



## Article

# Hybrid Metal-dielectric-metal sandwiches for SERS applications

Mikhail K. Tatmyshevskiy<sup>1,\*</sup>, Dmitry I. Yakubovsky<sup>1</sup>, Olesya O. Kapitanova<sup>1,2</sup>, Valentin R. Solovey<sup>1</sup>, Andrey A. Vyshnevyy<sup>1</sup>, Georgy A. Ermolaev<sup>1</sup>, Yuri A. Klishin<sup>1</sup>, Mikhail S. Mironov<sup>1</sup>, Artem A. Voronov<sup>1</sup>, Aleksey V. Arsenin<sup>1</sup>, Valentyn S. Volkov<sup>1</sup> and Sergey M. Novikov<sup>1,\*</sup>

<sup>1</sup> Center for Photonics and 2D Materials, Moscow Institute of Physics and Technology (MIPT), 9 Institutsky Lane, Dolgoprudny 141700, Russia; dmitrii.yakubovskii@phystech.edu (D.I.Y.); olesya.kapitanova@gmail.com (O.O.K.); valentinsr@mail.ru (V.R.S.); andrey.vyshnevyy@phystech.edu (A.A.V.); ermolaev-georgy@yandex.ru (G.A.E.); klishin.yuri@mail.ru (Y.A.K.); mironov.ms@phystech.edu (M.S.M.); voronov.artem@gmail.com (A.A.V.); arsenin.av@mipt.ru (A.V.A.); vsv.mipt@gmail.com (V.S.V.)

<sup>2</sup> Department of Chemistry, Lomonosov Moscow State University, 1-3 Leninskiye gory, Moscow 119991, Russia

\* Correspondence: mikhail.tatmyshevskiy@phystech.edu (M.K.T.); novikov.s@mipt.ru (S.M.N.); Tel.: +79056137678 (M.K.T.); +79032360487 (S.M.N.)

**Citation:** Tatmyshevskiy, M.K.; Yakubovsky, D.I.; Kapitanova, O.O.; Solovey, V.R.; Vyshnevyy, A.A.; Ermolaev, G.A.; Klishin, Y.A.; Mironov, M.S.; Voronov, A.A.; Arsenin, A.V.; et al. Hybrid Metal-Dielectric-Metal Sandwiches for SERS Applications. *Nanomaterials* **2021**, *11*, 3205. <https://doi.org/10.3390/nano11123205>

