

# Large Area Fabrication of Leaning Silicon Nanopillars for Surface Enhanced Raman Spectroscopy

Michael Stenbæk Schmidt,\* Jörg Hübner, and Anja Boisen

Surface enhanced Raman spectroscopy (SERS)<sup>[1]</sup> was discovered in 1974 and is now a powerful analysis technique which is becoming more and more widespread due to the development of cheaper lasers and spectrometer systems. SERS derives information about the type of chemical bonds in trace amounts of analyte molecules when these are adsorbed onto, or placed adjacent to, a metal surface or structure: a so-called SERS substrate. As it is vibrations in the chemical bonds of the analyte that cause a Raman shift, most chemical species can in theory be identified. For this reason SERS is used as a versatile analytical tool for both chemical and biochemical sensing in liquid and gas phases.<sup>[2–6]</sup>

It is widely recognized that the SERS phenomena is based on laser excitation inducing an electromagnetic field at the surface of noble metals. Areas with particularly large electromagnetic fields, also called “hot spots”, are found in between adjacent metal nanostructures if these are located sufficiently close to each other, i.e., on the order of a few nanometers. If an analyte molecule is located inside this hot spot, it will result in a comparably large Raman signal from the analyte. Recent studies have shown that hot spots account for a disproportionately large contribution to the total Raman signal from a SERS substrate.<sup>[7,8]</sup>

There is generally an emphasis on reproducibility and uniformity to ensure consistent chemical detection sensitivity across the surface of a SERS substrate. A trade-off between reproducibility and enhancement is often mentioned. The current dilemma is that the more uniform the enhancement is across a substrate, i.e. the better the reproducibility, which is often achieved using a top down lithographic approach, the lower the enhancement tends to be and vice versa.<sup>[9]</sup> Currently, the inability to mass produce large areas of cost effective nanostructured SERS substrates with large numbers of hot spots and hence suitable Raman enhancement is impeding the use of SERS sensors in both laboratories and mobile applications.

Ideally, a SERS substrate should enhance the Raman effect sufficiently to enable suitable chemical detection levels while at the same time being practical to use in a sensor system. Broadly speaking, SERS substrates can be classified into two categories, i) metallic nanoparticles in colloidal solution and ii) roughened metallic surfaces. Colloidal suspensions of metallic nanoparticles have so far been reported to have the largest enhancement factors and even single molecule detection has been demonstrated.<sup>[10–12]</sup> However, with colloidal solutions it is a challenge to bring the metal nanoparticles sufficiently close to form hot spots around the analyte, while at the same time preventing the formation of large conglomerations of nanoparticles before the analyte is introduced.

Rough silver and gold surfaces can be fabricated by a number of methods including chemical etching, mechanical deformation, electroplating and oblique angle deposition.<sup>[13–15]</sup> Processes where well defined metal coated silicon nanostructures are created, by for example electron beam lithography, have gained in popularity.<sup>[16]</sup> However this approach has a very high fabrication cost and is generally unfeasible for areas above a couple of mm<sup>2</sup>. As opposed to electron beam processes, bottom up processes based on co-block polymer patterned chemical seeding have been shown as a way of fabricating SERS substrates with good uniformity at relatively low process costs.<sup>[17]</sup> Another approach is to produce a rough surface on a given material with the desired topology and then cover it with gold or silver rendering it Raman active.<sup>[18–24]</sup> Recently, it has been demonstrated that freestanding nanopillars coated with silver or gold can act as effective SERS substrates.<sup>[25–29]</sup> The spacing between the pillars has been shown to have vital importance on the Raman signal.<sup>[26]</sup> Furthermore, it is illustrated through simulations and experimental measurements, that vertical nanopillar arrays can confine surface plasmons if the spacing between the nanopillars is sufficiently small.<sup>[27,28]</sup>

Recently an elegant concept of manufacturing flexible gold decorated InP nanowires<sup>[30]</sup> and gold capped polymer nanopillars<sup>[31–33]</sup> has been presented. These nanowires and nanopillars lean together as liquid solutions of analyte evaporate, hence trapping analyte molecules at the formed hot spots.<sup>[32]</sup> To fabricate regularly spaced nanopillars, electron beam lithography has been used to define the pillars in the fabrication process.<sup>[31]</sup> The feasibility of electron beam lithography can be improved using nanoimprint lithography. However, the high-cost task of producing large areas of nanostructures on the master stamp still remains and the imprint of high-aspect ratio structures is not trivial and can only be performed at dedicated or custom made facilities.

