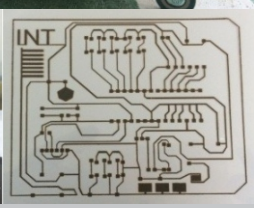
The 7th International Workshop on Nanotechnology and Application

IWNA 2019

6th - 9th November 2019, Phan Thiet, Vietnam

Proceedings



Organized by Vietnam National University Ho Chi Minh City
Institute for Nanotechnology
CEA - LETI - MINATEC, France

The 7th International Workshop on Nanotechnology and Application

IWNA 2019

Proceedings

6th - 9th November 2019, Phan Thiet, Vietnam

Organized by Vietnam National University Ho Chi Minh City
Institute for Nanotechnology
CEA - LETI - MINATEC, France

NANOMATERIALS AND NANODEVICES (NMD)

NFT-025-P

FACILE FABRICATION OF GOLD NANOPARTICLES BY SPUTTERING METHODS

Thi Ha Tran[1,2], Thi Huyen Trang Nguyen[1], Thanh Cong Bach[2], Nguyen Hai Pham[2], Cong Doanh Sai[2], Quang Hoa Nguyen[2], Trong Tam Nguyen[3], Khac Hieu Ho[4], Viet Tuyen Nguyen[2*]

[1]Department of Physics, Faculty of Basic Science, Hanoi University of Mining and Geology, Duc Thang, Tu Liem, Hanoi;

[2]Vietnam National University, University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi;

[3]Department of Physics, Faculty of Basic –Fundamental Sciences, Vietnam Maritime University, 484 Lach Tray – Le Chan - Hai Phong;

[4] Institute of Research and Development, Duy Tan University, 03 Quang Trung, Danang, Vietnam

Email: nguyenviettuyen@hus.edu.vn

ABSTRACT

Gold nanoparticles offer variety of applications in chemical and biological fields. Intensity and position of surface plasmon resonance (SPR) band in gold nanoparticles can be modulated by size and shape of the nanoparticles or the dielectric properties of the surrounding environment. This feature provides a convenient way to control the SPR of gold nanoparticles for surface enhance Raman scattering applications. It was popularly reported that gold nanoparicle can be synthesized favorably by chemical method but such approach also bring some limitation to applications due to surfactant often used in the synthesis process. In this report, we present the results of preparation of gold nanoparticles by combining sputtering and thermal annealing method. Size of the as-prepared gold nanoparticles, observed by scanning electron microscopy, increases monotonically with increasing sputtering time. Gold nanoparticles with size from 30 to 100 nm at high density and homogenous distribution was obtained when sputtering time is increased from 10s to 50 s. Gold thin film prepared at longer sputtering time could not be converted to gold nanoparticles as pointed out by absorption spectra. Variation of nanoparticle size results in corresponding shift of the SPR band.

Keywords: Gold nanoparticles; sputtering; thermal annealing; surface plasmon.

INTRODUCTION

Gold nanoparticles have shown its potential applications in various fields such as biomedical, electronics, photovoltaics … due to interesting properties such as: surface plasmon resonance, biocompatibility, excellent catalytic properties, multiple surface functionalities [1–5]. These applications have fostered research related to synthesis of gold nanostructures in general and gold nanoparticles in particular. A good synthetic process should provide gold nanoparticles of controllable morphology and shapes. Since its discovery, reduction method was broadly used as an effective way to prepare gold nanoparticles from solution phase [6,7]. Further modification of reduction method offered a convenient tool to obtain gold nanostructures of various shape including nanowires, nanorods, nanoflowers, nano-urchins… and of narrow size distribution. However the organic compounds used in the synthesis process might limit the applicability because purity is a key factor in many biological or electronic applications.

In this paper, we reported the fabrication of gold nanoparticles by a facile process with combining sputtering and thermal annealing methods. The obtained nanoparticles were characterized with different techniques such as: scanning electron microscope, diffuse reflectance spectroscopy. The results show that the products are of high quality. The major advantages of this approach are the homogeneity and uniformity of the nano products. The simple fabrication is also promising for scaling up for mass production.