Academic Editor: Maurizio Muniz-Miranda

Received: date

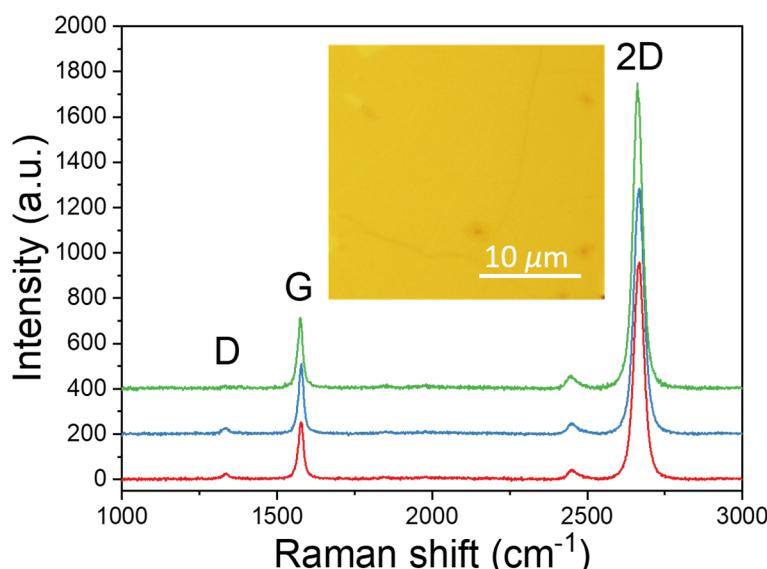
Accepted: date

Published: date

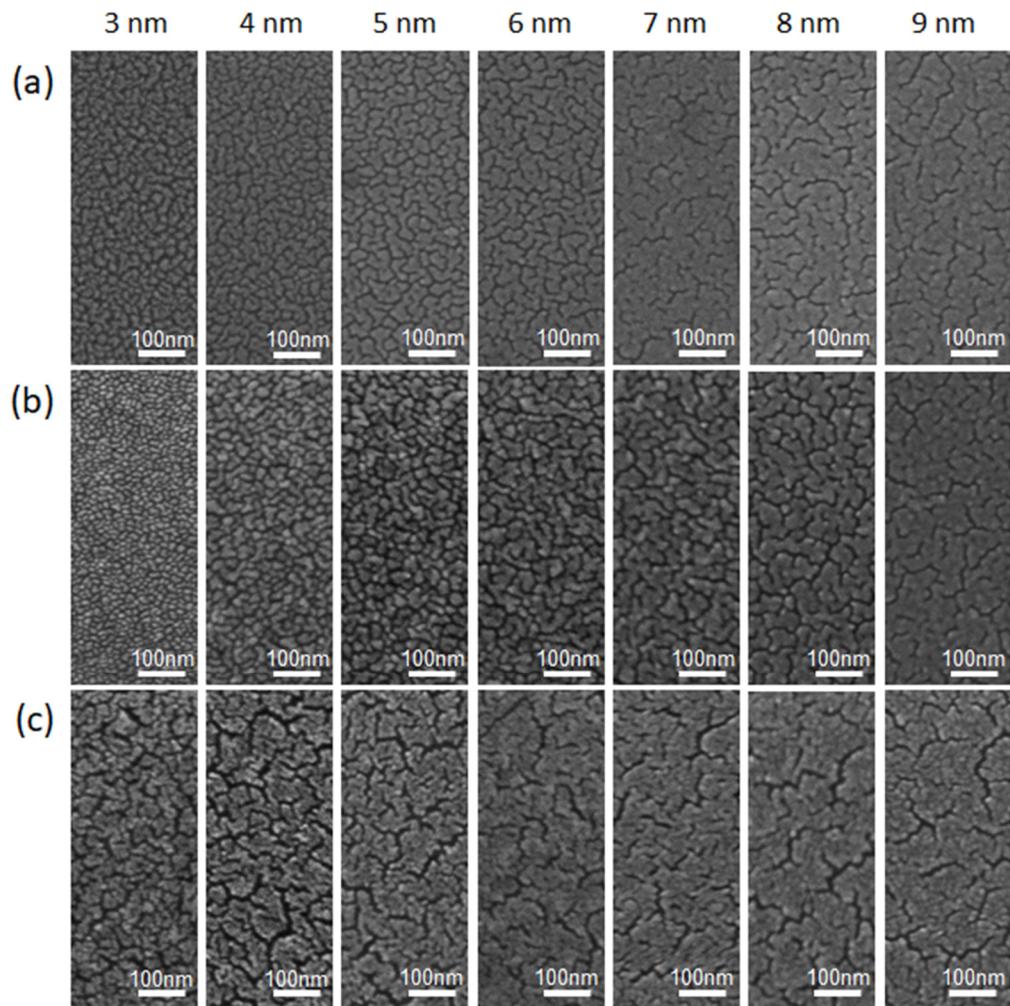
**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).



**Figure S1.** The typical Raman spectra of monolayer CVD graphene on top of an Au/SiO<sub>2</sub> substrate after transfer. The low intensity of D peak demonstrates the high quality of CVD graphene. Insert: the optical image of the substrate with graphene after transferring.



**Figure S2.** SEM images of gold films with thicknesses from 3 to 9 nm deposited on (a) glass/Au, (b) Au/SiO<sub>2</sub>/Au and (c) Au/SiO<sub>2</sub>/graphene/Au substrates.

**Table S1.** AFM measurements of the gold film thickness of glass/Au structures.

h(sensor), nm	glass/Au	
	h, nm	MSE, nm
3	4.3	0.3
4	6.1	0.3
5	6.2	0.3
6	8.7	0.3
7	8.3	0.2
8	9.1	0.3
9	9.7	0.3

**Table S2.** Average parameters of ultrathin gold films on glass/Au structures.

h(sensor), nm	occupancy, %	average particle size, nm
3	51.1	11.3
4	53.1	15.4
5	58.0	20.0
6	66.3	36.3
7	71.5	—
8	75.4	—

