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The influence of dielectric environment on the localized surface plasmon resonance of silver-based composite thin films



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ARTICLE INFO ABSTRACT Ag-based thin films with different topography were prepared by annealing process and laser irradiation, re-Keywords: LSPR spectively. The tunability of localized surface plasmon resonance (LSPR) was realized by adjusting the cover Plasmonic materials layer thickness of ITO or TiO₂. The effect of dielectric environment of Ag-based composite thin films on Optical absorption structure, surface morphology and optical property was investigated by X-ray diffraction (XRD), scanning Raman scattering electron microscope (SEM), atomic force microscopy (AFM), UV-VIS-NIR double beam spectrometer and Raman FDTD system, respectively. With the thickness of dielectric layer increasing, the topography of as-irradiated Ag-based thin films became smoother while the as-annealed Ag-based thin films had a rougher surface. LSPR absorption of both ITO/Ag and TiO₂/Ag bilayers showed red shift with the thickness of dielectric layer increasing. The electromagnetic field coupling between dielectric layers and Ag thin films contributed to increase significantly

domain (FDTD) simulation was in good agreement with that of the experiment.

1. Introduction

Localized surface plasmon resonance (LSPR) induced by collective electron charge oscillations in metallic nanoparticles (NPs) has the strong confinement and enhancement of near-field amplitude, which will occur when the resonance frequency of conduction electrons matches with the frequency of incident light [1,2]. LSPR has attracted a lot of attentions in recent years for its plentiful potential applications, such as surface enhanced Raman scattering (SERS) [3,4], biological sensors [5,6], plasmon enhanced fluorescence [7], photothermal therapy [8], nonlinear optics [9] and other photonics and optoelectronics devices [10]. To achieve the high intensity and efficiency of the above applications, it is of great significance to tune and extend the plasmon resonance wavelength. The tunable LSPR wavelength, which has been reported in various matrices like configurations of multilayers [11] and core-shell nanoparticles [12], is not only determined by the size, shape and composition of metal materials but also by the surrounding medium of metallic NPs [13,14]. It has been proved that strong tunable LSPR wavelength can be achieved by adjusting these factors appropriately [15].

Recently, a majority of researches focus on noble metals which have the unique LSPR properties for strong resonant oscillations to study surface plasmon resonance [16-18]. As a noble metal, silver (Ag) has been focused on for years because of its strong resonance absorption, low optical loss and low-cost fabrication. The size, shapes and surrounding medium of Ag thin film can be controlled appropriately to achieve the fine tunable LSPR. Nonetheless, the preparation of desirable size and shapes of Ag NPs and the difference of various surrounding mediums of Ag thin films are still worth exploring. On the one hand, laser irradiation technique has been studied theoretically and experimentally in recent years [19,20] to prepare the Ag thin films with various shapes. On the other hand, the effect of surrounding medium on Ag thin film, which can be structured through dielectric/metal bilayer, is of great importance to research about its LSPR tunability, plasmonic coupling and LSPR stability [21,22]. The dielectric/metal bilayer structure, such as indium tin oxide (ITO)/Ag, has been studied for years [23]. However, as a non-conductive material, TiO₂/Ag bilayer compared with ITO/Ag bilayer on LSPR property has little reports. In addition, the plasmonic coupling between the two materials and Ag thin films with different topography also needs an integrated study.

the sensitivity of surface enhanced Raman scattering (SERS). Additionally, the result of finite-difference time-

In this paper, we deposited ITO and TiO_2 layers as the dielectric layer upon Ag thin films which were fabricated by annealing process and laser irradiation to research the structure, morphology and optical properties of Ag-based composite thin films. LSPR wavelength of these

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bilayers was tuned in visible region with various thicknesses of dielectric layers, and the comparison of LSPR coupling between ITO/Ag and TiO₂/Ag bilayers was studied. Furthermore, the stability of LSPR wavelength in bilayer structures, which has a practical application in sensor devices, was discussed by air exposure with different days. Raman scattering properties of these bilayers were also investigated along with the simulation of finite-difference time-domain (FDTD) to figure out the electric field distribution of all samples.

