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Development of a glass-fiber-based spectrometer for the determination of drug residues in groundwater

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

Summary:

Within the scope of this project, a portable measuring device has been developed which enables a cost-effective analysis of organic substances from ppm to the sub-ppm range, such as drug residues in groundwater. The measurement is carried out by means of an exchangeable sensor head. The sensor head used is a nanostructured optical glass fiber glued into a fiber cannula. At the tip of the fiber is a surface-enhanced Raman scattering cell (SERS cell).

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

Background, Motivation an Objective

SERS based Raman spectroscopy is a powerful detection technique, which detects organic molecules by vibrational spectroscopy at very low concentrations, e.g. in groundwater or drinking water to the extent necessary for a risk assessment. The SERS effect is mainly due to the high local electric fields generated by the irradiation of suitable nanostructured highly electrically conductive materials such as silver or gold with a laser. Due to the resonances of the surface plasmons in the metallized nanostructures, there are local field increases (hot spots).

Design of measuring device

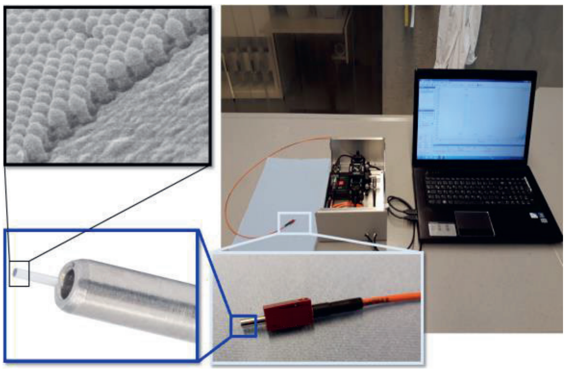

Fig. 1. Construction of a portable SERS-analyzer

Light source of the device is a laser with 785nm wavelength with maximum power of 75mW. The laser is connected to the measurement system via excitation fiber and fiber coupler. The laser beam get to sensor fiber via excitation collimator, line filter, dichroic mirror and objective. Nanopatterned optical fiber, glued into a fiber ferrule, is connected to the patch cable, sensor fiber respectively via an adapter (see Fig. 1). From the SERS-surface scattered light goes back via sensor fiber to the objective and get then to the spectrometer via dichroic mirror, line filter, eyepiece and detection fiber. The entire system is powered by a laptop via a USB cable. The spectrometer and laser are controlled also by the laptop.

Methods for structuring SERS-active areas

The following chapter describes methods for nanostructuring of SERS active areas on quartz substrates (see Fig. 2). All these methods can be used for structuring of optical quartz glass fiber.

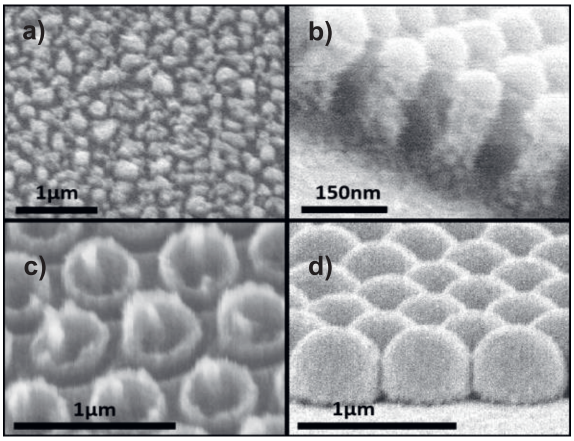

Fig. 2. SEM pictures: a) Metallized nano pillars on a quartz substrate produced by annealing a thin gold layer and dry etching in RIE; b) Metallized nano pillars and c) nano ring cavities on a quartz substrate produced by dry etching in RIE using of polystyrene spheres as an etch mask; d) Metallized polystyrene nano spheres

The first method is based on self-assembly structuring by annealing of a thin metal layer [1]. Other methods are based on Nano Sphere Lithography (NSL) [2]. Here, the spheres can be applied by means of a water technique [3] on the sample surface like a wafer or optical fiber.

First a quartz substrate is coated with 9nm gold via e-beam evaporatior and then annealed. This layer breaks up during annealing to very small structures similar islands. This self-assembled structure serves as a mask against CHF_3/Ar plasma [4] for dry chemical etching. Etching process creates small pillars among the Ag nano Islands. For SERS measurement, this structure is evaporated again with Au (see Fig. 2 a)).

Another SERS-active structure can be prepared by nano sphere lithography. This method allows creation of hexagonal grafted nano pillars. In this case, the nano spheres serve as an etching mask in the Reactive Ion Etching (RIE) process. After applying the polystyrene spheres (PS) on a substrate, the size of the spheres is reduced in RIE by oxygen plasma. In the next step, the substrate is dry chemical etched by CHF_3/Ar-Plasma. After the pillars have been etched, PS are removed by O_2-plasma. The quartz pillars are metallized with Au (see Fig. 2 b)).

For fabrication of Nano Ring Cavities with a pillar in the middle of ring (see Fig. 2 c)) as a SERS-active area, the nano sphere lithography is also used. After reducing the diameter of spheres by O_2-plasma, a thin layer of Cr is evaporated on spheres as a mask against CHF_3/Ar plasma. After etching process PS are removed by O_2-plasma. Lastly, the cavities are covered via e-beam evaporator with gold.

In the following method, the polystyrene spheres serves as a nanostructure directly. This technique calls Metal Film over Nanospheres (MFoN) or AgFoN if Ag is used. After applying the spheres on a quartz-substrate (see Fig. 2 d)) or an optical fiber, they can be covered with gold or silver without further treatments [5], for this experiment the PS are covered with Ag.

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 recordered.

The difference of Raman spectra obtained by different structuring methods of a quartz glass substrate is shown in Fig. 3.

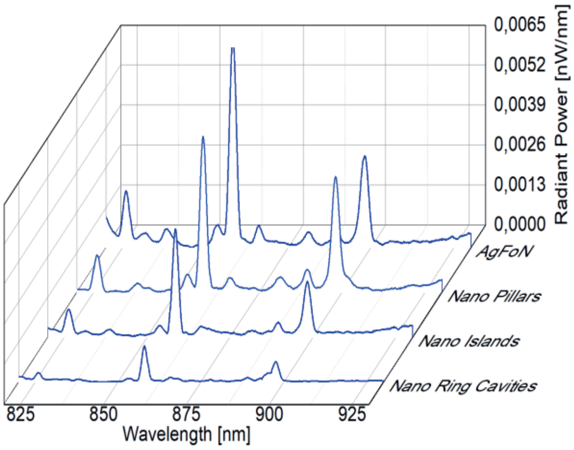

Fig. 3. SERS-spectra of p-thiocresol (10^{-4} mol/L) from quartz glass substrates with different nano structures: Silver Film over Nanospheres (AgFoN); Nano Pillars; Nano Islands; Nano Ring Cavities

Conclusion

With the measuring device and the SERS-active substrates, p-thiocresol with a concentration of 10^{-6} mol/L dissolved in ethanol could be determined. The measurement results show that the organic substances can be measured in the sub-ppm range.

References

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