanopillars can be reproduced with a uniform density on a wafer scale with uniform SERS enhancement as a result.

Raman spectra were obtained from DNT in the gas phase in the following manner. A saturated solution of DNT in ethanol was made. 1 ml of this solution was deposited onto a wad of ceramic wool which was inserted into a 12 cm long copper pipe with 10 mm diameter. The pipe was inserted into a cylindrical heater such that the two ends of the pipe protruded. Through fixtures nitrogen carrier gas was blown through the heated pipe. The nitrogen gas at the exit of the heated pipe was assumed to be saturated with DNT. The temperature of the outlet gas was 80 °C. At the outlet of the heated pipe a SERS substrate was placed for 120 seconds where after a Raman spectrum was recorded.

The excitation source for Raman spectroscopy was a near-infrared external cavity stabilized diode laser with a wavelength of 785 nm (Ahura) and a power of approximately 150 mW at the sample surface with a probe spot diameter of 160 μm (InPhotonics). For comparison, a commercial substrate [16] was used as a benchmark under identical DNT evaporation and spectroscopy conditions. The integration time on for spectra measured on SERS substrates was 1 second.

Raman spectra on bulk amounts of DNT crystals were performed with integration times of 10 seconds.

## VI. RESULTS

Examples of Raman spectra with integration times of 1 second from DNT evaporated onto the nanostructured silicon surfaces with silver coatings are shown in Fig. 3. The results obtained on a commercially available SERS substrate [16] are overlain for comparison. It is seen that the signal measured on the silver coated silicon nanopillars is a significant improvement compared to the commercial substrate. The Raman spectra for a bulk sample of DNT recorded with an integration time of 10 seconds is also shown.

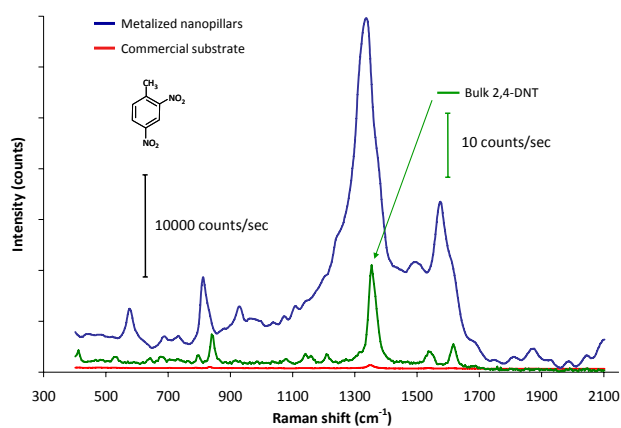


Figure 3. Raman spectra obtained after 120 seconds of 2,4-DNT / N<sub>2</sub> gas flow across silver nanopillar substrates (blue) and a commercially available substrate (red) using 785 nm excitation. An signal improvement of two orders of magnitude is seen with the novel substrate. The Raman spectrum of bulk amounts of 2,4-DNT crystals are overlain (green), however note the different scale.

## V. CONCLUSION

Numerous approaches of creating SERS substrates have been reported in literature. In general there is a trade-off between fabrication price / process complexity and Raman enhancement. Here we employ a cost effective fabrication method. This two step method produces large areas (wafer scale) of SERS active substrates which provide exceptionally large Raman enhancements. This process has been optimized to fabricate densely packed arrays of high aspect ratio silver pillars with large surface area and large numbers of electromagnetic hot spots which are responsible for the large Raman enhancement. The ability of these novel substrates to detect explosives vapours is demonstrated using 2,4-dinitrotoluene which is amongst the most common chemical species found around deployed landmines.

These new substrates enable explosives detection which is more than a factor 100 more sensitive than a commercially available SERS substrate. However it should be mentioned that the commercial substrate is a gold structure which is known to have a weaker Raman enhancement than silver. The concentration of DNT molecules exiting the heated pipe was

saturated at 80 °C and hence a large exaggeration of the concentrations found in actual minefields where ppb detection limits is a minimum requirement. Hence an effort to quantify the detection limit is being undertaken in continuation of the work presented here.

It is believed that these substrates can be used as cost effective consumables in existing SERS setups in use today. Under the framework of the Xsense project at DTU Nanotech these novel substrates will be coupled to a system comprising a micro-spectrometer to produce a handheld SERS based explosives sensor for demining actions [19].

