Organic Adhesion Layer for an Increased Waveguide-Excited Surface-Enhanced Raman Signal

N. Turk[1,2] , P. C. Wuytens[1,2,3], A. Raza[1,2], A. Skirtach[2,3] and R. Baets[1,2]

[1] Photonics Research Group, INTEC, Ghent University – imec, Belgium
[2] Center for Nano- and Biophotonics, Ghent University, Belgium
[3] Department of Molecular Biotechnology, Ghent University, Belgium

Author e-mail address: nina.turk@ugent.be

By replacing the titanium adhesion layer with 3-mercaptopropyltrimethoxysilane we show a 3-fold increase of the collected signal in on-chip Surface Enhanced Raman Spectroscopy using nanoplasmonic antennas integrated on a nanophotonic waveguide.

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The high field enhancement of nanoplasmonic antennas [1], combined with efficient light excitation and collection of high index contrast nanophotonic waveguides [2, 3] shows great promise for spectroscopy and biosensing. On-chip Surface Enhanced Raman Spectroscopy (SERS) has recently been demonstrated where gold bowtie antennas integrated on silicon nitride (SiN) waveguides were used to both excite and collect SERS spectra of gold-bound monolayers [4]. However, to date the sensitivity of waveguide-based SERS is insufficient for the detection of biomolecules which have small Raman cross-sections. Here, we propose the use of an organic adhesion layer to improve the field enhancement of the plasmonic antennas. This adhesion layer is a thin layer ensuring the attachment of gold antennas to the silicon nitride waveguide. Typically, a few nanometer adhesion layer of titanium (Ti) or chromium is used in the fabrication, however it has been demonstrated that metal adhesion layers dampen the localized surface plasmon resonance of the antennas, consequently lowering the SERS signal [5, 6]. The organic molecule 3-mercaptopropyltrimethoxysilane (MPTMS) has been proposed as a non-damping alternative to metal adhesion layers, and up to 10-fold enhancement of the SERS signal has been reported for top-down excitation [6]. In this paper, we experimentally compare the influence of titanium and MPTMS adhesion layers on the waveguide excited SERS signal of bowtie antennas on a single-mode photonic waveguide.

Gold bowtie antennas on a silicon nitride waveguide (as seen in Figure 1) were fabricated in a two–step electron beam lithography process. First, gold antennas and alignment markers were defined using a liftoff process. Next,
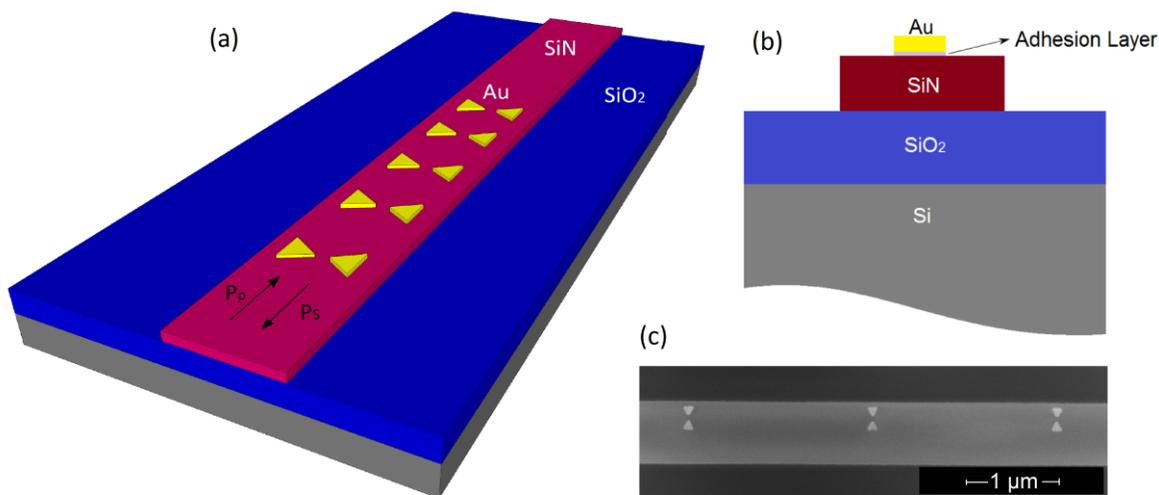
Figure 1 (a) Schematic of gold bowtie antennas on SiN rib waveguide. 10 bowtie antennas were fabricated on each waveguide, with the gap of 50 nm, length of 110 nm and the gold thickness of 30 nm. Antennas were excited with TE-polarized pump light P_p, and Raman signal P_S was collected in back reflection geometry. (b) Cross-section view of an antenna on a waveguide, showing the adhesion layer between the gold antenna and the SiN waveguide. In this work, we compared the influence of titanium adhesion layer, MPTMS adhesion layer and no adhesion layer on SERS signal. (c) SEM image of bowtie antennas on SiN waveguide.