EXPERIMENTAL

Sodalime glass was used as substrates for preparing gold thin films. The substrates were

first cleaned by ultrasonic bath in double distilled water, ethanol and acetone in sequences to remove any organic residue on the surface. The samples were then dried by air gun blowing. The substrates were then transferred into vacuum chamber of a DC sputtering system. The substrates were mounted onto an unheated copper plate. Thin films of gold were deposited on the prepared substrates by DC sputtering process at base pressure of 6 Pa. The used target is a gold disk (purity of 99.99%) of 2.5 inches. The current used in this research is fixed at 20 mA. The sputtering time was changed from 10s to 50s while the thickness of prepared films was estimated by using extrapolating plot provided by the sputtering system supplier.

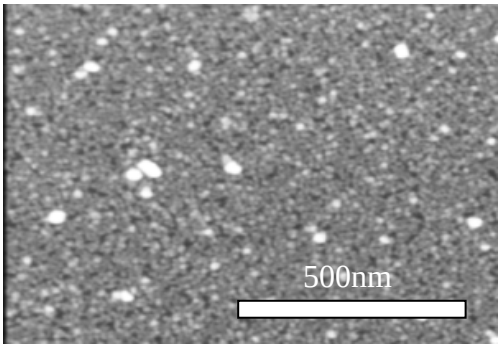
(a)

Figure 1. Image of DC sputtering system (a) and horizontal furnace (b) used to fabricate gold thin films in this research.

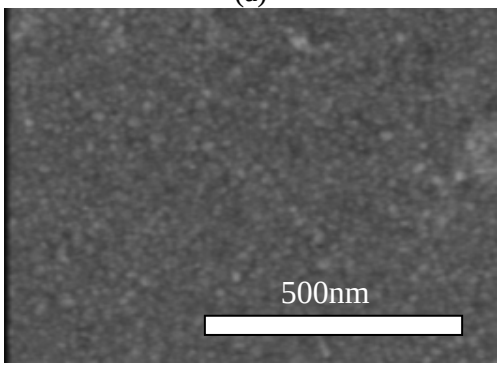
In order to transform gold thin films into nanoparticles, heat treatment at 300^{o}C in 2h was applied. Morphology of the obtained nano products were then characterized with scanning electron microscope Nova Nanosem while surface plasmon property was studied by diffuse reflectance spectroscopy.

RESULTS AND DISCUSSION

Figure 2 shows SEM images of gold thin films sputtered in 10 s and 40s. The images show that the films are smooth and homogeneous. It is likely that sputtering times does not change the morphology of surface morphology of thin films except thickness.



(a)



(b)

Figure 2. SEM images of gold thin films sputtered in 10s (a) and 40s (b)

After heat treatment at 300^{o}C in 2h, the gold layer was turned into array of gold nanoparticles of quite uniform size and shape. The nanoparticles has quasi spherical shape. The images also show that particle size is in a correlation with thickness of the as-prepared thin film. As the sputtering time increasing from 10s to 50s particle size increase accordingly from 30 nm to over 100 nm. It is also noted that at long sputtering time, size distribution becomes broader.

Figure 4 shows absorption spectra of the sputtered gold thin films. As can be seen that no plasmon peak was observed in the spectra which is in agreement with the fact that after sputtering gold was form as a continuous thin layer on substrates.

After heat treatment, clear plasmon peaks of gold appear in the absorption spectra. As sputtering time increasing, gold nanoparticles becomes bigger and size distribution is broader.

As a result, plasmon peak becomes broader and shifts to longer wavelengths. At sputtering time longer than 50s, plasmon peaks is faded out because of the large particle size.