This paper presents a far simpler method of producing flexible free standing nanopillars for SERS. The nanopillars are made from silicon and the resulting SERS substrate exhibit a

Dr. M. S. Schmidt, Dr. A. Boisen  
DTU Nanotech  
Technical University of Denmark  
Department of Micro- and Nanotechnology  
Ørstedes Plads, Building 345 east, 2800 Kgs. Lyngby  
Phone: +45 45 25 58 46  
E-mail: Michael.schmidt@nanotech.dtu.dk



Dr. J. Hübner  
DTU Danchip  
Technical University of Denmark  
Department of Micro- and Nanotechnology  
Ørstedes Plads, Building 345 east, 2800 Kgs. Lyngby  
Phone: +45 45 25 58 46

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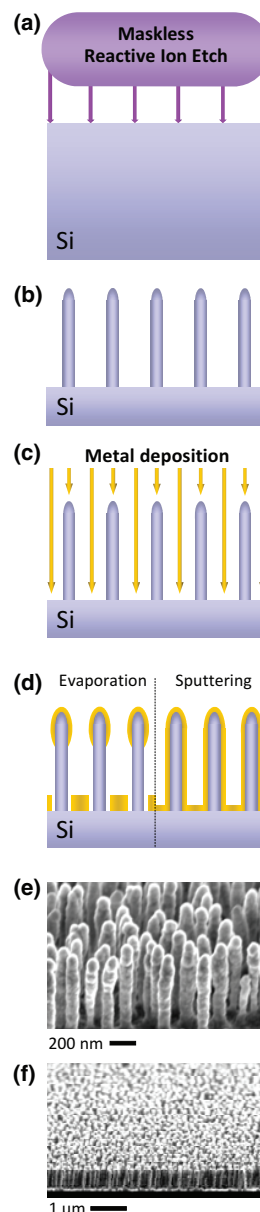
remarkably large Raman enhancement due to analyte trapping. The substrate can be fabricated in any silicon processing facility to produce large areas of SERS substrates at a minimal cost. The silicon nanopillars are defined by maskless dry etching. Previously, conical shaped silicon structures have been realised by a variety of maskless processes and used for SERS.<sup>[18,20,21,23,34–37]</sup> However, such conical structures can not bend and the reported Raman enhancements have consequently been relatively low. By fine tuning the etch process we demonstrate that it is possible to custom design the pillar height, width and nanopillar density. Furthermore, we demonstrate that these novel substrates can be used for gas sensing which until now has not been demonstrated with leaning nanopillars structures.

**Fabrication:** A fabrication process was developed using standard silicon plasma etching equipment<sup>[38]</sup> in an unconventional way not necessitating a lithographic step (Figure 1). Omitting a lithographic step by using maskless etching has clear advantages. Firstly, it significantly reduces the processing time hence facilitating cost effective consumable substrates. Also, it would be challenging to produce nanopillars this size on a large scale using conventional lithography-based silicon processing.

A broad variety of nanostructures can be produced by careful control of the reactive ion etching parameters.<sup>[34]</sup> For example, conical silicon micro- and nanostructures with a broad base, also reported in<sup>[34–37]</sup>, as well as low aspect ratio silicon nanopillars coated with silver or gold were tested for SERS activity.

For SERS applications we tuned and optimized a reactive ion etching process so that we are now able to fabricate free standing vertical silicon pillars in the range 50–80 nm wide. The pillar height scales linearly with the process time, so pillars with heights between 600 nm and 1600 nm were evaluated. The pillar density is controlled by varying the process chamber pressure and coil electrode power. As seen in Figure 1e, the nanopillars have the same height for a given process time. It is essential that the nanopillars have a uniform height for them to be able to “find” their nearest neighbours when leaning.

