Surface metalized polymer nanogratings as high-sensitive SERS substrates

Uwe Huebner[1], K. Weber[1,2], D. Cialla[1,2], H. Schneidewind[1], M. Zeisberger[1], H.-G. Meyer[1], J. Popp[1, 2]
[1]*Institute of Photonic Technology, Germany*
[2]*Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller-University Jena, Germany*

uwe.huebner@ipht-jena.de

Abstract

Within this contribution we introduce micro-fabricated and surface-metalized polymer gratings as highly homogenous and highly sensitive substrates for surface enhanced Raman spectroscopy (SERS). The field enhancement is caused by periodical grating structures which couple the light into the metallic surface, the generation of propagating surface plasmon polaritons (SPP) and their enhancement at the edges of the dot-like pattern. Used in Raman setups our plasmonic substrates strongly enhance the sensitivity and show homogenous SERS signal distribution. Employing thin silver films, enhancement factors in the range of 10^5 were achieved. On the way towards the final goal of establishing SERS as a routinely applied analytical tool in bio sensing and material science the proposed fabrication method and the obtained SERS substrates fulfil the need for low-cost and easy-to-handle SERS approaches.

1 Introduction

As Raman spectroscopy provides molecular information without the need to employ labels, it is an attractive tool in chemical and biological applications [1][2]. In order to increase the inherently small Raman signal by several orders of magnitude, surface enhanced Raman spectroscopy (SERS) can be applied [3]. The enhancement of the Raman signal allows the detection of analyte molecules in lowest concentration down to the single molecule level.. Since our goal is the establishment of SERS as a routinely applied analytical tool in bio sensing and material science for the detection of analytes in lowest concentrations, powerful SERS active surfaces are required providing homogenous signal distribution and adequate signal amplification.

Classical SERS active substrates are roughened metallic electrodes, aggregated colloids, and vacuum deposited metal films (silver, gold, copper). Applying silver nanoparticle cluster as SERS substrate very large enhancement factors up to 10^{10} (in hot spots) can be achieved; however the overall SERS signal distribution is generally very inhomogeneous and unsuitable for semi-automatic measurement setups. To achieve reproducible conditions across large measuring areas micro-fabricated SERS-substrates are developed [4]. These SERS substrates are two-dimensional dielectrically gratings fully-covered with a thin metallic film. The field enhancement is caused by periodical grating structures which couple the light into the metallic surface (generation of propagating surface plasmon polaritons – PSPP) and the associated field enhancement at the edges of the dot-like pattern. Compared to former investigations on silver deposited etched quartz SERS substrates [4] we present within this contribution polymer based SERS substrates which supply the same reproducible signal enhancement. These SERS arrays are much easier to fabricate thereby providing high potential for low-cost SERS approaches in the future.

2 Pattern and fabrication

As polymer material a PMMA resist on a fused silica substrate is used. The grating patterns were fabricated by e-beam lithography. For a later mass-production the resist or polymer gratings can be alternatively prepared using imprint techniques. The wafer scale fabrication starts with a 4 inch fused silica substrate, pre-fabricated with an arrangement of 72 numbered single chips with a size of 5 x 10 mm². Each single chip-layout contains 16 SERS-gratings with a size of 200 x 200 µm² for the Raman-measurements. The wafer surface was coated with a 70 nm thick PMMA electron beam resist (ARP671.04). The resist was baked 60 min at 180°C on a hotplate. After the exposure, performed using the shaped beam writer SB350 OS (from Vistec Electron Beam GmbH), the resist was developed 30 s in MIBK:IPA=1:1 and rinsed for 30 s in IPA. The grating dots are very angular and have steep sidewalls angles. After the development the resist mask is completely covered with a 10 nm thick Al_2O_3 film, deposited by atomic layer deposition (ALD). The Al_2O_3 film conserves the resist mask geometry and gives the possibility to trim the gap size inside the grating in a very precise way. On top of this Al_2O_3-enclosed PMMA grating a 20 nm thick metal layer serves as the structured plasmonic film for the enhancement of the light field. 2D-gratings with a period of 436 nm and covered with silver (see SEM images in Fig. **1**) are designed to provide a resonance for an excitation wavelength of 488 nm.