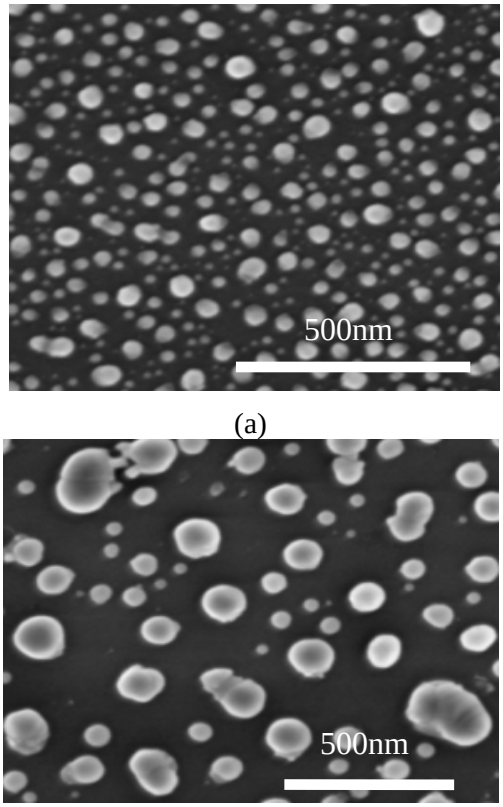


Figure 3. SEM images of gold thin films sputtered in 10 s (a) and 40s (b) after being annealed at 300ºC in 2h.

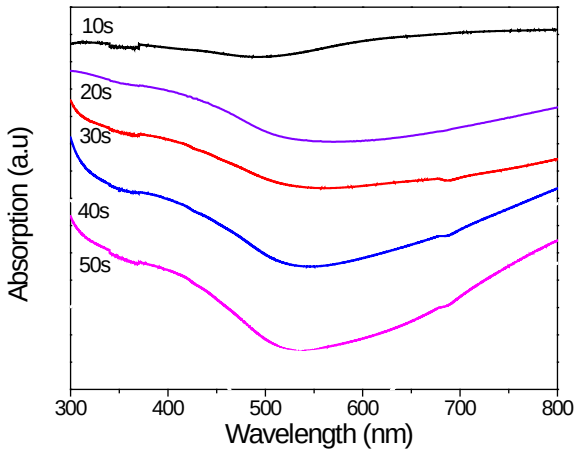


Figure 4. Absorption spectra of gold thin films prepared by sputtering method.

The results show that by controlling sputtering time, we can control the particle size, which in turn affect plasmon properties of the gold nano-particles.

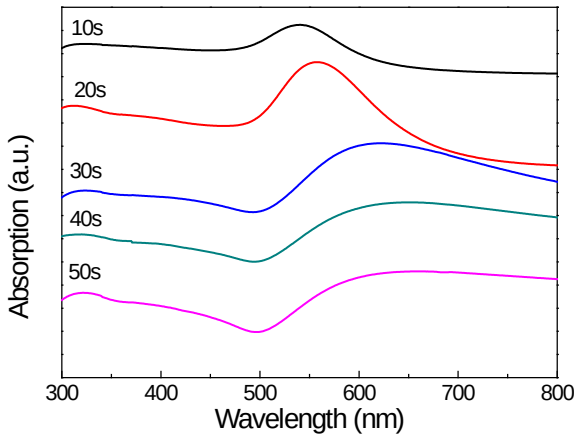


Figure 5. Absorption spectra of gold thin films prepared by sputtering method after heat treatment.

CONCLUSION

We successfully prepared gold nanoparticles on sodalime glass by combining sputtering and thermal annealing method. Particles size and surface plasmon property of gold nanoparticle can be conveniently controlled by sputtering time. The results demonstrate that combination of sputtering and annealing is a promising route to prepare gold nanoparticles array on flat substrates for various applications.

Acknowledgment

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2017.351. One of the author, Phd student Thi Ha Tran, would like to thank the Domestic Master/ PhD Scholarship Programme of Vingroup Innovation Foundation for supporting tution fee.

References

[1] B.B. Karakoçak, R. Raliya, J.T. Davis, S. Chavalmane, W.N. Wang, N. Ravi, P. Biswas, Biocompatibility of gold nanoparticles in retinal pigment epithelial cell line, Toxicol. Vitr. 37 (2016) 61–69. doi:10.1016/j.tiv.2016.08.013.

