

Tunable Nanopillars as surface enhanced Raman scattering (SERS) active structure for optical quartz glass fiber

E. Melekhov, V. Abb, T. Weidauer, M. Kammler, A. Lechner
 Regensburg University of Applied Sciences, Centre of Excellence NanoChem
 evgeny.melekhov@oth-regensburg.de

Summary:

In this work, a simple cost effective method to create tunable self-assembled three-dimensional nanostructure array-like nanoantennas on a tip of an optical quartz glass fiber is described. The structures are prepared using lithography-less dry etching. Gold nanoparticles are used as an etching mask using a thin metal-film thermal dewetting technique. The structures are applied as sensor for label-free analysis of organic substances in ppb range, such as drug residues in groundwater. The measurements are carried out by means of a Surface-enhanced Raman scattering (SERS) effect, an exchangeable sensor head, and a portable Raman device. This method allows in situ applications. Parathiocresol is used as a model substance to characterize the SERS cells. For metallization, gold and silver are compared. Reproducible SERS enhancement factors up to 10^7 are evaluated.

Keywords: Surface-enhanced Raman scattering (SERS); Nanostructuring; Analytical spectroscopy; Plasmonics; optical quartz glass fiber

Background, Motivation an Objective

Raman spectroscopy is a vibration spectroscopic technique using the inelastic scattering of light by vibrating molecules. Metallic nanostructures can induce a strong amplification of Raman signals by generation of local electrical fields induced by laser irradiation. Such signal amplification is caused on the one hand by localized surface plasmon resonances (LSPRs), and on the other hand by a charge transfer between substrate and molecules attached to the surface. Thus, it becomes possible to detect molecules by an amplification factor up to 10^{11} .

Design of measuring device

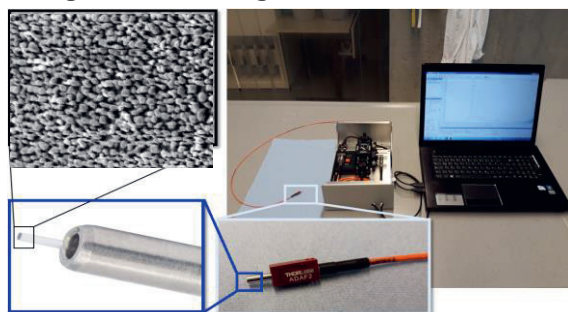


Fig. 1. Construction of a portable SERS-analyzer

The laser of $\lambda_{ex}=785\text{nm}$ is connected on one side to the excitation fiber and on the other side to the fiber coupler. The beam of the laser is collimated via an excitation collimator and passes through a line filter to the dichroic mirror

deflecting the light to the lens. The lens focuses the beam onto the sample surface. The same lens collimates the scattered Raman light from the SERS surface. The low energy Stokes bands pass through the dichroic mirror, the high energy anti-Stokes bands are almost completely suppressed. The dichroic mirror and the edge filter also reduce the highly intense Rayleigh bands and the excitation beam. The dichroic mirror deflects the light to the collimator, and in turn through an optical fiber to the spectrometer. The power supply for the system is provided via an USB cable from a laptop that is also employed for control of the laser and spectrometer.

Procedure of SERS-cells preparation

The following chapter describes a method for nanostructuring of SERS active areas on quartz substrates like plates or optical fibers (Fig. 2).

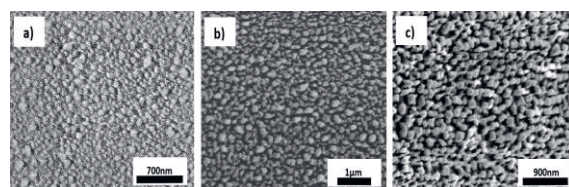


Fig. 2. Tilted SEM images of the preparation procedure of nanopillar arrays on a quartz plate: a) two-dimensional nanoislands, fabricated by thermal annealing of a gold layer; b) glass nanopillars, created by dry etching; c) quartz glass nanopillars after metallization with an additional silver film on top of the pillar array

The SERS substrate is prepared by reactive ion etching of quartz glass using nanoislands as an etching mask and an additive metallization with gold or silver. Creation of nanoislands is based on self-assembly structuring by annealing of a thin metal layer [1]. This can also be used for structuring of the tip of an optical quartz glass fiber.

Initially, a quartz substrate, e.g. a plate or an optical glass fiber, is covered with a thin gold film as a thermal dewetting layer via e-beam evaporator. In the next step, the metallized substrate is annealed to form closely packed gold nanostructures. During annealing, the thin gold layer breaks up forming nanoislands. These self-assembled structures serve as a mask [2] for etching the quartz glass substrate by CHF_3/Ar plasma.