single mode SiN waveguides were etched around these antennas. Samples with a titanium adhesion layer, an MPTMS adhesion layer and no adhesion layer were fabricated. The efficiency of the adhesion layer was defined as the percentage of antennas left on the waveguides at the end of processing (out of 60 antennas in total for each sample). It amounted to 100 % for the titanium adhesion layer, 92 % for the MPTMS adhesion layer and 53 % when no adhesion layer was used. SERS experiments were performed only with the Ti and MPTMS samples.

Samples with Ti and MPTMS adhesion layer were immersed in 4-Nitrothiophenol (NTP). This molecule binds selectively to the bowties through a gold-thiol bond, ensuring that the collected SERS signal originates exclusively from the antennas. Bowtie antennas were then excited through the waveguide and SERS spectra of NTP were collected on a confocal Raman microscope (100x/0.9 objective, 785 nm laser, 0.5 mW laser power) in a back reflection geometry. The input polarization was aligned to the TE-mode of the waveguide, and the spectra were obtained as an average of 10 measurements with integration time of 5 s each. The integrated number of counts at the 1339 cm^{-1} NTP peak was calculated in order to quantify the strength of the SERS signal (Figure 2b). The SERS signal from the MPTMS sample was on average (2.9 ± 0.6)-fold stronger than the signal of the titanium sample. We however noticed the high variability in the SERS signal for the MPTMS sample, which together with less than 100% efficiency of adhesion suggests that the SERS signal from the MPTMS sample is not as reproducible as that from the titanium sample. We currently attribute the high variability of the signal to the small variations in electron beam lithography processing that affect the antenna geometry and therefore its signal enhancement. We aim to optimize the process parameters to improve the reproducibility of SERS signal obtained with the MPTMS adhesion layer.
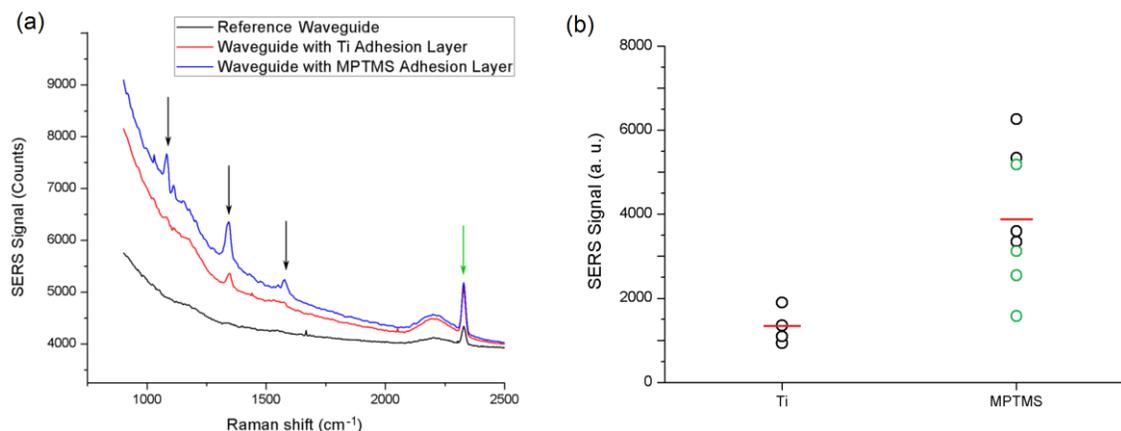
Figure 2 (a) Raman spectra of NTP measured on a SiN waveguides functionalized with 10 gold bowtie antennas for both titanium and MPTMS adhesion layer, compared to the spectrum of a reference waveguide. Black lines indicate peaks characteristic of NTP, whereas the green line marks the position of SiN peak that is used as a reference peak to achieve maximum coupling of the light to the waveguide. (b) Comparison of SERS signal for titanium and MPTMS adhesion layers. Circles indicate individual measurements, and the red line represents the average signal. For the MPTMS, measurements from two different samples are indicated in green and black. The SERS signal increases (2.9 ± 0.6)-fold when titanium adhesion layer is replaced with MPTMS.

In this paper, we have experimentally demonstrated an average 3-fold increase in waveguide-excited SERS signal of bowtie antennas integrated on a single-mode SiN waveguide by replacing the titanium adhesion layer with 3-mercaptopropyltrimethoxysilane. Increasing the sensitivity by using an alternative adhesion layer therefore takes us a step further towards on-chip SERS for the detection of biomolecules.

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