[2] S. Dutta Roy, M. Ghosh, J. Chowdhury, Adsorptive parameters and influence of hot geometries on the SER(R) S spectra of methylene blue molecules adsorbed on gold nanocolloidal particles, J. Raman Spectrosc. 46 (2015) 451–461. doi:10.1002/jrs.4675.

[3] I. Unlu, J.W. Soares, D.M. Steeves, J.E.

Whitten, Photocatalytic Activity and Fluorescence of Gold/Zinc Oxide Nanoparticles Formed by Dithiol Linking, Langmuir. 31 (2015) 8718–8725. doi:10.1021/acs.langmuir.5b01632.

[4] G. Sinha, L.E. Depero, I. Alessandri, Recyclable SERS substrates based on Au-Coated ZnO nanorods, ACS Appl. Mater. Interfaces. 3 (2011) 2557–2563. doi:10.1021/am200396n.

[5] T. Barman, A.A. Hussain, B. Sharma, A.R. Pal, Plasmonic hot hole generation by interband transition in gold-polyaniline, Sci. Rep. 5 (2015) 1–5. doi:10.1038/srep18276.

[6] E. Satheeshkumar, J. Yang, Photochemical decoration of silver nanoparticles on ZnO nanowires as a three-dimensional substrate for surface-enhanced Raman scattering measurement, J. Raman Spectrosc. 45 (2014) 407–413. doi:10.1002/jrs.4477.

[7] D. Wang, P. Schaaf, Nanoporous gold nanoparticles, J. Mater. Chem. 22 (2012) 5344–5348. doi:10.1039/c2jm15727f.

AMN-044-P

SURFACE ENHANCE RAMAN SCATTERING OF METHYLENCE BLUE ADSORBED ON GOLD NANOPARTICLES

Thi Ha Tran[1,2], Thi Huyen Trang Nguyen[1], Thanh Cong Bach[2], Nguyen Hai Pham[2], Cong Doanh Sai[2], Quang Hoa Nguyen[2], Trong Tam Nguyen[3], Khac Hieu Ho[4], Viet Tuyen Nguyen[2*]

[1]Department of Physics, Faculty of Basic Science, Hanoi University of Mining and Geology, Duc Thang, Tu Liem, Hanoi

[2]Vietnam National University, University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi

[3]Department of Physics, Faculty of Basic –Fundamental Sciences, Vietnam Maritime University, 484 Lach Tray – Le Chan - Hai Phong

[4]Institute of Research and Development, Duy Tan University, 03 Quang Trung, Danang, Vietnam

Email: nguyenviettuyen@hus.edu.vn

ABSTRACT

Gold nanoparticles are well-known for surface plasmon resonant related applications such as: surface enhanced Raman scattering, photovoltaics. In these applications, particle size is extremely important due to its effect on surface plasmon resonant peak position. In this report, thin films of gold were first fabricated by sputtering methods. Gold nanoparticles were developed by annealing the as prepared gold thin films at 300ºC. The as-prepared nanoparticles was characterized with scanning electron microscopy, absorption spectroscopy while Raman spectroscopy was used to study the surface enhanced Raman scattering. The as-prepared arrays of gold nanoparticles show excellent SERS activity with organic dye methylence blue as probe. Particle size shows clear effect on enhancement of Raman signal methylence blue.

Keywords: Gold nanoparticles; sputtering; thermal annealing; surface plasmon.

INTRODUCTION

Since its discovery, surface enhanced Raman scattering (SERS) is expected to provide a sensitive tool for chemical and biomedical sensing and imaging [1–3]. In this technique, preparation of noble metals nanoparticles is extremely important because they serve as the platform for Raman enhancement. Self assembled monolayer of gold or silver nanoparticles developed from solution phase is reported to provide good enhancement of Raman signal [4–6]. However, one main limitation of this method is the randomness of the aggregation of nanoparticles during synthesis, which often leads to poor repeatability of the prepared SERS substrates. This in turn prevents the capability of using these substrates for quantitative study. Hence, development of SERS substrates based on evenly distributed array of noble metal is of great interest.