Results

For Raman measurements, the samples are immersed in 10^{-4} mol/l solution of p-thiocresol in ethanol. After the sample solution is evaporated, the SERS spectrum is recorded.

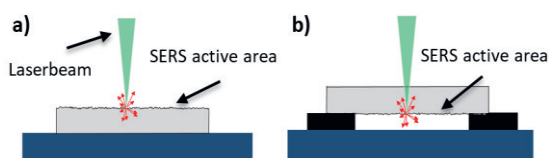


Fig 3: Schematic representation of the SERS measurements of quartz substrates from a) the upper side and b) from the underside of the substrate (comparable with a SERS-measurement using an optical fiber)

Figure 4 illustrates SERS-spectra of p-thiocresol using quartz plates covered by gold (right) or silver (left) on the top of the pillars from the underside (dashed red lines) and from the upper side (solid blue lines) of substrates (see Fig. 3).

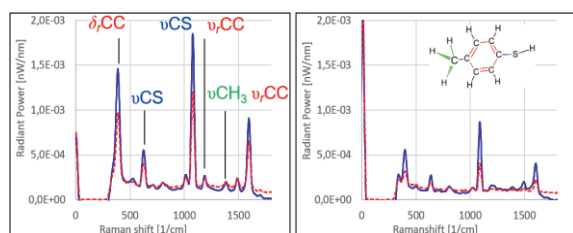


Fig 4: SERS Spectra of p-thiocresol with a concentration of 10^{-4} mol/l measured on structured quartz glass substrate. Dashed red lines represent SERS measurements from the underside of the substrates. The solid blue lines correspond to the measurements from the upper side of the substrates. Structures are metallized with 50 nm Ag (left) and 50nm Au (right)

Figure 5 shows SERS spectra of p-thiocresol recorded using a structured quartz glass fiber. In this figure, the solid blue line represents the background spectrum of the glass fiber im-

mersed in pure ethanol. The dashed red line represents the overlay of the Raman spectrum of the quartz glass fiber and the SERS spectrum of p-thiocresol with a concentration of 10^{-4} mol/l. The corrected SERS spectrum of p-thiocresol after subtracting the background spectrum of the quartz glass fiber is illustrated on the right.

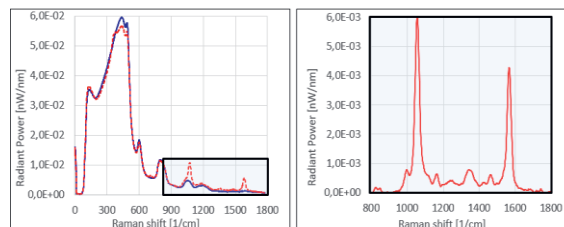


Fig 5: Raman spectrum of a SERS active structured quartz glass fiber immersed in ethanol as background spectrum (solid blue line) and SERS spectrum of thiocresol (dissolved in ethanol) with a concentration of 10^{-4} mol/l overlaid with the Raman spectrum of the glass fiber (dashed red line, left); SERS spectrum of p-thiocresol solution 10^{-4} mol/l (background Raman spectrum from the glass fiber already subtracted)

Conclusion

By thermal dewetting technology, quartz glass substrates such as optical fibers can be structured over large areas homogeneously in order to prepare nanopillars at low temperature. The pillars have diameters between 30nm and 80nm with the depth of 200nm. For creation of SERS activity, these pillars can be covered with silver or gold. In this way, nanogaps between metallized tops of pillars can be precisely adjusted.

Using the presented construction of the portable analyzer, SERS measurements can be performed in the field. With the measuring device and the SERS-active structure, p-thiocresol with a concentration of 10^{-8} mol/l dissolved in ethanol could be determined. The measurement results show that the organic substances can be measured in the ppb range.

References

- [1] R. P. V. Duyne, J. C. Hulteen und D. A. Treichel, „Atomic force microscopy and surface-enhanced Raman spectroscopy.I. Ag island films and Ag film over polymer nanosphere surfacessupported on glass,“ *The Journal of Chemical Physics*, pp. 2101-2115, 1993.
- [2] T.-W. Chang, M. R. Gartia, S. Seo, A. Hsiao und G. L. Liu, „A wafer-scale backplane-assisted resonating nanoantenna array SERS device created by tunable thermal dewetting nanofabrication,“ *Nanotechnology* 25, 2014.