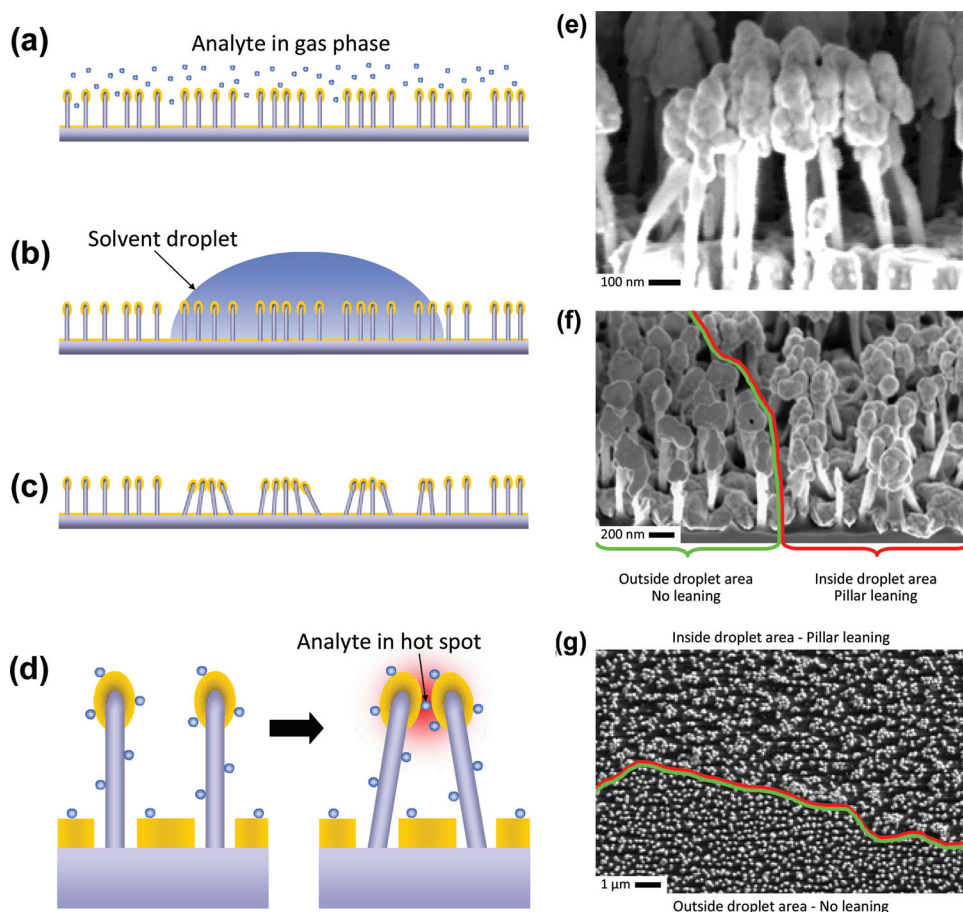
To prevent contamination in the subsequent SERS spectra, the silicon nanopillars were manufactured without the fluorocarbon passivation cycles normally used in deep reactive ion etching and reported in.<sup>[35]</sup> Furthermore, after the reactive ion etch the nanostructured silicon was exposed to a one minute argon plasma to physically remove any remnants of the SF<sub>6</sub> etchant gas and its decomposition products. The silicon nanopillars are coated with silver by electron beam evaporation to facilitate a Raman active surface. The metallization thickness was optimized for a laser excitation wavelength of 785 nm. More conformal silver coatings by magnetron sputtering as shown in Figure 1e,f, were also fabricated. However the conformal silver coatings yielded lower Raman signals than from those fabricated using the evaporated metallization technique and will thus not be discussed in the following. Background signals from the substrate become an issue when very small amounts of analyte are to be detected. Thus, it is advantageous to use silicon as the nanopillar material compared to various polymers as the background signal from the single silicon peak is very easily identified in subsequent Raman spectra. The leaning ability of the nanopillars is instrumental for the task of metallization. If rigid pillars were fabricated with a spacing



**Figure 1.** The fabrication process. a) Maskless reactive ion etching forms silicon nanopillars b). c) Silver is deposited by electron beam evaporation or magnetron sputtering onto the silicon nanopillars to form SERS-active substrates. d) Evaporation results in silver lumps at the top of the silicon pillars while sputtering yields conformal coatings as shown in the SEM image in e). f) The pillars produced across large areas have a uniform height.

necessary to form hot spots without leaning (<5 nm) then metallization would be virtually impossible as a continuous silver layer would form on top of the pillars. However, because of the leaning effect, the density of nanopillars can be tuned to facilitate the optimal diameter of the silver tip with respect to the wavelength of the laser used for the Raman analysis.

**Leaning Effect:** As also shown in<sup>[31]</sup> the ability of the nanopillars to lean is crucial for a large Raman enhancement. To demonstrate that the same mechanism is taking place on the