#### ACKNOWLEDGMENT

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

#### REFERENCES

- [1] International Campaign to Ban Landmines, Landmine Monitor 2009
- [2] R. Aroca, "Surface-enhanced vibrational spectroscopy," John Wiley & Sons Ltd, 2006.
- [3] T. Kang, I. Yoon, K-S. Jeon, W. Choi, Y. Lee, K. Seo, Y. Yoo, Q-H. Park, H. Ihee, Y. D. Suh, B. Kim, "Creating Well-Defined Hot Spots for Surface-Enhanced Raman Scattering by Single-Crystalline Noble Metal Nanowire Pairs", *J. Phys. Chem. C*, 113, 2009, pp. 7492–7496.
- [4] Y. Fang, N-H. Seong, D. D. Dlott, "Measurement of the distribution of site enhancements in surface-enhanced Raman scattering". *Science*, vol 321 (5587), 2008, pp. 388-392.
- [5] R. S. Golightly, W. E. Doering, M. J. Natan, "Surface-Enhanced Raman Spectroscopy and Homeland Security: A Perfect Match?", *J. Am. Chem. Soc. Nano*, 3 (10), 2009, pp. 2859-2869.
- [6] K. Kneipp, Y. Wang, R. R. Dasari, M. S. Feld, B. D. Gilbert, J. Janni, J. I. Steinfeld, "Near-infrared surface-enhanced Raman scattering of trinitrotoluene on colloidal gold and silver", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol 51 (12), 1995, pp. 2171-2175.
- [7] E. Le Ru, P. Etchegoin, "Principles of Surface-Enhanced Raman Spectroscopy and related Plasmonic Effects" Elsevier, 2008.
- [8] D-K. Lim, K-S. Jeon, H. M. Kim, J.-M. Nam, Y. D. Suh, "Nanogap-engineerable Raman-active nanodumbbells for single-molecule detection", *Nature Materials*, vol 9 (1), 2010, pp. 60-67.
- [9] 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, pp. 665-670.
- [10] A. K. Misra, S. K. Sharma, P. V. Zinin, L. Melnick, L. Kamemoto, Q. Iu, N. Hu, "Novel micro-cavity substrates for improving the raman signal from submicrometer size materials". *Applied Spectroscopy*, vol 63 (3), 2009, pp. 373-377.
- [11] J. D. Driskell, S. Shanmukh, Y. Liu, S. B. Chaney, X.-J. Tang, Y.-P. Zhao, R. A. Dluhy, "The Use of Aligned Silver Nanorod Arrays Prepared by Oblique Angle Deposition as Surface Enhanced Raman Scattering Substrates", *J. Phys. Chem. C*, vol. 112 (4), 2008, pp. 895-901.
- [12] E.C. Le Ru, P.G. Etchegoin, J. Grand, N. Féliđj, 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.
- [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-73120I-6.
- [15] J. Tang, F. S. Ou, H. P. Kuo, M. Hu, W. F. Stickle, Z. Li, R. S. Williams, "Silver-coated Si nanoglass as highly sensitive surface-enhanced Raman spectroscopy substrates", *Appl Phys A*, vol 96 (4), 2009, pp. 793–797.
- [16] Klarite™: Renishaw Diagnostics.
- [17] M. S. Schmidt, J. Hübner, A. Boisen, "Towards easily reproducible nano-structured SERS substrates", *Proceedings of IEEE Sensors conference*, 25-28 Oct. 2009, pp. 1763-1767.
- [18] V. George, T.F. Jenkins, D.C. Leggett, J.H. Cragin, J.M. Phelan, J.C. Oxley, J. Pennington, Progress on determining the vapor signature of a buried land mine, *Proc. SPIE*, Vol. 3710, 1999, pp 258-269.
- [19] M. S. Schmidt, N. Kostasheva, F. Bosco, J. K. Olsen, C. Johnsen, K. A. Nielsen, J. O. Jeppesen, T. S. Alstrøm, J. Larsen, M. H. Jakobsen, T. Thundat, Anja Boisen, "Xsense: using nanotechnology to combine detection methods for high sensitivity handheld explosives detectors", *Proc. SPIE*, Vol. 7664, 2010, pp. 76641H1-6.