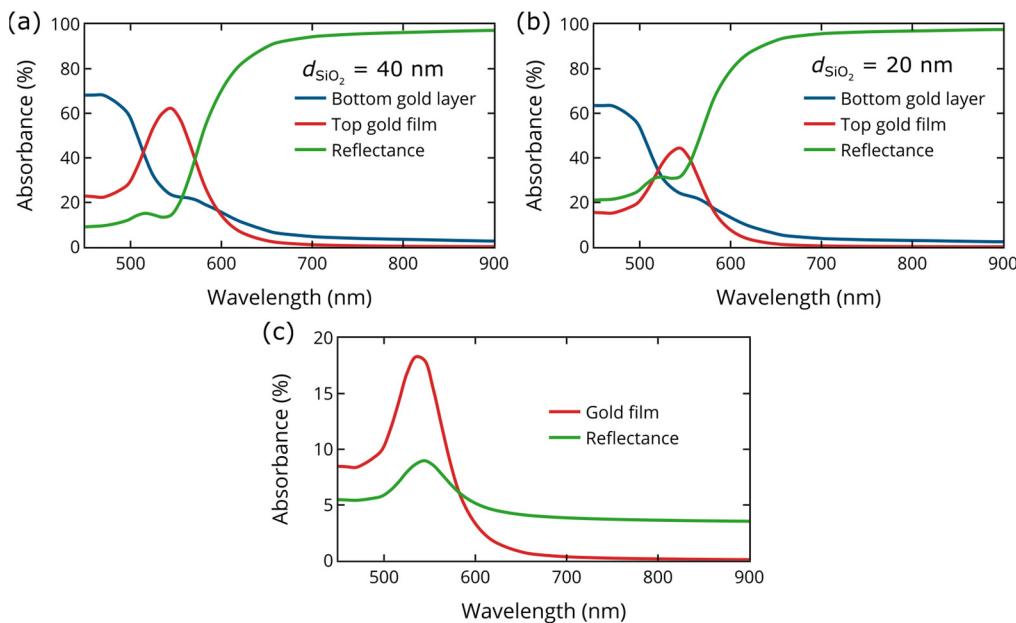
9	81.2	—
---	------	---

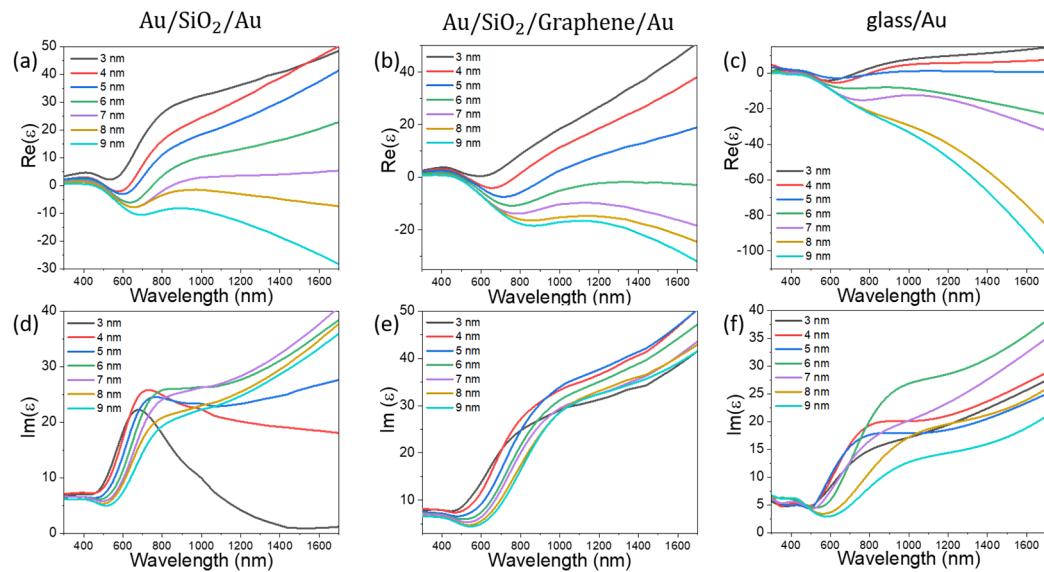
**Table S3.** Average parameters of ultrathin gold films on Au/SiO<sub>2</sub>/Au structures.

