On-chip surface enhanced Raman spectroscopy using ALD grown plasmonic nanotrenches integrated with a silicon nitride slot waveguide

('Student Paper')

Ali Raza [*,1,2], Stéphane Clemmen [1,2,3], Michiel Van Daele [4], Jolien Dendooven [4], Matthew B. E. Griffiths [5], Seán T. Barry [5], Andre Skirtach[2,6], Christophe Detavernier [4], Roel Baets [1,2]

[1]*Ghent University - imec, Technologiepark 126, 9052 Ghent, Belgium*
[2]*Center for Nano- and Biophotonics, Ghent University, Belgium*
[3]*Laboratoire d'information quantique, Université Libre de Bruxelles, 1050 Bruxelles, Belgium*
[4]*Department of Solid State Sciences, COCOON Research Group, Krijgslaan 281, 9000 Ghent, Belgium*
[5]*Department of Chemistry, Carleton University, 1125 Ottawa, Canada*
[6]*Department of Biotechnology, Ghent University, 9000 Ghent, Belgium*
***e-mail: ali.raza@ugent.be**

ABSTRACT

We present an enhanced Raman spectroscopy using sub 10 nm plasmonic nanotrenches directly grown on a silicon nitride slot waveguide using atomic layer deposition (ALD). A novel ALD process for gold deposition at 100° C is used, the precursor and reactant used for this process are Me_3AuPMe_3 and H_2 plasma, respectively. The fabricated Raman sensor exhibits $\sim 1.5 \times 10^{-8}$ pump to Stokes conversion efficiency for a monolayer of 4-Nitrophenol. This is at least an order of magnitude higher than the state of art nanoplasmonic waveguide based Raman sensors.

Keywords: Nanoplasmonics, Integrated Optics, Surface enhanced Raman spectroscopy, Waveguide enhanced Raman spectroscopy, Monolayer sensing, Atomic layer deposition.

1 INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is a sensing technique that uses a nanoplasmonic structure to enhance the light in a nanometer-sized gap hence producing high electric field hot spots [2]. The analyte molecules present in these hot spots are then excited and the scattered Raman signal is collected either by a high NA microscope objective or a higher index contrast waveguide. The former technique is called free space SERS and the latter is known as waveguide based SERS [5]. Various nanoplasmonics structures i.e. nanobowties [5], [6] and nanotriangles [10] etc. have been integrated on a photonic platform to demonstrate waveguide based SERS. The fabrication of these plasmonics structures demands high resolution and alignment dependent patterning techniques. Recently, enhanced Raman spectroscopy using a hybrid nanoplasmonic waveguide [1], [7] has been demonstrated whereby mass scalable UV-photolithography is used. Despite all these design and technological advancements, the detection of an ultra-small concentration of weak Raman scatterers, demands further sensitivity improvement. One of the key applications in this regard is the single molecule spectroscopy [12] on a photonic chip.

In this work, we present an on-chip Raman sensor that uses plasmonic nanotrenches directly defined on a single mode silicon nitride Si_3N_4 slot waveguide using atomic layer deposition. Highly conformal ALD of Al_2O_3 and Au allows defining the nanotrenches in a more controlled and uniform fashion all along the waveguide width and length. Furthermore, the gold layer is deposited by a novel gold ALD process. The SERS performance of the resulting sensor is characterized using a monolayer of 4-Nitrophenol.