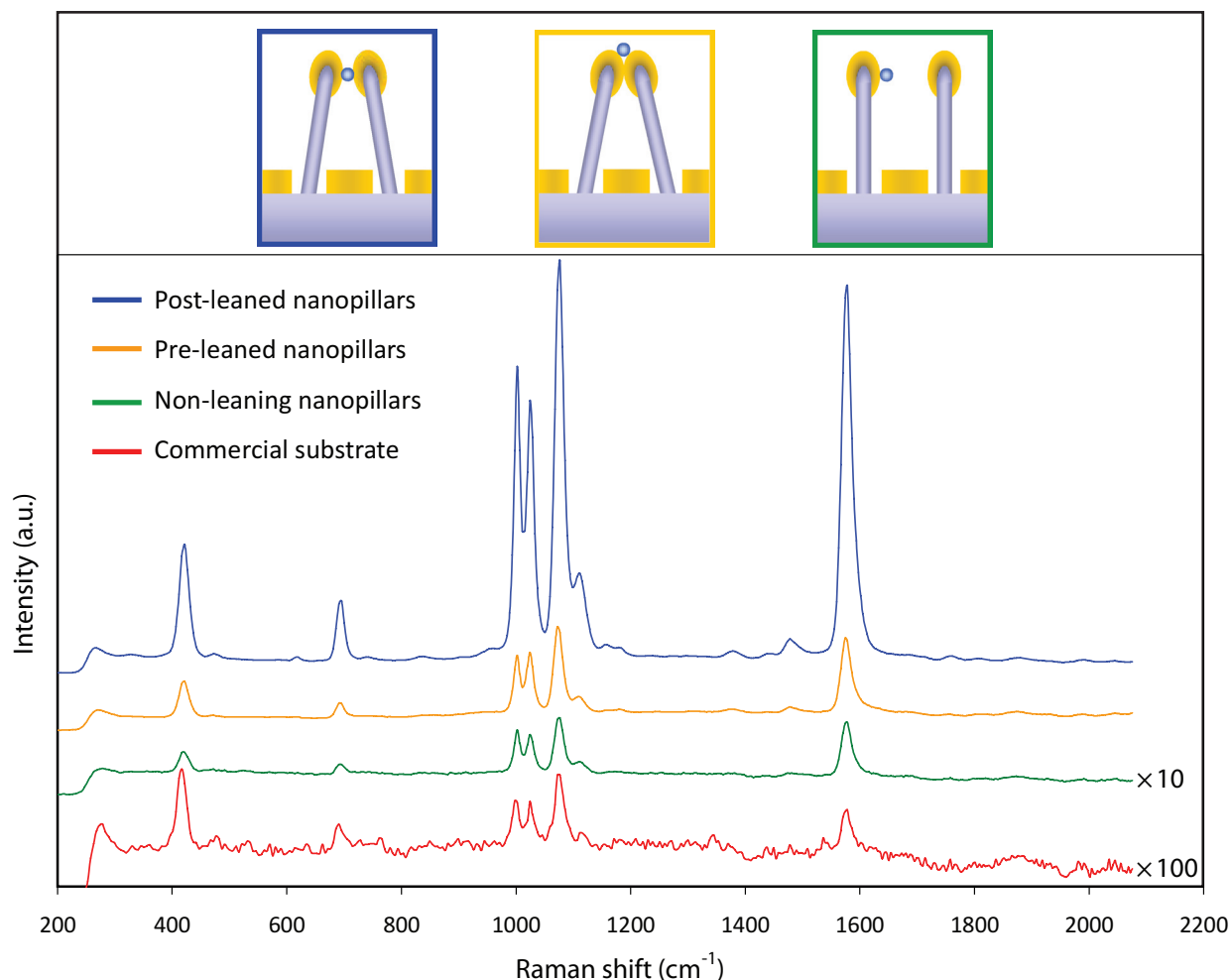
**Figure 2.** Concept of the leaning nanopillar substrate. a)–c), Schematic of the leaning mechanism. d) Schematic of hypothesized enhancement mechanism. When the solvent evaporates, surface tension will pull the silicon nanopillars together, trapping the analyte at the hot spot giving rise to a large Raman signal. e) SEM image of a cluster of leaning silver coated silicon nanopillars. f) Tilted SEM image of the outer perimeter of the evaporated solvent droplet area. The nanopillars to the right have leaned to form hot spots while the nanopillars to the left remain vertical and free standing. g) SEM image of nanopillar surface seen perpendicular to the surface. The line indicates the outer perimeter of the evaporated solvent droplet. Bottom: individual freestanding nanopillars. Top: clusters of nanopillars have formed.

substrate presented here the following measurements were performed. At the same time we present the novel use of this substrate as a gas sensor. When the substrate is exposed to analyte in gas phase, it is assumed that the analyte adsorbs uniformly all over the nanopillars, including the silver coated tips (Figure 2a,d). We exposed a silver coated nanopillar substrate to thiophenol vapor for 30 seconds. From these non-leaning nanopillars we measured a Raman enhancement an order of magnitude larger than from a commercially available substrate<sup>[24]</sup> used as a benchmark under identical conditions (Figure 3). The signal from the commercial substrate has been multiplied by a factor 100 for clarity in Figure 3.

By subsequently depositing a droplet of solvent (in this case water) onto the substrate, (Figure 2b), and letting it evaporate, surface tension will cause the nanopillars to lean towards their nearest neighbours (Figure 2c,d), thus creating self assembled hot spots. Analyte molecules adsorbed at the tips of the pillars will now be located exactly in the hot spots as the pillars lean together (Figure 2d). This self assembling mechanism creates a large number of electromagnetic hot spots inside

the laser excitation area. Using a 160  $\mu\text{m}$  diameter laser spot we observe a drastic increase in the Raman signal by a factor of 72 compared to the non-leaning pillars just outside the droplet area (Figure 3). Inside the droplet area the measured Raman signal is 620 times larger than the commercially available benchmark substrate (Figure 3). From scanning electron microscopy (SEM) investigations it is seen that most nanopillars have paired with their nearest neighbours, (Figure 2e-g). As it is the size of the analyte molecule which determines the spacing between the nanopillar tips, the smallest possible gaps are created with respect to the analyte molecule size. The nanopillars remain clustered over time and have not been observed to become freestanding even after 12 months of storage.

If the pillars are brought to lean before exposure to thiophenol vapor (pre-leaning), the signal is 16 times stronger than for surrounding non-leaning pillars. However, the Raman signal from pre-leaning pillars is approximately 4.5 times lower than from the post-leaning pillars that are brought to lean after analyte exposure (Figure 3). This indicates that some potential



**Figure 3.** Raman spectra recorded from the silicon nanopillars substrate in both leaning and non-leaning configurations with a commercial substrate included as a benchmark. For clarity the signal from the commercial substrate and the non-leaning nanopillars have been multiplied by 100 and 10, respectively. The substrates were exposed to thiophenol vapours for 30 seconds. The subsequent Raman spectra were recorded with an integration time of 1 second at a laser excitation wavelength of 785 nm (160  $\mu\text{m}$  diameter laser spot with a power of 150 mW). The leaning nanopillars create a much larger Raman enhancement than the non-leaning nanopillars. The pillars leaning prior to thiophenol exposure have a 4.5 times weaker signal than the pillars brought to lean after thiophenol exposure.