2. Experiment

Prior to deposition, fused quartz substrates were ultrasonically cleaned in acetone, ethanol and deionized water for 20 min respectively and then dried with a flow of nitrogen. Ag thin films with a thickness of 15 nm were deposited on the substrates by electron beam evaporation with a base pressure of the chamber less than 4.0×10^{-4} Pa. The asdeposited Ag thin films were subsequently annealed in situ in the same vacuum chamber with the temperature of 100 °C for 30 min. After annealing process, laser irradiation with a continuous wave CO₂ laser source with the wavelength of $10.6 \,\mu m$ was applied in the experiment. The laser parameters were as follow: laser beam power was set as 3 W, the beam diameter was 0.1 mm, and the scan speed was set at 50 mm/s. Following the laser irradiation, ITO and TiO2 layers with the thicknesses of 10, 20 and 30 nm were deposited upon as-irradiated Ag thin films by electron beam evaporation, respectively (ITO/as-irradiated Ag (ITO/as-ir Ag) and TiO₂/as-irradiated Ag (TiO₂/as-ir Ag)). The chamber was evacuated to a base pressure of less than 8.0×10^{-4} Pa. For comparison, Ag thin film without being irradiated was also used in the study (ITO/as-annealed Ag (ITO/as-an Ag) and TiO₂/as-annealed Ag (TiO₂/as-an Ag)). The thicknesses of all thin films were monitored by a quartz crystal microbalance. To better understand the whole process, a schematic of the experiment is shown in Fig. 1.

The crystal structure of the samples were analyzed by X-ray diffraction (XRD) using a Rigaku MiniFlex600 system with Cu k\alpha radiation ($\lambda = 0.15408$ nm). The surface morphology and roughness were characterized by scanning electron microscope (SEM) (S-4800, Hitachi) and atomic force microscopy (AFM) (XE-100, Park System) with the scanning area of 3 µm × 3 µm. The optical absorption of the samples was measured with an UV-VIS-NIR double beam spectrophotometer (Lambda 1050, Perkins Elmer). Raman scattering spectra were examined using a confocal microprobe Raman system (inVia Raman Microscope, Renishaw) with 633 nm laser. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Structural properties

Fig. 2 shows the XRD patterns of all samples prepared by electron beam evaporation. In both Fig. 2(a) and (b), there is only one diffraction peak at around 38.184° (2 θ), which is corresponding to the (111)

crystallographic plane of Ag (JCPDS: 04–0783). No other grain growth can be observed during the deposition of dielectric layers. With the thickness of dielectric layer increasing in each bilayer, the intensity of the diffraction peak has a slight decrease because of the protection of dielectric layers [24]. For ITO/as-ir Ag (in Fig. 2(a)) and TiO₂/as-ir Ag (in Fig. 2(b)) bilayers, the XRD intensity of as-irradiated Ag is respectively stronger than that of as-annealed Ag in ITO/as-an Ag and TiO₂/ as-an Ag bilayers. It indicates the preferential orientation of Ag grains along the (111) crystallographic direction by laser irradiation. When ITO and TiO₂ are at the same thickness in bilayers, such as the wine lines (with the thickness of dielectric layer for 30 nm) in Fig. 2(a) and (b), the diffraction peaks are almost indistinguishable in XRD intensity. These results reveal that the dielectric layers have no obvious effect on the grain growth of Ag thin films.

3.2. Surface morphology

Fig. 3 shows the representative AFM images of Ag thin films and ITO/Ag bilayer structures with different ITO thicknesses. The morphology of as-annealed Ag thin film presents disorders (in Fig. 3(a)). After laser irradiation, the thin film was transformed into orderly spheroidal or ellipsoidal structures (in Fig. 3(e)). According to Fig. 3(a)-(d) and (e)-(h), the changes in morphology are closely related to the thickness of ITO layer. For as-annealed Ag thin film, with the ITO thickness increasing, it grows from small and sharp islands into rough and undulate accumulated island structures. At the same time, the surface of as-irradiated Ag thin film becomes relatively smooth during the deposition of ITO layer. As shown in Fig. 4, the values of the root mean square (RMS) surface roughness of the two groups are 2.477, 2.243, 2.263, 2.440 nm (ITO/as-an Ag) and 5.762, 5.501, 5.464, 5.415 nm (ITO/as-ir Ag), respectively, which are in accord with the surface morphology. The RMS values of TiO₂/Ag bilayer are shown in Fig. 4 as well, they are 2.477, 2.586, 2599, 2.697 nm and 5.762, 5.557, 5.477, 5.320 nm for TiO₂/as-an Ag and TiO₂/as-ir Ag, respectively.