2 METHODS

2.1 Fabrication

The sensor is fabricated in three steps. In the first step, Si_3N_4 slot waveguides are fabricated using 193 nm optical lithography and subsequently etched by fluorine based inductive coupled plasma-reactive ion-etch process [8] to get the final structure as depicted in Fig. 1. Then a 40 nm layer of Al_2O_3 is deposited using ALD. Finally, a 100 μm window is defined using DUV lithography followed by an ALD deposition of a 24 nm thick gold layer composed of 7.9 nm wide nanotrenches. A home built ALD reactor with a base pressure of 2×10^{-6} mbar is used to deposit the Al_2O_3 and Au layers [3]. Both layers are deposited at a substrate temperature of 100°C. The Al_2O_3 layer is deposited using TMA and H_2O as the precursor and reactant, respectively. The used pressure for both gases is $6\text{x}10^{-3}$ mbar. Au is deposited with a new ALD process, using Me_3AuPMe_3 and H_2 plasma (20% H_2 in Ar) as the precursor and reactant. A pressure of 1 mbar is used for the Au reactant and

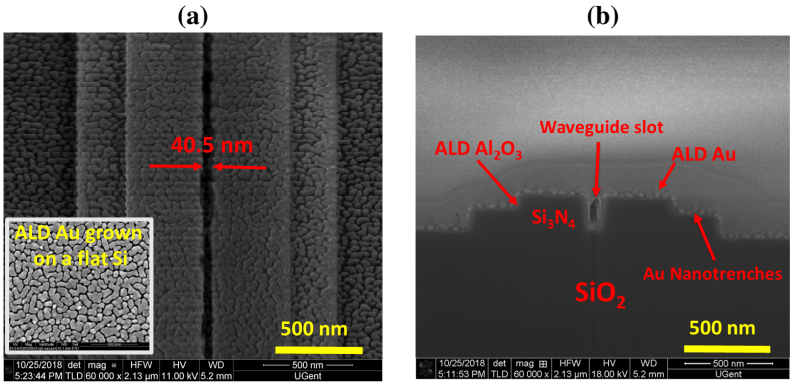

Figure 1. The SEM images of the fabricated on-chip SERS device. a) Top view. Inset shows the Au island directly grown on a flat Si substrate. b) The SEM cross section of the waveguide showing the stack of the material layers.

6x10^{-3} mbar for the hydrogen gas. In order to characterize the free space SERS strength of the ALD gold islands, a nanostructured gold layer is also grown on a flat silicon substrate as shown in Fig. 1.a (inset).

After the patterning, the chip was thoroughly cleaned with Acetone/IPA/DI water and dried with N_2 gun. For the monolayer coating, the chip was immersed in 1mM solution of 4-Nitrophenol (pNTP) in Ethanol. pNTP selectively binds to the gold using a thiol−gold bond.

2.2 Experiment

A confocal Raman microscope (WITEC Alpha 300R+) equipped with 100x/0.9 objective is used to characterize the Raman sensor. We acquire Raman spectra in a back-reflection geometry. A 785 nm laser and -70°C cooled Andor IDUS 401 CCD camera is used. All spectra are recorded using 1 mW pump power and a 1 sec integration time. For on-chip Raman measurements, the light is edge coupled to the waveguide and the polarization is aligned to the TE-mode of the waveguide. Also, same experimental conditions are used for free space SERS substrates. Further details about the experiment are reported in [7].

3 RESULTS AND DISCUSSION

In the first set of experiments, free space SERS performance of ALD gold layers is characterized. In order to optimize the gold thickness, four different thicknesses of ALD gold are deposited on a flat Si substrate using 100, 200, 400 and 800 ALD cycles. The measured Raman spectra are shown in Fig. 2.a (inset). Each spectrum is recorded by optimizing the CCD counts for the 1339 cm^{-1} ($\nu_s(NO_2)$) [4] Raman mode of pNTP . Very weak pNTP peaks were measured with the gold substrate where 100 ALD cycles are used. On the other hand, the stronger pNTP Raman modes appear in a Raman spectrum measured from substrate with 800 ALD gold cycles. This is attributed to the formation of nanotrenches $\simeq$ 7.9 nm size that lead to a huge field enhancement. Based on the 1339 cm^{-1} Raman mode, the pump to Stokes conversion efficiency (P_s/P_p) is measured using the method reported in [6]. The measured values of P_s/P_p are shown in Fig. 2.a. A highest value of P_s/P_p = $(8.7 \pm 0.4) \times 10^{-9}$ is recorded for the 800 ALD cycles SERS substrate. This is almost one order of magnitude weaker than state of art free space SERS substrates such as a nanodome substrate [11] with $P_s/P_p \sim 7 \times 10^{-8}$. However, it is worth mentioning that in the present case, a nanoplasmonic gap of 7.9 nm is achieved without any patterning technique and with further optimization of ALD gold process, P_s/P_p can be greatly enhanced.