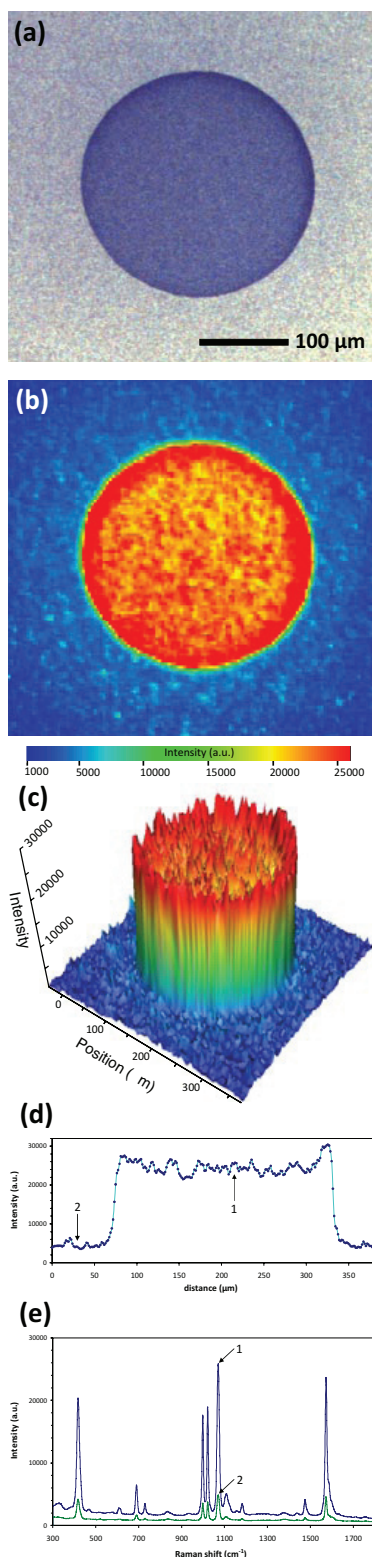
hot spots and/or adsorption sites are negated by leaning prior to analyte exposure.

The substrates can also be used with liquid analytes by dipping the substrate into an analyte solution. Alternatively, a liquid analyte can be simply deposited onto the substrate where it is allowed to evaporate. It should be noted that any organic solvent can be used as the silicon is not dissolved as is the case for some types of polymers. When the analyte evaporates, the pillars lean to form hot spots with the analyte molecules trapped in between. The sheer number of formed hot spots makes it very likely that the analyte species will be located in a large number of hot spots giving rise to a large average Raman signal.

SEM investigations have shown that the silicon nanopillars will snap towards each other during electron raster scanning. Hence, electrostatically induced leaning is seen as another approach of forming hot spots without using evaporating

liquids. Although it is a possibility, it is unlikely that it is localized heating which causes the leaning in the SEM. To support this there hasn't been any observations of leaning being induced on free standing pillars by laser exposure after Raman measurements.

In order to study the uniformity of the Raman signal across an area of leaning nanopillars, mappings were performed on a substrate with a pillar density of  $18.0 \mu\text{m}^{-2}$ . Using a  $\mu$ -Raman system and a laser spot diameter of 3.1  $\mu\text{m}$ , spectra were recorded every 3.5  $\mu\text{m}$  across the surface of a substrate exposed to thiophenol in the gas phase followed by nanopillar leaning induced by evaporation of a single water droplet. The resulting Raman map comprising of 14274 spectra and showing the relative intensity of the  $1071 \text{ cm}^{-1}$  peak is shown in **Figure 4b** together with an optical microscope image of the same area (**Figure 4a**). It should be noted that the area with leaned nanopillars is visibly darker and thus easy to identify. From **Figure 4b,c,d**,



**Figure 4.** a) Optical microscope image of a nanopillar surface on which a water droplet has been deposited to induce nanopillar leaning after exposure to thiophenol gas. Note that the leaning area is clearly identifiable. b) Raman map of the same area as shown in a) using a laser spot diameter of 3.1 μm and a step-size of 3.5 μm. The normalized intensity