Fig. 5 shows the representative SEM images of Ag thin films and ITO/Ag bilayer structures with increased ITO thicknesses. Comparing Fig. 5(a) and (e), it is obvious that laser irradiation makes as-annealed Ag thin films broken into defined particles. With increased ITO thickness, as shown from Fig. 5(b)–(d), morphology on as-annealed Ag thin film grows into accumulated island with bulky NPs. While the surface of as-irradiated Ag thin films shows almost unchanged with the deposition of dielectric layer between Ag NPs (as shown in Fig. 5(f)–(h)). The SEM results reflect the uniformity with AFM images.

Laser energy is transferred to Ag thin films by laser irradiation and this thermal energy causes the films breakup into droplets with certain nanosize solid metallic particles [19,20]. In the experiment, this breakup results in the as-annealed Ag thin films readily transformed into Ag NPs with ellipsoidal structures. For ITO/as-an Ag bilayer structure, the increased thickness of ITO layer causes the higher grain size, broadened height distribution and low valleys which result in an increasing RMS of Ag thin film [25]. Whereas the deposition of ITO



Fig. 1. A schematic diagram of the experiment process.



Fig. 2. XRD patterns of (a) Ag thin films and ITO/Ag bilayer with different ITO thicknesses and (b) Ag thin films and TiO₂/Ag bilayer with different TiO₂ thicknesses.



Fig. 3. AFM images of (a) as-annealed Ag thin film, (b) ITO10/as-an Ag, (c) ITO20/as-an Ag and (d) ITO30/as-an Ag bilayers; (e) as-irradiated Ag thin film, (f) ITO10/as-ir Ag, (g) ITO20/as-ir Ag and (h) ITO30/as-ir Ag bilayers.



Fig. 4. Surface roughness of all thin films with the thicknesses of dielectric layer from 0 to 30 nm.

layer in ITO/as-ir Ag structure may fill the spacing between Ag NPs and then makes the particle morphology smoother, leading to the decrease of RMS, also occurs in TiO_2 /as-ir Ag bilayer.

3.3. Optical absorption

The absorption spectra of ITO/Ag and TiO₂/Ag bilayers with different dielectric layer thicknesses are shown in Fig. 6. According to Fig. 6(a) and (c), the increased thickness of ITO and TiO₂ layer influences the as-annealed Ag films on their LSPR wavelengths which respectively red-shift about 148 and 104 nm and both have gradually weaker absorption peaks in bilayer structures. While with the deposition of ITO and TiO₂ layer on as-irradiated Ag (in Fig. 6(b) and (d)), there is a red shift of LSPR wavelength with a wider range about 206 and 138 nm respectively, and the absorption intensity increases first and then decreases in the bilayer structures.

For as-annealed (black curve in Fig. 6(a)) and as-irradiated (black



Fig. 5. SEM images of (a) as-annealed Ag thin film, (b) ITO10/as-an Ag, (c) ITO20/as-an Ag and (d) ITO30/as-an Ag bilayers; (e) as-irradiated Ag thin film, (f) ITO10/as-ir Ag, (g) ITO20/as-ir Ag and (h) ITO30/as-ir Ag bilayers.