a) b)

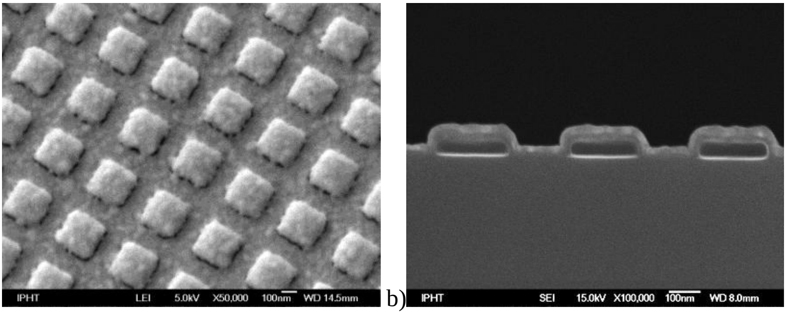

Figure 1: a) SEM micrograph of the covered 2D-PMMA grating (tilt 25°); b) SEM cross-section image of the silver/Al_2O_3 covered PMMA grating (period: 436 nm).

3 Application

SERS spectra were recorded using a micro-Raman spectrometer (alpha 300 RS, WITec, Germany, a scheme of the measurement setup is shown in Figure 2a). As excitation source the 488 nm line of an argon ion laser was employed. The sample is irradiated through a 100x Nikon microscope objective (NA=0.90) having a laser power of ~ 20 µW incident on the surface. The scattered light is detected with a CCD camera. Line scans with 20 points per line were measured using an x/y motorized piezo stage. The integration time was adjusted to 1 s. A representative spectrum of crystal violet is depicted in Figure 2b. To estimate the enhancement factor, the SERS measurements on the unpatterned silver surface are used as reference. The ratio of the intensity detected on the patterned surface and the intensity detected on the unpatterned surface is approximately 10^3, which represents the electromagnetic contribution to the overall signal enhancement. Following this definition, the contribution of the chemical enhancement is neglected. Thus, the given enhancement factor represents an estimation of the minimal signal amplification when using the described SERS substrates. To high quality and reproducibility of the micro-fabricated grating pattern is proved by the fact that high signal homogeneities across the whole measurement area are obtained.

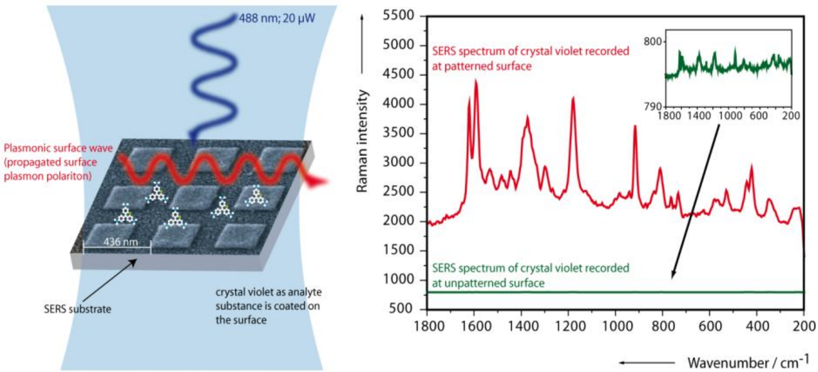

Figure 2: a) Principle of the surface enhanced Raman measuring procedure; b) mean value SERS spectra of a crystal violet monolayer on the grating area and the comparison to the spectra obtained on the unpatterned metallic surface (inset).

4 Summary

We introduce micro-fabricated and surface-metalized 2D-polymer gratings as powerful substrates for SERS. Used in Raman setups the plasmonic substrates show highly sensitive and highly homogenous SERS signals. Employing thin silver films, enhancement factors in the range of at least 10^3 were achieved.

References:

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