



## Statistical analysis of large areas of Raman mapped DNA functionalized gold coated silicon nanopillar SERS substrates

Frøhling, Kasper Bayer; Alstrøm, Tommy Sonne; Bache, Michael; Schmidt, Michael Stenbæk; Schmidt, Mikkel Nørgaard; Larsen, Jan; Jakobsen, Mogens Havsteen; Boisen, Anja

*Publication date:*  
2015

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Frøhling, K. B., Alstrøm, T. S., Bache, M., Schmidt, M. S., Schmidt, M. N., Larsen, J., ... Boisen, A. (2015). Statistical analysis of large areas of Raman mapped DNA functionalized gold coated silicon nanopillar SERS substrates. Abstract from 8th International Conference on Advanced Vibrational Spectroscopy, Vienna, Austria.

## 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.

# Statistical analysis of large areas of Raman mapped DNA functionalized gold coated silicon nanopillar SERS substrates

Kasper B. Frøhling<sup>1</sup>, Tommy S. Alstrøm<sup>2</sup>, Michael Bache<sup>1</sup>, Michael S. Schmidt<sup>1</sup>, Mikkel N. Schmidt<sup>2</sup>, Jan Larsen<sup>2</sup>, Mogens H. Jakobsen<sup>1</sup> and Anja Boisen<sup>1</sup>

<sup>1</sup>Department of Micro- and Nanotechnology, Technical University of Denmark, Ørsted's Plads, 2800, Kgs. Lyngby, Denmark

<sup>2</sup>Department of Applied Mathematics and Computer Science, Technical University of Denmark, Asmussens Alle, 2800, Kgs. Lyngby, Denmark

Keywords: SERS, area map, peak fitting, statistics, sensor

Detection of small molecules at low concentration by Surface Enhanced Raman Spectroscopy (SERS) has mostly been done using metal nanoparticles<sup>1</sup>, where data is normally limited to a few measurements of different clusters. The emergence of SERS substrates with well-defined, uniform 2D layers of nanostructures has created an opportunity to increase the amount of data tremendously. The amount of data calls for new approaches for data processing and data visualization, especially when batches of large area maps are collected. However to our knowledge only limited statistical analysis on SERS maps have been published<sup>2-4</sup>.

In this work we demonstrate new ways to analyze DNA and 6-mercapto-1-hexanol (MCH) surface functionalization of a uniform gold covered silicon nanopillar SERS substrate<sup>5</sup> (Figure 1; SEM images) by using a peak-fitting approach on 30x10 point area maps. Using the fitted model it is possible to observe behavior of peak creation and peak shifts during different functionalization steps. Direct characterization of a DNA and MCH functionalized SERS substrate is of high value for use in different diagnostic assays<sup>3,6,7</sup>.

The analysis is carried out by jointly fitting a Voigt profile (a combination of

Lorentzian and Gaussian shaped curve) and a linear baseline correction to a given spectral window (Figure 1; graph).

The gold heads of the SERS substrate were functionalized with thiolated 75-mer DNA. The remaining gold binding sites were subsequently blocked with the small molecule MCH (Figure 1; schematic). The SERS signal was then captured in a 30x10 point area map using a 780 nm laser with 0.1 mW power and a 50x objective.

By analyzing the large amount of data, it is possible to get a statistical view of the position of SERS peaks for a given surface functionalization. Current data shows the appearance of a specific DNA peak after 15 minutes incubation in thiolated DNA solution (data not shown). Incubation for longer time does not narrow the peak position distribution nor increase the intensity distribution of the peaks. Data on MCH backfilling show significant change in peak position of the DNA peak for different MCH concentrations (Figure 1; histogram). Smaller concentrations show only a slight shift of the DNA peak position, while the largest show only the MCH peak.

The statistical tool presented allows for direct inspection, interpretation and comparison of batches of SERS maps on uniform SERS substrates that would otherwise not be possible.