Fig. 6. Absorption spectra of (a) ITO/as-an Ag and (b) ITO/as-ir Ag bilayer with different ITO thicknesses and (c) TiO₂/as-an Ag and (d) TiO₂/as-ir Ag bilayer with different TiO₂ thicknesses.

curve in Fig. 6(b)) Ag thin films, laser irradiation causes the resonance absorption shifted to the longer wavelength with a stronger absorption intensity. As a result, both ITO/as-ir Ag and TiO₂/as-ir Ag bilayer with the same thickness (such as 30 nm) of dielectric layer have a prominent shift of LSPR wavelength, an effective increase of absorption intensity and a relatively narrower absorption peak compared with those of asannealed Ag thin films. Moreover, the difference between ITO and TiO₂ layers can be observed in Fig. 6. It indicates the absorption wavelengths of TiO₂/Ag bilayers show a stronger resonant frequency with narrower absorption peak and higher absorption intensity than those of ITO/Ag bilayers when they have the same thickness of dielectric layer. How-ever, compared with TiO₂/Ag bilayers, ITO/Ag bilayers have a wider tunable range of LSPR wavelength.

In our previous study [26], by laser irradiation, the thermal energy of laser is transferred to Ag thin film, leading to the thin film transformed into nano-ellipsoid structure with different size and spacing of Ag NPs. So the increased size and spacing of Ag NPs cause the red shift and the higher absorption intensity of LSPR wavelength between asannealed (black curve in Fig. 6(a) and (c)) and as-irradiated Ag thin film (black curve in Fig. 6(b) and (d)) [27,28]. When the dielectric layer is deposited upon Ag thin film, plasmonic coupling takes place between the two layers, consequently, the plasmon resonance of Ag thin films is affected by the plasmon resonance of ITO or TiO₂ [24]. Also, the deposition of dielectric layer upon Ag thin films is equal to increasing the size of Ag NPs, resulting in the resonant absorption shifts to the longer wavelength with higher absorption intensity [29]. With the thickness of dielectric layers increasing, the red shift of LSPR wavelength in Fig. 6 is related to the surface morphology of bilayers, as shown in AFM images (Fig. 3(a)-(h)). Furthermore, the various thicknesses lead to the shift in electric field density on the surface along with a change of the electron oscillation frequency, thereby generating different cross-sections of optical absorption [24]. As a result, the smaller interface between dielectric layer and Ag thin film causes a red shift of LSPR wavelength with a lower cross section due to the increased thickness of dielectric layer in dielectric/as-an Ag bilayers. While for dielectric/as-ir Ag bilayers, with the thickness of dielectric layer increasing, the interface increases first and then decreases due to the existence of structured Ag NPs. In addition, there is a relatively lower free electron density of dielectric materials, therefore the absorption intensity increases first and then decreases (as shown in Fig. 6(b) and (d)) along with the weaker LSPR frequency. In general, different thickness of dielectric layer directly causes the shift of the plasmon resonance peak, and the tunable LSPR in visible region provides an opportunity for these bilayers about their applications in LSPR sensing [30,31].



Fig. 7. (a) LSPR wavelength of a representative sample of TiO_2/as -an Ag and TiO_2/as -ir Ag bilayers with the TiO_2 thickness of 30 nm in air exposure for 0, 30 and 60 days; (b) LSPR shifts of all samples after air exposure.

In LSPR sensing application, one of the important properties of these thin films is stability. Therefore, Fig. 7 illustrates the stability of all samples in ambient air exposure for 0, 30 and 60 days. A representative sample of TiO₂/Ag bilayer with the TiO₂ thickness of 30 nm after air exposure is indicated in Fig. 7(a). The absorption spectrum shows an obvious red shift with an increased absorption peak both in TiO₂/as-an Ag and TiO₂/as-ir Ag bilayers after 30 days exposure. Nevertheless, a slight difference can be observed between the spectra of 30 and 60 days exposure. To comprehensively analyze the phenomenon, the LSPR shifts of all samples after exposure with various days are demonstrated in Fig. 7(b). It is apparent that the resonant wavelength of all samples red-shifts after 30 days exposure (shift between dark and red polyline in each diagram of Fig. 7(b)) and then the LSPR peak keeps relatively steady during the air exposure from 30 to 60 days (shift between red and blue polyline in each diagram of Fig. 7(b)). Especially for ITO/as-ir Ag bilayer structure (as shown in Fig. 7(b(b))), the LSPR wavelength stays almost unchanged by air exposure. It is demonstrated that Ag thin films with the laser irradiation are more stable. Meanwhile, as a dielectric layer, ITO keeps LSPR wavelength more stable than TiO₂. As a result, ITO/as-ir Ag bilayer has the best stability among all samples.