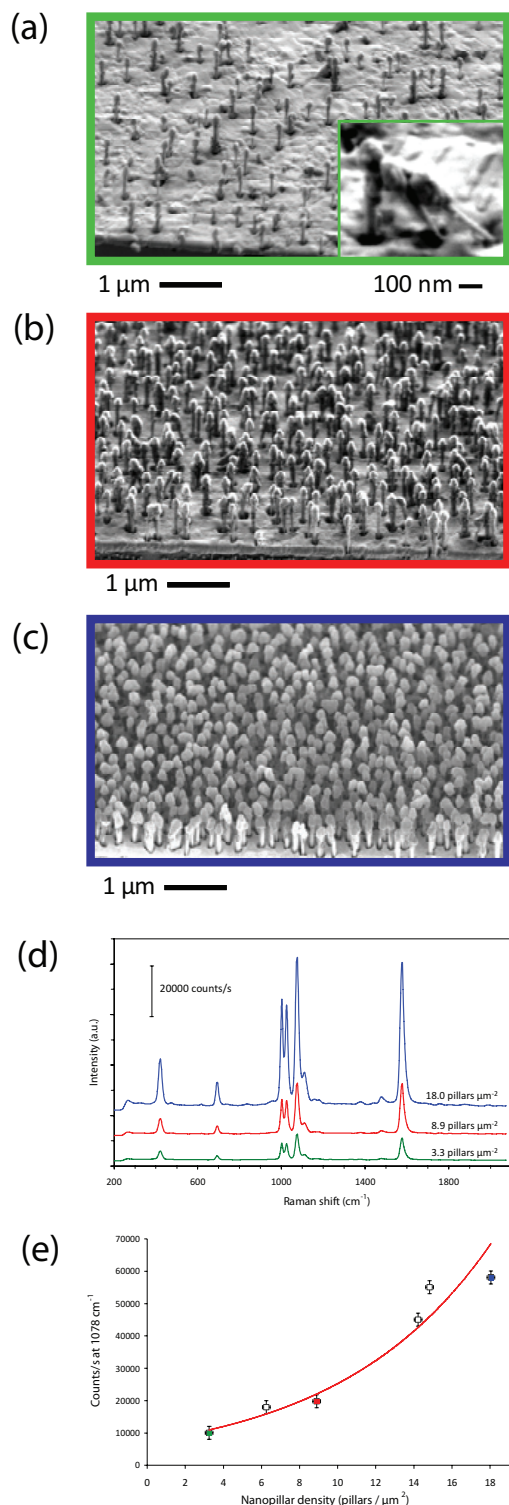
it is seen that the signal from within the leaned nanopillar area is relatively uniform with a 7% deviation from the average signal across the leaned area. Figure 4d shows a line scan across the leaned area with a step size of 1.5 μm. There is a slight increase in signal at the perimeter of the leaned area. As nanopillars at the border to the non-leaning pillars can only lean inwards towards the leaning area (Figure 2f,g) it is hypothesized that the stronger Raman signal at the perimeter is due to more pillars per unit area forming hot spots.

In order to investigate the influence of pillar density on the Raman signal, substrates with six different pillar densities (3.3, 6.2, 8.9, 14.2, 14.8 and 18.0 pillars μm<sup>-2</sup>) were fabricated and used for gas phase thiophenol detection. The recorded Raman signals are plotted as a function of nanopillar density in Figure 5. The Raman signal is seen to increase with increasing pillar density. Even at relatively low pillar densities (3.3 μm<sup>-2</sup>) a significant Raman signal is observed and thus hot spot formation must still be possible. SEM investigations confirm that nanopillars, even at these low densities, form clusters—now with remarkably large angles of leaning (Figure 5a inset). The ability to define the sensitivity of a spread of SERS substrates is seen as a pathway to enable semi-quantitative measurements of analyte gas concentrations as discussed in the following conclusion.

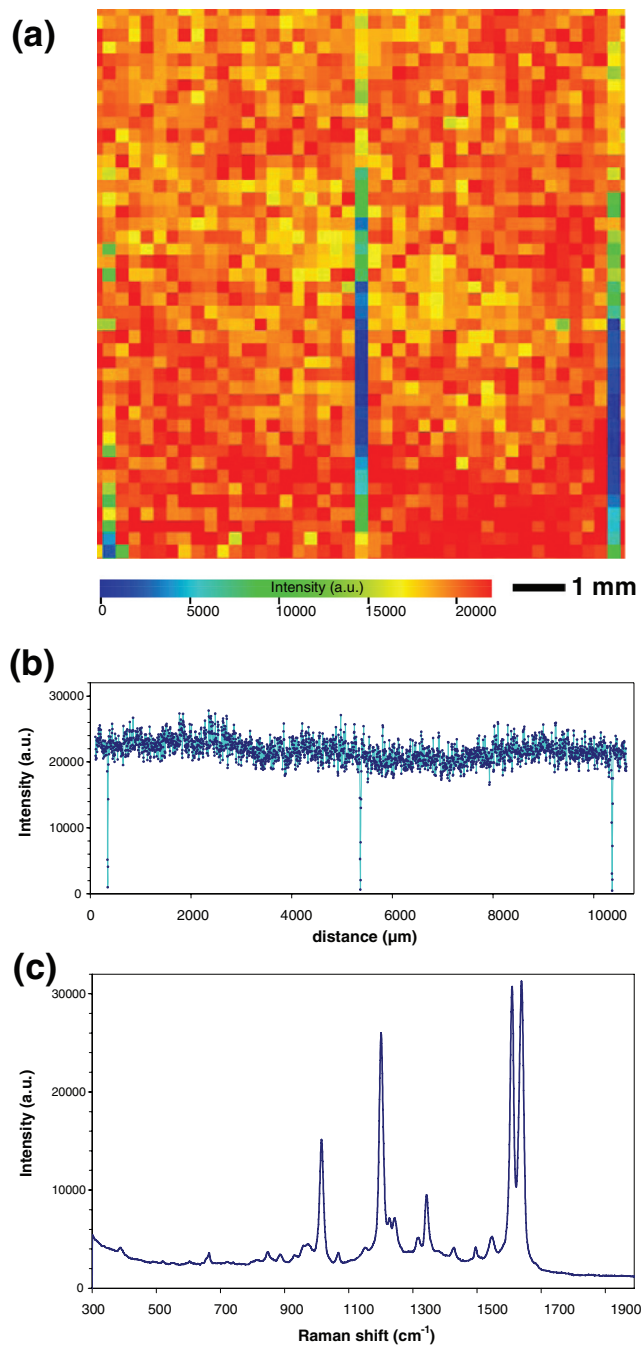
To evaluate the large scale uniformity of the substrate as in<sup>[31]</sup> we immersed a 1 × 1 cm piece of silicon nanopillar substrate into 1mM of trans-1,2-bis(4-pyridyl)ethylene (BPE) in ethanol solution for 10 minutes. Hereafter the substrate was allowed to air dry to cause nanopillar leaning. After rinsing the substrate with ethanol in order to remove non-adsorbed BPE, the substrate was Raman mapped using steps of 100 μm and a laser spot diameter of 3.1 μm. Once the pillars lean during the first evaporation process the pillars are irreversibly attached and will not detach during the rinsing process. In Figure 6a, the intensity of the 1200 cm<sup>-1</sup> peak is shown as a function of position on the entire substrate. The blue lines, corresponding to a very low Raman signal, stem from scribed lines made every 5 mm after fabrication to serve as orientation marks. A line scan with steps of 2 μm on the same chip is shown in Figure 6b where the relative intensity of the 1200 cm<sup>-1</sup> peak is plotted. When excluding the signal from the scribed lines the standard deviation from the average signal from the line scan in Figure 6b is 8%.