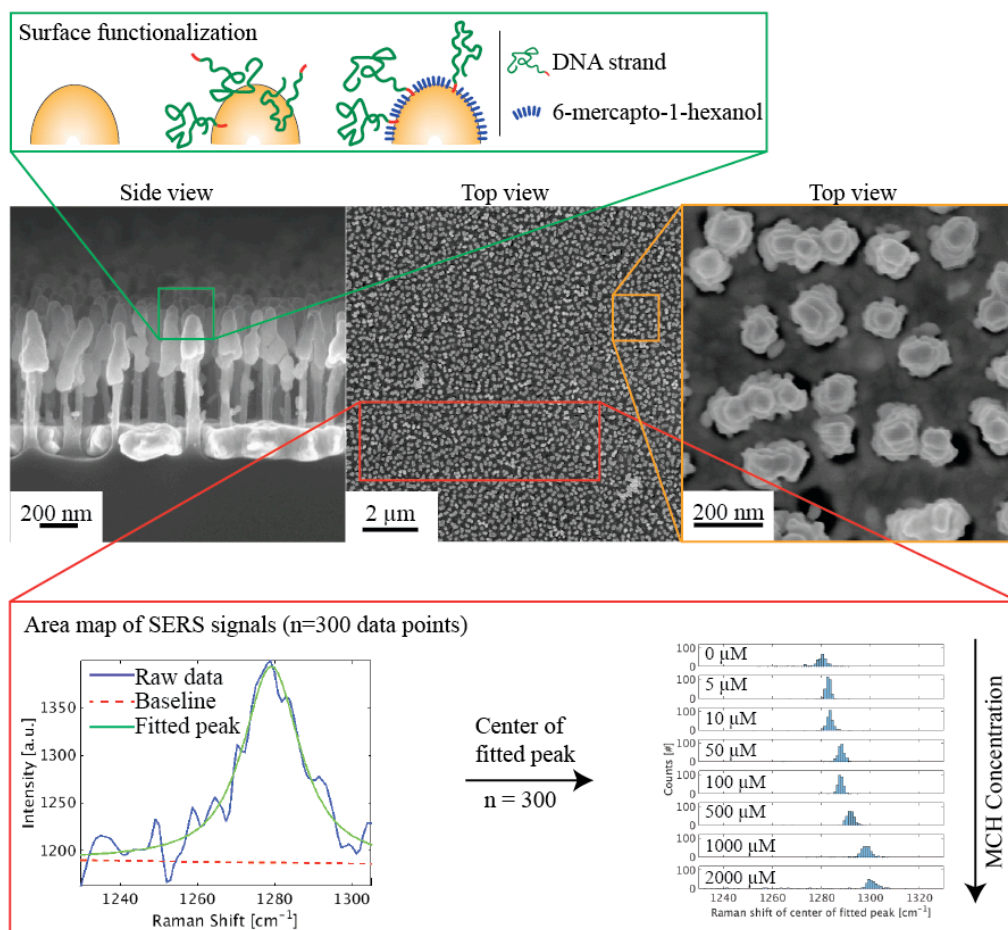


Figure 1. Top: schematic of the surface functionalization used in the experiments. Thiolated DNA was conjugated to the gold covered silicon nanopillar heads followed by backfilling with 6-mercapto-1-hexanol (MCH). Middle: SEM images of the SERS substrate seen from the side (left) and the top (middle and right). The gold heads of the silicon nanopillars are clearly seen. Bottom: overview of the peak-fitting model (left) used on 300 individual SERS spectra. The histogram (right) shows a clear shift of center peak position as a function of MCH concentration.

- 1 B. Sharma, M. Fernanda Cardinal, S. L. Kleinman, N. G. Greeneltch, R. R. Frontiera, M. G. Blaber, G. C. Schatz and R. P. Van Duyne, (2013), *MRS Bull.*, 38, 615–624.
- 2 C. M. S. Izumi, M. G. Mo and A. G. Brolo, (2011), *J. Phys. Chem. C*, 115, 19104–19109.
- 3 J. Yang, M. Palla, F. Bosco, T. Rindzevicius, T. S. Alstrøm, M. S. Schmidt, A. Boisen, J. Ju and Q. Lin, (2013), *ACS Nano*, 7, 5350–5359.
- 4 T. S. Alstrøm, K. B. Frøhling, J. Larsen, M. N. Schmidt, M. Bache, M. S. Schmidt, M. H. Jakobsen and A. Boisen, in *24th International Workshop on Machine Learning for Signal Processing (MLSP)*, IEEE, 2014.
- 5 M. S. Schmidt, J. Hübner and A. Boisen, (2012), *Adv. Mater.*, 24, OP11–OP18.
- 6 M. Culha, D. Stokes, L. R. Allain and T. Vo-Dinh, (2003), *Anal. Chem.*, 75, 6196–201.
- 7 E. A. Josephs, T. Ye, N. Sciences and U. States, (2013), *ACS Nano*, 7, 3653–3660.