3.4. SERS performance

All samples were used as SERS substrates in the experiment, which study the potential application of their LSPR properties. The probing Rhodamine B (Rh B) molecule, a typical artificial dye, was chosen as a test compound to study the SERS of the ITO/Ag and TiO₂/Ag bilayers. In this study, the Rh B molecule solutions with the concentration of 10^{-3} mol/L were dosed onto the surface of these bilayers. As shown in Fig. 8, three strongest Raman peaks at about 1648, 1504 and 1361 cm⁻¹, which are corresponding to C=C stretching modes of aromatic rings, can be observed in the samples. For as-annealed Ag thin films (Fig. 8(a)), the Raman signal intensities enhance with the thickness of dielectric layers increasing. While in as-irradiated Ag thin films, the intensities have the decrease tendency with the thickness of TiO₂ and ITO (as shown in Fig. 8(b)) layers increasing. With the same thickness of ITO and TiO₂ layers, ITO shows a stronger Raman intensity than that of TiO₂ on as-annealed Ag thin films, while TiO₂ has a higher intensity of Raman scattering compared with ITO upon as-irradiated Ag thin films.

It is well known that the Raman signal is affected by the surface morphology of samples (in Fig. 3). With the deposition of dielectric layer, morphology of as-irradiated Ag thin films has the smoother surface with decreased RMS (as shown in Fig. 4). According to the electromagnetic enhancement theory [32], there are less "hot spots" to excite local electrical fields, resulting in the decrease of Raman intensity. On the contrary, the dielectric/as-an Ag bilayers have the enhanced Raman signal along with the increased RMS. Moreover, the Raman intensity has a direct relation with LSPR wavelength [24]. In Fig. 6, TiO₂/Ag bilayers show stronger absorption intensity and resonance frequency than ITO/Ag bilayers in as-irradiated Ag thin films, so TiO_2 shows the higher Raman intensity. In addition, the absorption intensity of wavelength at 633 nm indicates that ITO/as-an Ag bilayer has higher LSPR absorption than TiO_2 /as-an Ag bilayer. At the same time, ITO itself has the plasmon resonance, therefore the Raman scattering of ITO/as-an Ag bilayer is stronger. For bilayer structure, the coupling between dielectric layer and Ag thin film also affects the Raman scattering. Plasmon resonance is sensitive to the surrounding medium and the distance between NPs. ITO has a stronger influence on LSPR wavelength than TiO_2 , causing the larger Raman signal in asannealed Ag thin films. However, with the deposition of dielectric layer, the increased distance between Ag NPs results in the weaker interparticle plasmon coupling strength. As a result, the Raman intensity in as-irradiated Ag thin films has declined.

To further verify the analysis above, the simulation of FDTD was employed to calculate the electric field distribution of these Ag-based composite thin films. In this simulation, a 633 nm laser irradiated perpendicularly to the x-y plane of the bilayers with the polarization along the y-axis direction. In the model structures, the size and spacing of Ag NPs were 64 nm in the diameter of a spherical structure and 20 nm in a distance respectively, and the increased thickness of dielectric layers were 10, 20 and 30 nm, which were in accord with the experimental data. Fig. 9 illustrates the electric field of Ag-based composite thin films with various thicknesses of dielectric layers. In Fig. 9(a) and (b), the electric field intensity enhances with the increased dielectric layer thickness upon Ag continuous thin films. The "hot spots", aggregation of the red spots in the pictures, located on the surface of dielectric layer which is between Ag NPs reflect the simulated intensity of electrical field, indicating the Raman signal for Ag NPs structure. The electric filed intensity tends to be decreasing with the thickness of dielectric layer between Ag NPs increasing (as shown in Fig. 9(c) and (d)). At the same time, when the dielectric layers are at the same thickness, ITO layer shows a stronger Raman intensity than TiO₂ layer on continuous thin films, and TiO₂ layer has a higher intensity of Raman scattering than ITO layer between Ag NPs. On the whole, the simulation results of FDTD are in good agreement with the SERS results above.