Although the evaluation of the SERS enhancement factor has been the cause of some debate in the SERS community, attempts at determining the enhancement factor as described in<sup>[28]</sup> and<sup>[31]</sup> were carried out, see supporting information for details. Assuming complete coverage of the nanopillars with the test molecule, BPE, we arrive at an enhancement factor on

for the 1071 cm<sup>-1</sup> peak across the surface of the leaning nanopillars area is shown on a colour scale. c) Three dimensional representation of the Raman map in b). Note the very well defined difference in signal intensity between the leaned nanopillars and the non-leaning nanopillars. d) The intensity of the 1071 cm<sup>-1</sup> peak across the diameter of the leaning nanopillar area using a laser spot diameter of 3.1 μm and a step-size of 1.5 μm. A 7% deviation from the average signal was measured from the leaning nanopillars. e) Representative spectra (not baseline corrected) recorded from (1) the leaned nanopillars and (2) from the non-leaning nanopillars.



**Figure 5.** Raman spectra from 785 nm laser excitation and a laser spot diameter of 160 μm from substrates with varying nanopillar densities. The pillars were exposed to thiophenol in the gas phase and the pillars were brought to lean by an evaporating water droplet. The colours of the frames around the SEM pictures. a)–c) correspond to the Raman spectra in d) and the intensities in e). Inset in a): note the large possible angle of leaning.



**Figure 6.** Map showing the uniformity of the Raman signal across a 10 × 10 mm piece of nanopillar surface. BPE was used as the analyte molecule and the relative intensity of the 1200 cm⁻¹ peak is plotted. Lines are scribed every 5 mm into the surface to act as orientation marks. b) A line scan plotting the intensity of the 1200 cm⁻¹ peak across the same sample shows a uniform signal intensity (8% deviation). c) Representative BPE spectra from the nanopillars surface.

the order of  $2.4 \times 10^6$ . If we assume that it is only the molecules located on the silver tips of the nanopillars, approximated to be spheres, that produce a Raman signal, we arrive at an enhancement factor on the order of  $7.8 \times 10^6$ . If we use the assumptions and method presented in<sup>[31]</sup> where it is primarily the