After the free space SERS characterization, the Raman spectrum is measured using an on-chip SERS sensor. The spectrum is shown in Fig. 2. b. In order to reduce the silicon nitride background [9], the length of the access waveguide is limited to 1 μm. The measured spectrum contains all the pNTP Raman modes. The measured P_s/P_p measured for the 1339 cm^{-1}mode is $\sim 1.5 \times 10^{-8}$. Note that a coupling loss of 4.2 dB/facet has been taken into account for the on-chip P_s/P_p value. This is $\sim$ 2 times stronger than its free space counterpart. This is attributed to the long interaction length (few microns), leading to an efficient excitation and collection of Raman signal. Also, this is an order of magnitude stronger than the previously reported nanoplasmonic waveguide based on-chip Raman sensor where P_s/P_p = $(1.0 \pm 0.057) \times 10^{-9}$ [7]. This substantial improvement is ascribed to the formation of 7.9 nm wide nanotrenches inside Si_3N_4 slot waveguide. This leads to an efficient modal overlap between a photonic and a plasmonic mode hence producing a huge Raman enhancement $|E|^4$.

CONCLUSION

We have reported a SERS sensor for an on-chip Raman spectroscopy using a novel ALD process of gold. Me_3AuPMe_3 and H_2 plasma are used as the precursor and reactant, respectively. The formation of 7.9 nm wide nanotrenches along the width and length of the Si_3N_4 slot waveguide leads to a large pump to Stokes

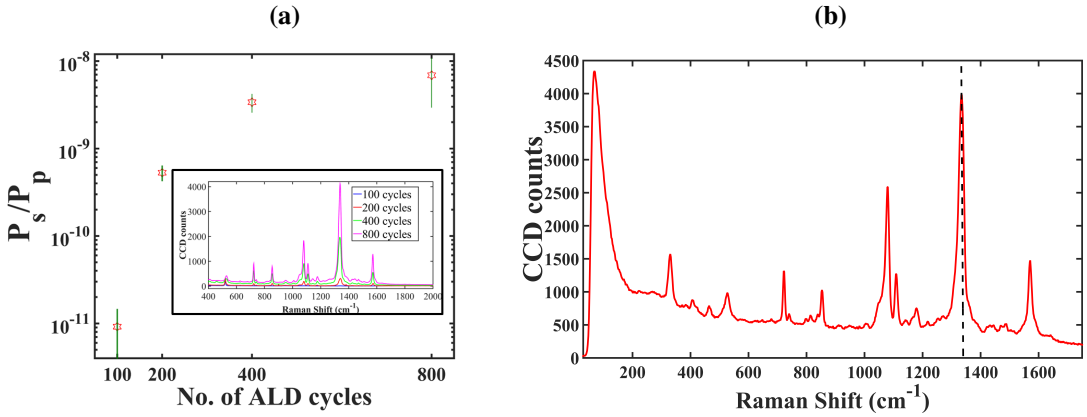

Figure 2. a) The pump to Stokes (P_s/P_p) conversion efficiency of ALD grown Gold on a flat Si substrate. The inset shows the Raman spectra of NTP measured from SERS substrates grown with four different number ALD cycles. b) The NTP Raman spectrum measured from an on-chip Raman sensor. The dotted line at 1339 cm^{-1} represents the strongest mode of pNTP ($\nu_s(NO_2)$).

conversion efficiency of 1.5 $\times$ 10^{-8}. This is the highest on-chip pump to Stokes conversion efficiency known to the date.

