

Non-Lithographic Au Film over Nanosphere SERS Substrate

Agnes Purwidyantri¹ and Chao-Sung Lai^{2,3,4}

¹ Biomedical Engineering, Chang Gung University, Taoyuan, Taiwan

² Department of Electronic Engineering, Chang Gung University, Taoyuan, Taiwan

³ Department of Nephrology, Chang Gung Memorial Hospital, Taiwan

⁴ Department of Materials Engineering, Ming Chi University of Technology, Taiwan

Abstract

In this research, SERS substrates were prepared by producing Au-nanoarray grown on polystyrene (PS) nanospheres-coated ITO. Al₂O₃ and Cr adhesion layers were applied to support the growth of 10 nm Au generated by thermal evaporation. Findings showed that Al₂O₃ as adhesion layer yielded higher particles density than the typical Cr layer especially in the application of SERS detection.

1. Introduction

One noticing technique in SERS substrate preparation is the application of metal film over nanosphere (MFON) [1]–[3] and metallic nanoparticles (MNPs) in suspension. Au film over nanosphere (AuFON) and Ag film over nanosphere (AgFON) are the two commonly used MFON SERS substrates easily produced by NSL techniques that use spin-coated microspheres layers as templates for silver or gold deposition. Thermal evaporation of gold film can also be one effective route to obtain a uniform thin film on to the PS contour.

The introduction of Al₂O₃ as new adhesion inter-layer has been proven to be a good solution when high temperatures and in biological environment involved in the process. Al₂O₃ is a ceramic electrical insulator and has a relatively high thermal conductivity appropriate for heating systems [4]. In this study, AuFON deposited by Al₂O₃ adhesion layer is employed as the backbone of the research which could be regarded as a potential route for a simple non-lithographic nanopatterning technique in SERS substrate preparation.

2. Materials and Methods

A 100 nm PS nanospheres was drop-coated onto the surface of the ITO. Two nm of Al₂O₃ and/or Cr adhesion layer was deposited to support thermally evaporated 10 nm thick of Au (Fig. 1). Field electron scanning electron microscope (FE-SEM) was used to capture the surface. SERS system using 473 nm laser was used for the detection of 1 μ M Rhodamine (R₆G) molecules. A 2D-FDTD (finite domain time difference) was employed for hot spots localization simulation.

3. Results and Discussion

Fig.2 shows that self-assembly drop-coating methods of 100 nm PS nanospheres yielded a highly periodic monolayer coating. After Au deposition, thick nanofilm was visible and the globular nanostructure had a tendency to disappear. However, further increase of Au thickness led to the increase of layer's homogeneity and the globular structure was being less pronounced as well as the surface roughness [5], [6]. The information regarding the particle size and nanogap formation

on the PS nanobeads in this work is summarized in Table 1.

To further investigate the SERS effect of the PS on the surface, in Fig. 3, the whole AuFON substrate regardless of the adhesive layer, achieved the more optimum peak for R₆G molecule detection at 1 μ M concentration than directly on bare ITO. Carried out in the calculation of SERS enhancement factor (EF_{SERS}), the optimum value was achieved when Au nanofilm was combined with Al₂O₃ adhesion layer. Moreover, PS nanobeads modification resulted in a more prominent enhancement factor than the Au nanofilm on flat ITO. Such structure on the PS spherical crystal dramatically gained about 3 times higher order EF_{SERS} than those on flat ITO. In 2D FDTD simulation, it is found that the distribution of the near field intensity was greatly augmented in the boundary between the adjacent Au spheres. In addition, stronger electromagnetic (EM) fields can be clearly seen between the crevices formed by the two adjacent Au spheres which can be regarded as where SERS hotspots are located.

3. Conclusions

AuFON has been proven to constitute a confirmed nanopatterning techniques where surface plasmon polaritons is likely to be more intense in nanofilm clusters. We also point out that the SERS hotspot generation is typically located in the interim of the adjacent spherical Au based on the simulation. Results point out that Al₂O₃ holds the potency as a new adhesion layer material for gas and biological sensors and in biomedical applications. Finally, a novel non-lithographic nanostructuring technique using AuFON is realized for the SERS substrate fabrication.

Acknowledgements

We would like to express sincere thanks to Chang Gung Memorial Hospital, Taiwan for the financial support under contract no. CMRPD2D0072, CMRPD2F0021 and CMRPD3D0112 and Taiwan Ministry of Science and Technology under contract number MOST 104-2632-E-182-001 and MOST 104-2221-E-182-041.

References

- [1] L. A. Dick, A. D. McFarland, C. L. Haynes, and R. P. Van Duyne, *J. Phys. Chem. B*, vol. 106, no. 4, pp. 853–860, 2002.
- [2] C. Farcau and S. Astilean, *J. Phys. Chem. C*, vol. 114, no. 27, pp. 11717–11722, 2010.
- [3] J. McPhillips, C. McClatchey, T. Kelly, A. Murphy, M. P. Jonsson, G. A. Wurtz, R. J. Winfield, and R. J. Pollard, *J. Phys. Chem. C*, vol. 115, no. 31, pp. 15234–15239, 2011.

[4] V. Guarnieri, L. Biazzi, R. Marchiori, and A. Lago, *Biomatter*, vol. 4, no. 1, p. e28822, 2014.