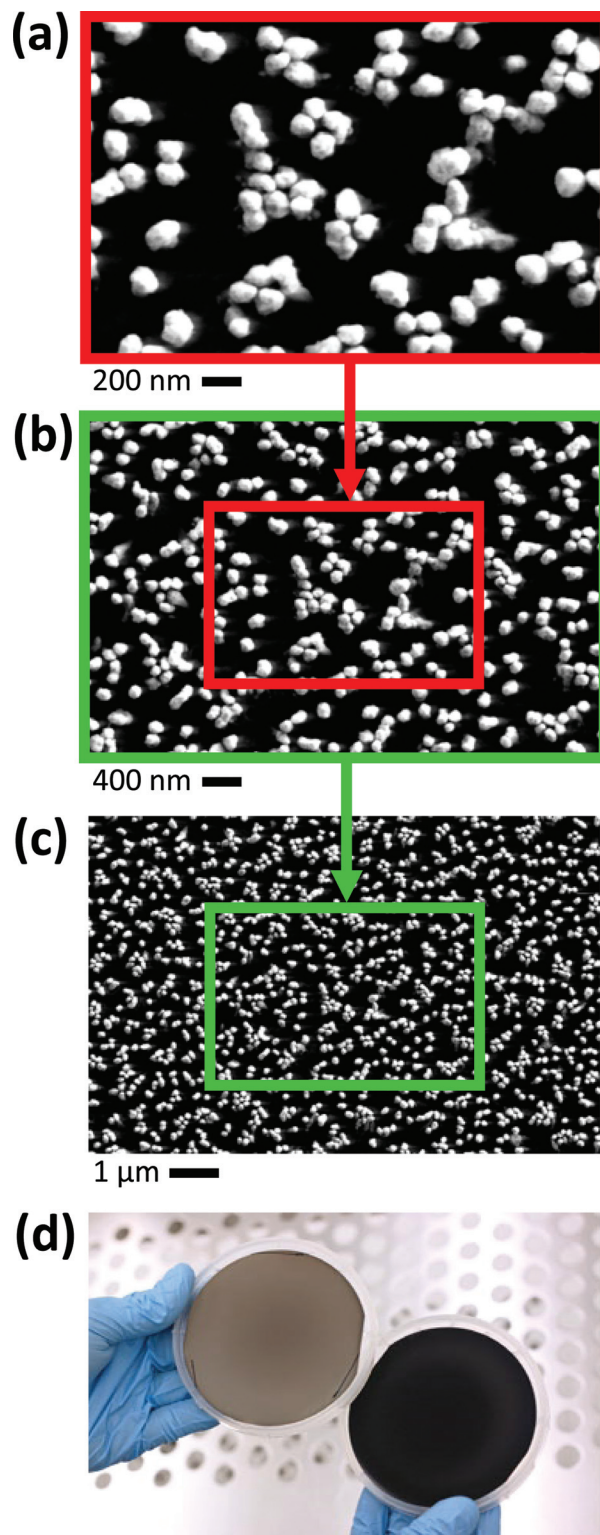
few molecules trapped in the hot spots which account for the Raman signal we arrive at an enhancement factor of  $2.1 \times 10^{11}$ . This value is comparable, albeit slightly larger, than reported from gold coated polymer pillars. Since these values vary significantly depending on ones initial assumptions we compared our substrate with a readily available commercial substrate. The 620 times increase in Raman signal compared to the commercial substrate provides an alternative and purely experimental estimate of our substrates performance.

In summary, we have reported a simple two step fabrication method for square-centimeter-sized silicon nanopillar substrates with a highly uniform Raman enhancement. The estimated enhancement factor is comparable to that of the imprinted polymer nanopillar substrate when committed to the same experimental procedure and calculation method.<sup>[28,31]</sup> In addition to having a minimal and easily recognized background signal from silicon it should be noted that silicon based substrates can, as opposed to some polymer substrates, also be used at elevated temperatures and in organic solvents. However, our major point is not the large enhancement—here we believe more can be done by optimizing pillar height, metal coverage, and pillar cluster formation. Instead, we focus on demonstrating the possibility of simple, reliable, reproducible large scale fabrication of this new class of analyte trapping SERS substrates using standard silicon processing equipment available in most research institutions.

In order to make SERS substrates economically viable as a disposable consumable the use of lithography in general and electron beam lithography in particular, is seen as a prohibitively costly process step. Hence, we selected maskless reactive ion etching to realize wafer scale nanostructured surfaces for SERS, **Figure 7**. Our substrates are today fabricated on 4 and 6 inch silicon wafers with standard deviations from the average signal of approximately 10% (excluding an approximately 1 cm wide rim at the edge of the wafer). These wafers can easily be diced into smaller chips to be used as consumables. In addition to being very cost effective the ability to form hot spots with the analyte inside is seen as fundamental for obtaining a sufficient SERS enhancement for trace chemical detection.

As shown in **Figure 5**, it is possible to control the sensitivity of the substrates in well controlled increments by reducing the density of pillars. Hence, an array of SERS substrates with varying pillar densities could possibly be used as a method for semi-quantitative Raman measurements. The principle being that if an analyte species is able to be detected on the least sensitive substrate (lowest pillar density) it is presumably present in high concentrations and if the analyte is only detected on the most sensitive substrate (highest pillar density) it is presumably present in low concentrations.

The SERS substrate presented here can be stored easily in a protective atmosphere/vacuum until needed and can be employed for both liquid and gas phase detection in various chemical and biochemical applications such as explosives detection.<sup>[39,40]</sup> Furthermore, this technique opens up for the possibility to tune the size of the silver nanoparticles on the silicon pillars to optimally absorb the excitation laser light of any given wavelength of interest to resonant Raman scattering. As large areas can be produced at a low cost it is the hope that this will facilitate widespread use of the powerful SERS sensing



**Figure 7.** Uniformity of the nanopillar substrate. a)–c) SEM images using secondary electrons taken at a right angle to the surface. A uniform distribution of metal covered nanopillars is seen over the area of a 4" silicon wafer. d) Using maskless reactive ion etching, nanostructures (here shown with several  $\mu\text{m}$  tall structures for clarity) can be created on a wafer scale (right). After metallization with silver the wafer changes colour from black (right) to grey (left).

technique in numerous applications where trace level chemical detection is necessary.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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