<b>h(sensor), nm</b>	<b>occupancy, %</b>	<b>average particle size, nm</b>
3	49.3	9.3
4	53.8	17.2
5	56.4	19.6
6	63.7	34.8
7	67.7	—
8	71.3	—
9	79.9	—

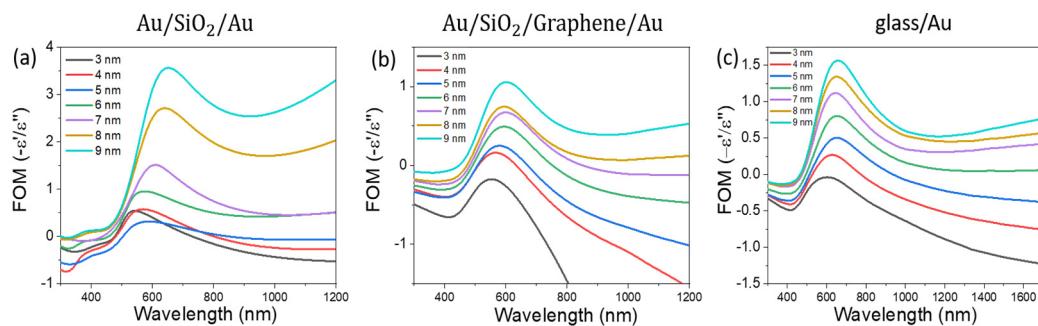
**Table S4.** Average parameters of ultrathin gold films on Au/SiO<sub>2</sub>/graphene/Au structures.

<b>h(sensor), nm</b>	<b>occupancy, %</b>	<b>average particle size, nm</b>
3	57.9	28.3
4	64.3	69.2
5	69.0	89.2
6	74.1	—
7	83.1	—
8	85.2	—
9	87.9	—

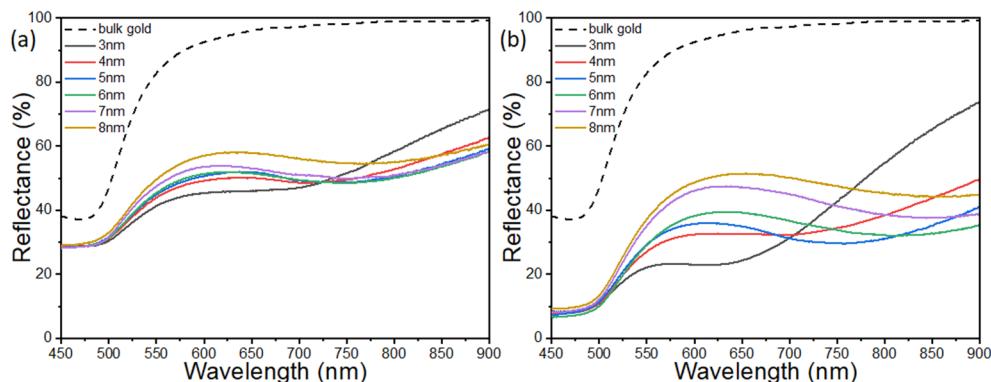
**Figure S3.** Calculated spectra of reflectance, absorbance in different gold layers in the Au/SiO<sub>2</sub>/Au structure with h(sensor) = 3 nm and SiO<sub>2</sub> layer with a thickness of (a) 40 nm and (b) 20 nm. The optical properties of the sub-percolation gold layer were homogenized using the Maxwell-Garnett approximation. (c) Calculated absorbance and reflectance of the nano-Au film on a semi-infinite SiO<sub>2</sub> substrate.