In this research, we report of using gold nanoparticles array on sodalime glass to effectively enhanced Raman scattering. The 2D arrays of gold nanoparticles were fabricated by sputtering and annealing method. Morphology and surface plasmon resonance property of the samples were then characterized with scanning electron microscope and absorption spectroscopy, respectively. Surface enhanced Raman scattering on the as prepared gold nanoparticle array was also studied.

EXPERIMENTAL

Thin films of gold were prepared on sodalime glass substrates. Ultrasonic bath was applied to clean the substrates. The substrates were cleaned with double distilled water, ethanol and acetone in 10 min each cycle several times to clean the surface. The samples were then dried before being transferred into vacuum chamber for sputtering process. DC sputtering system integrated in Scaning electron microscope was utilized to prepare gold thin films. Heat treatment was not applied during sputtering process. Base pressure in vacuum chamber is maintained at 6 Pa. A gold disk (purity of 99.99%) of 2.5 inches was used as target. The current for sputtering was fixed at 30 mA while sputtering time was from 10s to 50s. The thickness of obtained films was estimated

by the correlation between sputtering time and thickness given by the manufacture of sputtering system.

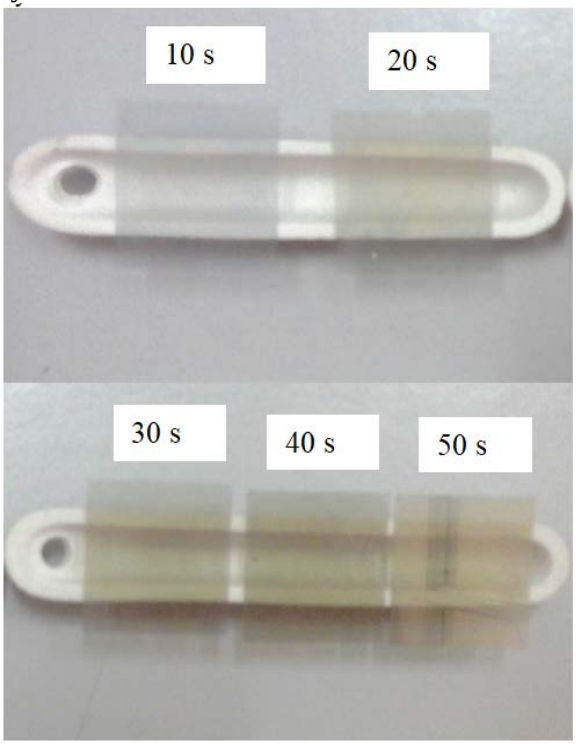


Figure 1. Image of gold nanoparticles array prepared by sputtering and thermal annealing method. The sputtering time is 10s, 20s, 30s, 40s and 50s.

In the next step, the as-prepared thin films were annealed at 300ºC in 2h. The heat treatment helps to form array of gold nanoparticle distributed quite evenly on the substrates.

The samples were then studied with scanning electron microscope and absorption spectroscopy. Raman spectrometer Lamram HR 800 was used to investigate surface enhanced Raman scattering of the as-fabricated substrates with Methylence blue as Raman probe. Laser power was estimated as 0.2 mW at the surface sample. Raman signal was collected with a 50x long working distance lens.

RESULTS AND DISCUSSION

Figure 2 presents SEM images of array of gold nanoparticles formed by annealing gold thin films sputtered in 10 s and 40s. As can be seen from the figure that the nanoparticles have uniform size and quasi spherical shape.

It is noted that particles size increases with increasing sputtering time. Average particles size of gold nanoparticles developed from thin films sputtered in 10s is about 30nm while that of the sample sputtered in 40s is over 100nm with a broad size distribution.