[5] S. Szunerits, V. G. Praig, M. Manesse, and R. Boukherroub, *Nanotechnology*, vol. 19, no. 19, p. 195712, 2008.

[6] A. Schaub, P. Šlepička, I. Kašpárková, P. Malinský, A. Macková, and V. Svorčík, *Nanoscale Res. Lett.*, vol. 8, no. 1, p. 249, 2013.

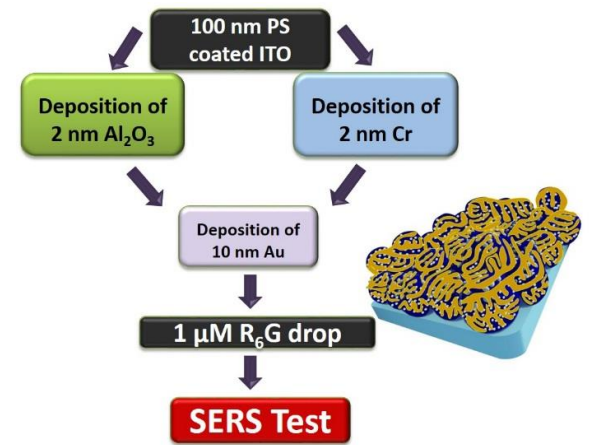


Fig.1 Schematic workflow of the proposed SERS substrate fabrication

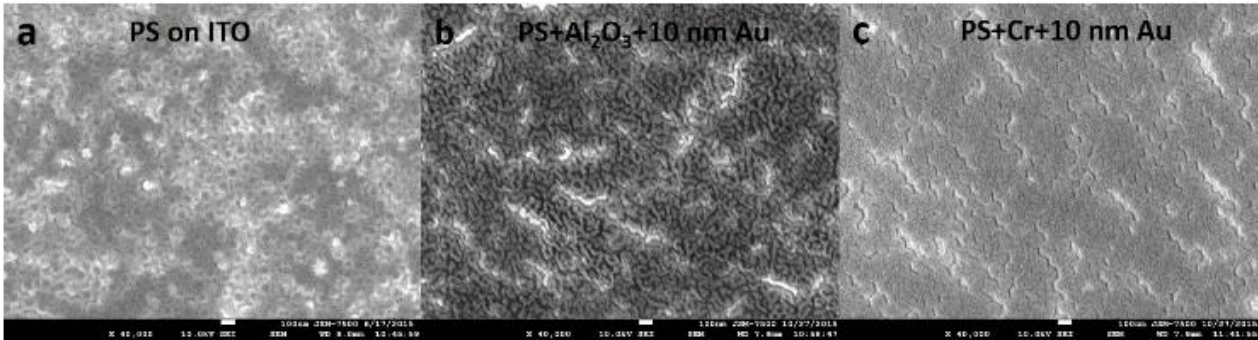


Fig 2. FESEM picture of (a) monolayer PS on ITO, Au nanofilm on PS nanobeads with (b) Al₂O₃ and (c) Cr adhesion layer

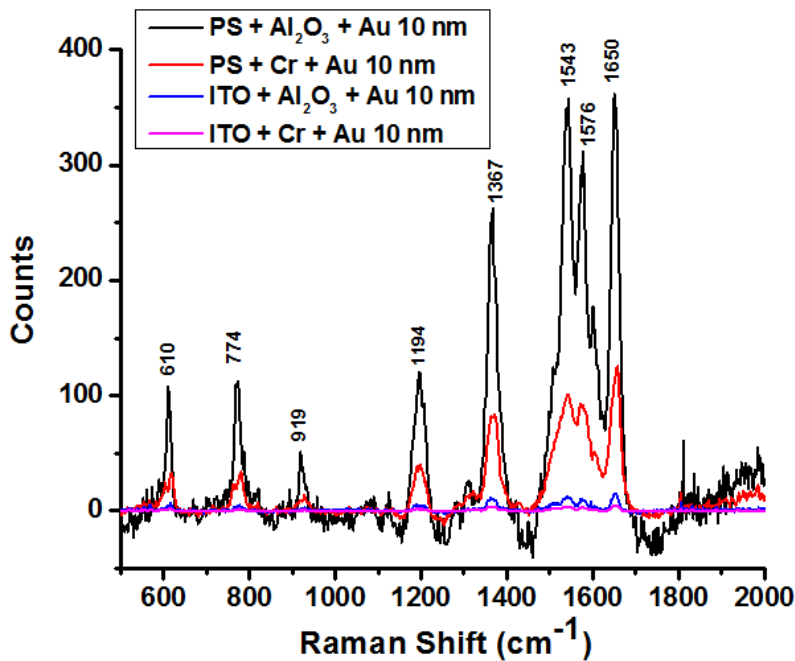


Table I. AuFON particles arrangement on PS nanobeads covered substrate

| | PS+ Al ₂ O ₃ + Au 10 nm | PS+ Cr+ Au 10 nm |
|--------------------|---|---------------------------|
| Particle Size (nm) | 33-38 | 40-45 |
| Nanogap (nm) | 25-27 | 20-25 |

Fig 3. SERS activity measured using R6G as reporter molecule on Au nano-film on PS nanobeads patterned and/or flat ITO substrate