ACKNOWLEDGMENT

The authors acknowledge Liesbet Van Landschoot (UGent) for taking the SEM images. This research was funded by the FWO Belgium. Stéphane Clemmen thanks the F.R.S-FNRS for financial support. We also acknowledge the support of BOF (UGent, Belgium).

REFERENCES

[1] Q. Cao, J. Feng, H. Lu, H. Zhang, F. Zhang, and H. Zeng. Surface-enhanced Raman scattering using nanoporous gold on suspended silicon nitride waveguides. *Opt. Express*, 26(19):24614–24620, Sep 2018.

[2] E. Le Ru and P. Etchegoin. *Principles of Surface-Enhanced Raman Spectroscopy: and related plasmonic effects*. Elsevier, 2008.

[3] E. Levrau, K. Van de Kerckhove, K. Devloo-Casier, S. Pulinthanathu Sree, J. A. Martens, C. Detavernier, and J. Dendooven. In situ ir spectroscopic investigation of alumina ald on porous silica films: Thermal versus plasma-enhanced ald. *The Journal of Physical Chemistry C*, 118(51):29854–29859, 2014.

[4] M. A. Mahmoud. Surface-enhanced Raman spectroscopy of double-shell hollow nanoparticles: Electromagnetic and chemical enhancements. *Langmuir*, 29(21):6253–6261, 2013. PMID: 23647422.

[5] F. Peyskens, A. Dhakal, P. Van Dorpe, N. Le Thomas, and R. Baets. Surface enhanced Raman spectroscopy using a single mode nanophotonic-plasmonic platform. *ACS Photonics*, 3(1):102–108, 2016.

[6] F. Peyskens, P. Wuytens, A. Raza, P. Van Dorpe, and R. Baets. Waveguide excitation and collection of surface-enhanced Raman scattering from a single plasmonic antenna. *Nanophotonics*, 2018.

[7] A. Raza, S. Clemmen, P. Wuytens, M. Muneeb, M. Van Daele, J. Dendooven, C. Detavernier, A. Skirtach, and R. Baets. ALD assisted nanoplasmonic slot waveguide for on-chip enhanced Raman spectroscopy. *APL Photonics*, 3(11):116105, 2018.

[8] A. Z. Subramanian, P. Neutens, A. Dhakal, R. Jansen, T. Claes, X. Rottenberg, F. Peyskens, S. Selvaraja, P. Helin, B. D. Bois, K. Leyssens, S. Severi, P. Deshpande, R. Baets, and P. V. Dorpe. Low-loss singlemode pecvd silicon nitride photonic wire waveguides for 532 x2013;900 nm wavelength window fabricated within a cmos pilot line. *IEEE Photonics Journal*, 5(6):2202809–2202809, Dec 2013.

[9] N. L. Thomas, A. Dhakal, A. Raza, F. Peyskens, and R. Baets. Impact of fundamental thermodynamic fluctuations on light propagating in photonic waveguides made of amorphous materials. *Optica*, 5(4):328–336, Apr 2018.

[10] P. C. Wuytens, A. G. Skirtach, and R. Baets. On-chip surface-enhanced Raman spectroscopy using nanosphere-lithography patterned antennas on silicon nitride waveguides. *Opt. Express*, 25(11):12926–12934, May 2017.

[11] P. C. Wuytens, A. Z. Subramanian, W. H. De Vos, A. G. Skirtach, and R. Baets. Gold nanodome-patterned microchips for intracellular surface-enhanced Raman spectroscopy. *Analyst*, 140(24):8080–8087, 2015.

[12] R. Zhang, Y. Zhang, Z. Dong, S. Jiang, C. Zhang, L. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. e. Luo, et al. Chemical mapping of a single molecule by plasmon-enhanced Raman scattering. *Nature*, 498(7452):82, 2013.