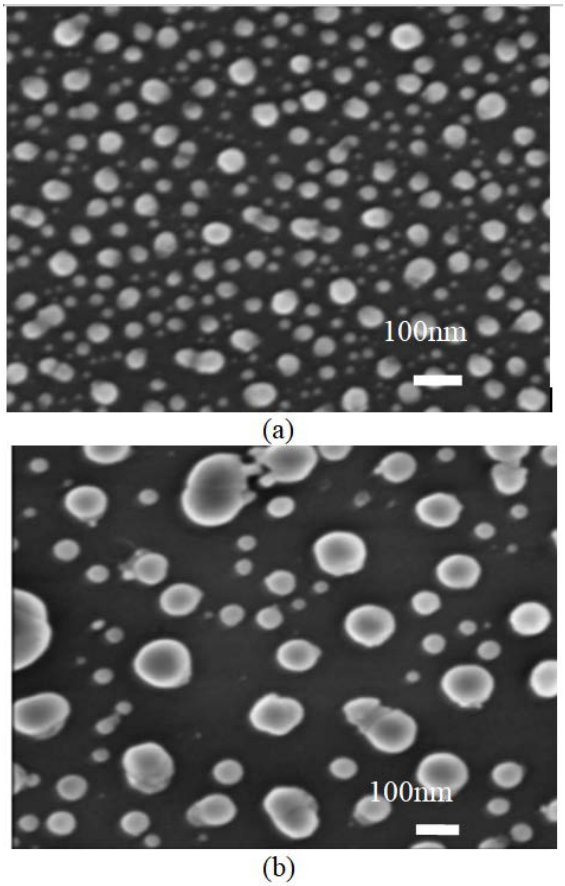


Figure 2. SEM images of gold nanoparticles obtained by annealing gold thin films sputtered in 10 s (a) and 40s (b).

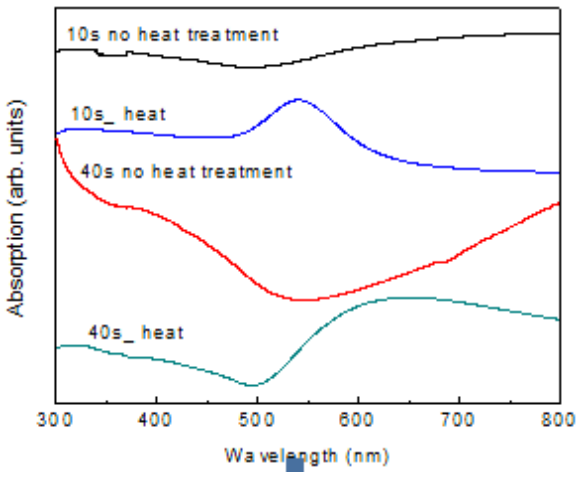


Figure 3. Absorption spectra of gold thin films with and without heat treatment.

Figure 3 shows absorption spectra of the sputtered gold thin films before and after annealing at 300ºC in 2h. The absence of plasmon peak in the absorption spectra before

annealing process implies that gold was formed as a continuous thin layer on substrates.

After heat treatment, clear plasmon peaks of gold in the absorption spectra demonstrate that gold layers were transformed into nanoparticles due to the shrinkage induced by heat treatment. Absorption data show agreement with SEM images where broader plasmon peaks and red shift of plasmon peak correspond to growth of particle size as well as size distribution.

SEM images and absorption data show that gold nanoparticles of different size, and tunable surface plasmon resonance were obtained by controlling sputtering time. Surface enhanced Raman scattering of methylence blue adsorbed on these gold nanoparticle was studied to demonstrate the application of surface plasmon resonance in biomedical field. Figure 4 shows Raman spectra of methylence blue adsorbed on gold nanoparicles array prepared from thin films of 40s sputtering.

Raman spectra clearly illustrate characteristic Raman peaks of methylence blue at 1299, 1393, 1497, 1621 cm^{-1}. Table 1 summarizes the corresponding vibration modes of methylence blue. The Raman peaks in our study agree well with those reported previously for this material.

Raman data shows that the asprepared gold nanoparticles are good SERS substrates of high sensitivity, which allow detecting methylence blue at very low concentration of 10^{-10} M.

Estimated enhancement factor of the asprepared SERS substrates based on gold nanoparticles was 3.8×10^{7}. The result is promising and show that SERS substrate based on gold nanoparticles has some advantages such as simple processing, high puritiy.