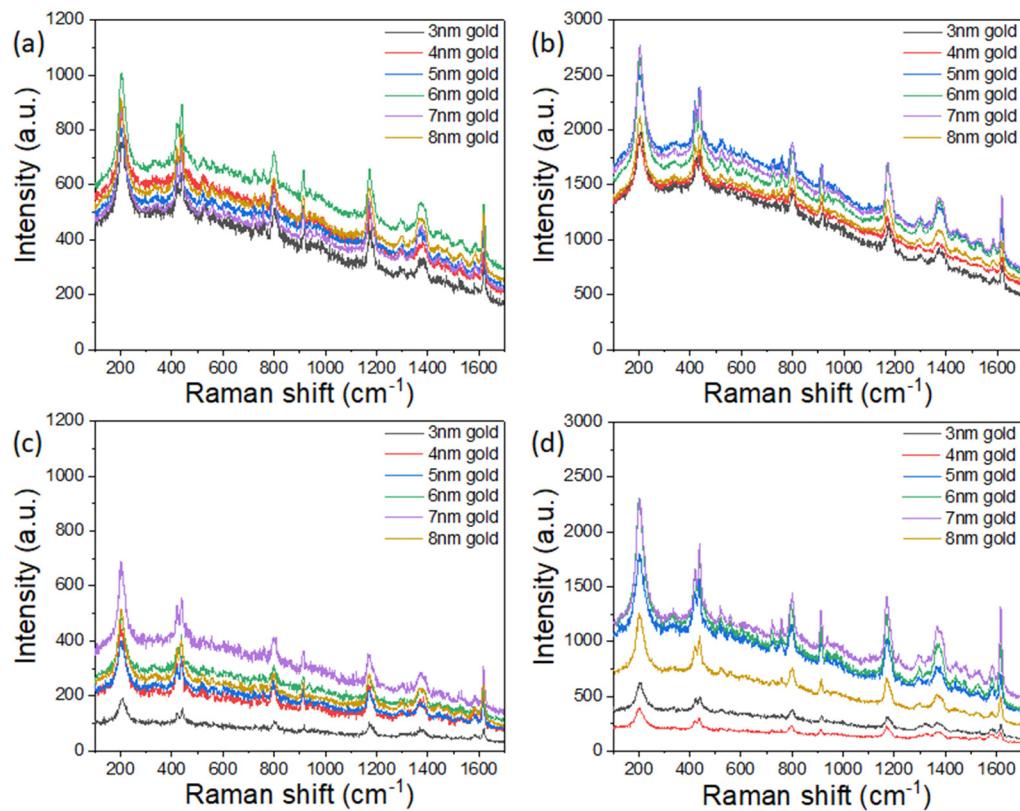
**Figure S4.** Dependence of the real and imaginary parts of dielectric function of the thin gold films in (a,d)  $\text{Au}/\text{SiO}_2/\text{Au}$ , (b,e)  $\text{Au}/\text{SiO}_2/\text{graphene}/\text{Au}$  and (c,f)  $\text{glass}/\text{Au}$  structures.



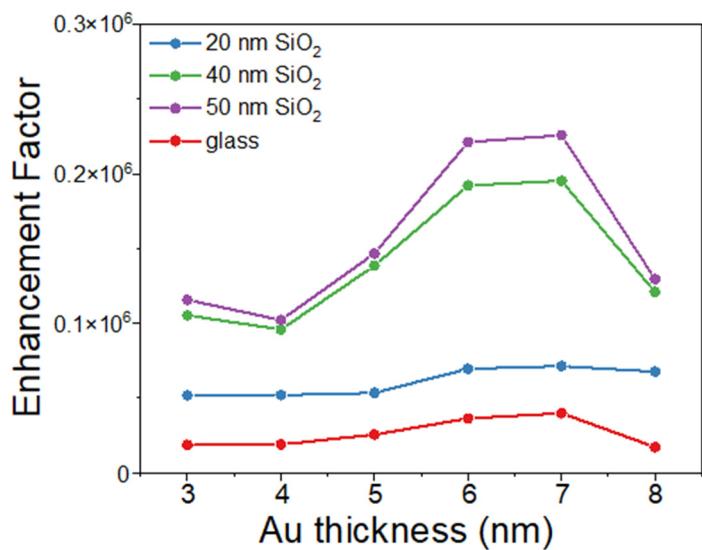
**Figure S5.** Ellipsometric figures of merit (FOM) of the thin gold films in (a)  $\text{Au}/\text{SiO}_2/\text{Au}$ , (b)  $\text{Au}/\text{SiO}_2/\text{graphene}/\text{Au}$  and (c)  $\text{glass}/\text{Au}$  structures.



**Figure S6.** Reflection spectra of the fabricated structures with different thicknesses of gold films for  $\text{Au}/\text{SiO}_2/\text{Au}$  substrates with (a) 20 nm and (b) 40 nm thick  $\text{SiO}_2$  layer. All of the achieved spectra were normalized to the reflection spectrum of a silver mirror.



**Figure S7.** SERS spectra of the Crystal Violet dye with a concentration of  $10^{-6}$  M, acquired with a laser excitation wavelength of 633 nm for (a,b) Au/SiO<sub>2</sub>/Au and (c,d) Au/SiO<sub>2</sub>/graphene/Au structures with 20 nm and 40 nm SiO<sub>2</sub> thickness.



**Figure S8.** Dependence of SERS enhancement factors (EF) on the thickness of the gold film for Au/SiO<sub>2</sub>/Au substrates with different SiO<sub>2</sub> layer thickness (20 nm, 40 nm and 50 nm), calculated by the intensity of 207 cm<sup>-1</sup> Raman mode.