4. Conclusions

In conclusion, the influence of dielectric environment of silverbased composite thin films on structure, morphology and optical properties were investigated in this paper. The results indicate that with the thickness of dielectric layer increasing, the LSPR wavelength of ITO/Ag and TiO₂/Ag bilayers both red-shifts in visible region, meanwhile ITO/Ag bilayer has a wider tunable range of LSPR wavelength. It also demonstrates that as a dielectric layer upon Ag thin films, LSPR absorption of TiO₂ presents a narrower peak and a higher absorption intensity compared with that of ITO layer. For LSPR applications, ITO/ as-ir Ag bilayer shows the best stability among all samples. Moreover, the differences of Raman scattering due to the variation of LSPR are in agreement with the results of FDTD simulation in this study.



Fig. 8. Raman scattering spectra of Rh B on (a) dielectric/as-an Ag and (b) dielectric/as-ir Ag bilayer structures.



Fig. 9. FDTD simulated electric field amplitude patterns for (a) ITO/Ag continuous thin films, (b) TiO_2/Ag continuous thin films, (c) ITO/Ag NPs bilayers and (d) TiO_2/Ag NPs bilayers with the thickness of dielectric layers increasing.

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References

- E. Hutter, J.H. Fendler, Exploitation of localized surface plasmon resonance, Adv. Mater. 16 (2004) 1685–1706.
- [2] D. Gaspar, A.C. Pimentel, T. Mateus, et al., Influence of the layer thickness in plasmonic gold nanoparticles produced by thermal evaporation, Sci. Rep. 3 (2013) 1469.
- [3] C. Zhu, G. Meng, Q. Huang, Z. Zhang, Q. Xu, G. Liu, Z. Huang, Z. Chua, Ag nanosheet-assembled micro-hemispheres as effective SERS substrates, Chem. Commn 47 (2011) 2709–2711.
- [4] H.-Y. Wu, C.J. Choi, B.T. Cunningham, Plasmonic nanogap-enhanced Raman scattering using a resonant nanodome array, Small 8 (2012) 2878.
- [5] A.V. Kabashin, P. Evans, S. Pastkovsky, W. Hendren, G.A. Wurtz, R. Atkinson, R. Pollard, V.A. Podolskiy, A.V. Zayats, Plasmonic nanorod metamaterials for biosensing, Nat. Mater. 8 (2009) 867–871.
- [6] D. Rodrigo, O. Limaj, D. Janner, et al., Mid-infrared plasmonic biosensing with graphene, Science 349 (2015) 165–168.

- [7] R.M. Bakker, H.-K. Yuan, Z. Liu, et al., Enhanced localized fluorescence in plasmonic nanoantennae, Appl. Phys. Lett. 92 (2008) 043101.
- [8] J. Song, P. Huang, H. Duan, X. Chen, Plasmonic vesicles of amphiphilic nanocrystals: optically active multifunctional platform for cancer diagnosis and therapy, Acc. Chem. Res. 48 (2015) 2506–2515.
- [9] P. Muhlschlegel, H.-J. Eisler, O.J.F. Martin, B. Hecht, D.W. Pohl, Resonant optical antennas, Science 308 (2005) 1607–1609.
- [10] X. Zheng, W. Xu, C. Corredor, S. Xu, J. An, B. Zhao, J.R. Lombardi, Laser-induced growth of monodisperse silver nanoparticles with tunable surface plasmon resonance properties and a wavelength self-limiting effect, J. Phys. Chem. C 111 (2007) 14962–14967.
- [11] Y. Tachibana, K. Kusunoki, H. Ohsaki, Optical properties of Ag/dielectric-material multilayers, Vacuum 74 (2004) 555–559.
- [12] Y. M, W. Li, E.C. Cho, et al., Au@Ag core-shell nanocubes with finely tuned and well-controlled sizes, shell thicknesses, and optical properties, ACS Nano 4 (2011) 6725–6734.
- [13] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment, J. Phys. Chem. B 107 (2003) 668–677.
- [14] P.K. Jain, M.A. El-Sayed, Plasmonic coupling in noble metal nanostructures, Chem. Phys. Lett. 487 (2010) 153–164.
- [15] I. Mejac, W.W. Bryan, T.R. Lee, C.D. Tran, Visualizing the size, shape, morphology, and localized surface plasmon resonance of individual gold nanoshells by near-infrared multispectral imaging microscopy, Anal. Chem. 81 (2009) 6687–6694.
- [16] N.J. Halas, S. Lal, W.S. Chang, S. Link, P. Nordlander, Plasmons in strongly coupled

metallic nanostructures, Chem. Rev. 111 (2011) 3913-3961.