Table 1. Raman peak position and assignment of the corresponding vibration mode

Observed Raman peak	Raman vibration mode [1,7]
1299	(CH); (C-N) ring
1393	(C9-N10); (C3-N2); (C-N) ring; (CH)
1497	(CH2)twist ; (CH)
1621	(C-C)/(C-N)

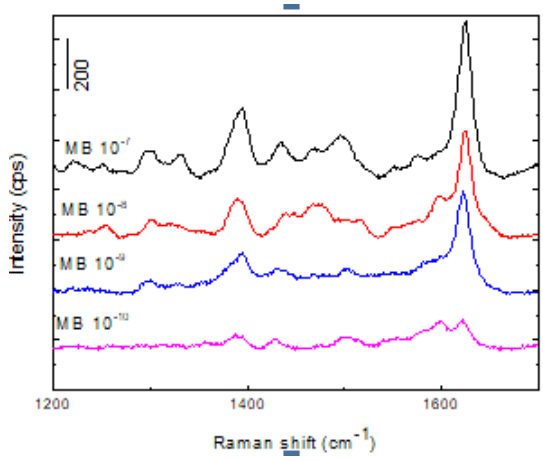


Figure 4. Raman spectra of methylence blue adsorbed on gold nanoparticles prepared from gold thin films sputtered in 40s.

CONCLUSION

Uniform gold nanoparticles were prepared on sodalime glass by combining sputtering and thermal annealing method. Surface plasmon peak position of gold nanoparticle is dependent upon particle size, which can be tuned conveniently by controlling sputtering time. The as-prepared gold nanoparticle array can serve as good surface enhanced Raman scattering platform and can be applied in biomedical analyzing. Further optimization of enhancement factor is being conducted.

Acknowledgment

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2017.351. One of the author, Phd student Thi Ha Tran, would like to thank the Domestic Master/ PhD Scholarship Programme of Vingroup Innovation Foundation for supporting tution fee.

References

[1] S. Dutta Roy, M. Ghosh, J. Chowdhury, *Adsorptive parameters and influence of hot geometries on the SER(R) S spectra of methylene blue molecules adsorbed on gold nanocolloidal particles*, J. Raman Spectrosc. **46** (2015) 451–461. doi:10.1002/jrs.4675.

[2] Y. Li, J. Dykes, T. Gilliam, N. Chopra, *A new heterostructured SERS substrate: Free-standing silicon nanowires decorated with graphene-encapsulated gold*

nanoparticles, Nanoscale. **9** (2017) 5263–5272. doi:10.1039/c6nr09896g.

[3] P.G. Yin, L. Jiang, T.T. You, W. Zhou, L. Li, L. Guo, S. Yang, *Surface-enhanced Raman spectroscopy with self-assembled cobalt nanoparticle chains: Comparison of theory and experiment*, Phys. Chem. Chem. Phys. **12** (2010) 10781–10785. doi:10.1039/c002662j.

[4] A. Vincenzo, P. Roberto, F. Marco, M.M. Onofrio, I. Maria Antonia, *Surface plasmon resonance in gold nanoparticles: a review*, J. Phys. Condens. Matter. **29** (2017) 203002. http://stacks.iop.org/0953-8984/29/i=20/a=203002.

[5] B.S. Lee, D.Z. Lin, T.J. Yen, *A low-cost, highly-stable surface enhanced raman scattering substrate by si nanowire arrays decorated with au nanoparticles and Au backplate*, Sci. Rep. **7** (2017) 1–7. doi:10.1038/s41598-017-04062-4.

[6] W.R. Premasiri, J.C. Lee, A. Sauer-Budge, R. Théberge, C.E. Costello, L.D. Ziegler, *The biochemical origins of the surface-enhanced Raman spectra of bacteria: a metabolomics profiling by SERS*, Anal. Bioanal. Chem. **408** (2016) 4631–4647. doi:10.1007/s00216-016-9540-x.

[7] G.N. Xiao, S.Q. Man, *Surface-enhanced Raman scattering of methylene blue adsorbed on cap-shaped silver nanoparticles*, Chem. Phys. Lett. **447** (2007) 305–309. doi:10.1016/j.cplett.2007.09.045.