[17] E.R. Encina, E.A. Coronado, Near field enhancement in Ag Au nanospheres heterodimers, J. Phys. Chem. C 115 (2011) 15908–15914.

- [18] L.A. Austin, M.A. Mackey, E.C. Dreaden, M.A. El-Sayed, The optical, photothermal, and facile surface chemical properties of gold and silver nanoparticles in biodiagnostics, therapy, and drug delivery, Arch. Toxicol. 88 (2014) 1391–1417.
- [19] F. Mafune, J. Kohno, A. Yoshihiro Takeda, T. Kondow, H. Sawabe, Formation and size control of silver nanoparticles by laser ablation in aqueous solution, J. Phys. Chem. B 104 (2000) 9111–9117.
- [20] S.J. Henley, J.D. Carey, S.R.P. Silva, Pulsed-laser-induced nanoscale island formation in thin metal-on-oxide films, Phys. Rev. B 72 (2005) 195408.
- [21] V.A.G. Rivera, Y. Ledemi, S.P.A. Osorio, et al., Efficient plasmonic coupling between Er³⁺: (Ag/Au) in tellurite glasses, J. Non-cryst. Solids 358 (2012) 399–405.
- [22] M. Potara, A.M. Gabudean, S. Astilean, Solution-phase, dual LSPR-SERS plasmonic sensors of high sensitivity and stability based on chitosan-coated anisotropic silver nanoparticles, J. Mater. Chem. 21 (2011) 3625–3633.
- [23] S. Szunerits, X. Castel, R. Boukherroub, Preparation of electrochemical and surface plasmon resonance active interfaces: deposition of indium tin oxide on silver thin films, J. Phys. Chem. C 112 (2008) 10883–10888.
- [24] R. Hong, X. Wang, J. Ji, C. Tao, D.H. Zhang, D. Zhang, ITO induced tunability of surface plasmon resonance of silver thin film, Appl. Surf. Sci. 356 (2015) 701–706.

- [25] W.J. Stemp, B.E. Childs, S. Vionnet, C.A. Brown, The quantification of microwear on chipped stone tools: assessing the effectiveness of root mean square roughness (Rq), Lithic Technol. 33 (2008) 173–189.
- [26] R. Hong, W. Shao, W. Sun, C. Deng, C. Tao, D. Zhang, Laser irradiation induced tunable localized surface plasmon resonance of silver thin film, Opt. Mater. 77 (2018) 198–203.
- [27] S. Link, M.A. El-Sayed, Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles, J. Phys. Chem. B 103 (1999) 4212–4217.
- [28] R.G. Nikov, N.N. Nedyalkov, P.A. Atanasov, D. Hirsch, B. Rauschenbach, K. Grochowska, G. Sliwinski, Characterization of Ag nanostructures fabricated by laser-induced dewetting of thin films, Appl. Surf. Sci. 374 (2016) 36–41.
- [29] H. Chen, L. Shao, Q. Li, J. Wang, Gold nanorods and their plasmonic properties, Chem. Soc. Rev. 42 (2013) 2679–2724.
- [30] E.M. Larsson, J. Alegret, M. Käll, D.S. Sutherland, Sensing characteristics of NIR localized surface plasmon resonances in gold nanorings for application as ultrasensitive biosensors, Nano Lett. 7 (2007) 1256–1263.
- [31] J. Ye, P.V. Dorpe, L. Lagae, G. Maes, G. Borghs, Observation of plasmonic dipolar anti-bonding mode in silver nanoring structures, Nanotechnology 20 (2009) 465203.
- [32] M. Fan, A.G. Brolo, Silver nanoparticles self-assembly as SERS substrates with near single molecule detection limit, Phys. Chem. Chem. Phys. 11 (2009) 7381–7389.