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Investigation of the performance of thermally generated Au/Ag nanoislands for SERS and LSPR applications

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Abstract

In this work the performance of Au/Ag nanoislands was investigated for Surface Enhanced Raman Spectroscopy (SERS) and Localized Surface Plasmon Resonance (LSPR) applications. The nanoislands were generated by thermally annealing thin layers of silver and gold (having thickness in the 5-15 nm range), which were previously sputtered onto glass surfaces. Both pure (silver and gold nanoparticles – AuNP and AgNP) and composite metallic systems (silver-gold core-shell structures – Ag-Au core-shell) were evaluated based on their plasmonic and SERS sensitivity. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to measure the size, shape and distribution of the nanoparticles to correlate them with the obtained plasmonic/Raman capabilities. The technological parameters of nanoisland fabrication for optimal sensitivities are presented.

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1. Introduction

Gold and silver nanoparticles are widely used as signal amplification elements in various electrochemical and optical sensor applications. Although these NPs can be synthesized in several ways, perhaps one of the simplest

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methods is the thermal annealing of pre-deposited thin films on glass or silicon surfaces. With this method the parameters of the annealing process (time, temperature) and the pre-deposited thin film thickness influence and define the resulting size and distribution of the NPs (nanoislands) on the surface [1].

Localized surface plasmon resonance (LSPR) is a very sensitive optical phenomenon and can be utilized for a large variety of sensing purposes (chemical sensors, gas sensors, biosensors, etc.). The sensitivity of LSPR based devices strongly depends on the used material and also on the size and geometry of the metallic nanoparticles [2]. By controlling these parameters the plasmon absorption band can be tuned and the sensitivity can be optimized even in a way, that (considering molecular or biosensing applications) it reaches the sensitivity of classic Kretschmann-configuration based SPR devices on the market [3, 4].

Surface enhanced Raman spectroscopy (SERS) is an analytical method which can significantly increase the yield of Raman scattering of target molecules adsorbed on the surface of metallic nanoparticles. Depending on the nanoparticles and some other conditions the enhancement factor can reach the order of 10^{10}-10^{11}, which would enable even the detection of single molecules on the surface.

The aim of the current work is the investigation and optimization of the technological parameters of thermally generated pure Au/Ag nanoislands and core-shell nanostructures in order to fabricate cheap but sensitive SERS and LSPR photonic elements.

2. Experimental

For nanoparticle fabrication previously cleaned glass slides were coated with silver/gold thin films in various thickness with a vacuum thermal evaporation system. The thin films were subsequently thermally annealed for given time periods in a ceramic oven. The technological parameters of the investigated samples are collected in Table 1, while Fig. 1 gives on overview of the whole technological and investigation sequence on our experiments.

Atomic force microscope (AFM) measurements were done with a Veeco (lately Bruker) diInnova type microscope in full contact and tapping mode with 512x512 sampling rate and 1 Hz scan rate. The PID values were optimized according to the user manual. Bruker TAP150A and ART D160 probes were used for tapping mode imaging. For data evaluation the freeware Gwyddion 2.27 software was used.

The optical spectroscopy measurements were performed with an Avantes Avaspec 2048-4DT spectrometer and an Avantes Avalight DHS halogen light source between 400 nm and 750 nm.

SERS measurements were performed with a Renishaw 1000 micro-Raman spectrometer. The 514 nm line of an Ar ion laser was used for the excitation and the excitation spot was focused into a spot having diameter of 1 micron. The spectra were recorded with 10 s integration time. The SERS enhancement was tested using benzophenon-izopropyl alcohol solution that was dripped onto the substrate so that the same drop covered partially both the nanoparticle coated region and the clean glass substrate. The latter was used for the reference measurements.

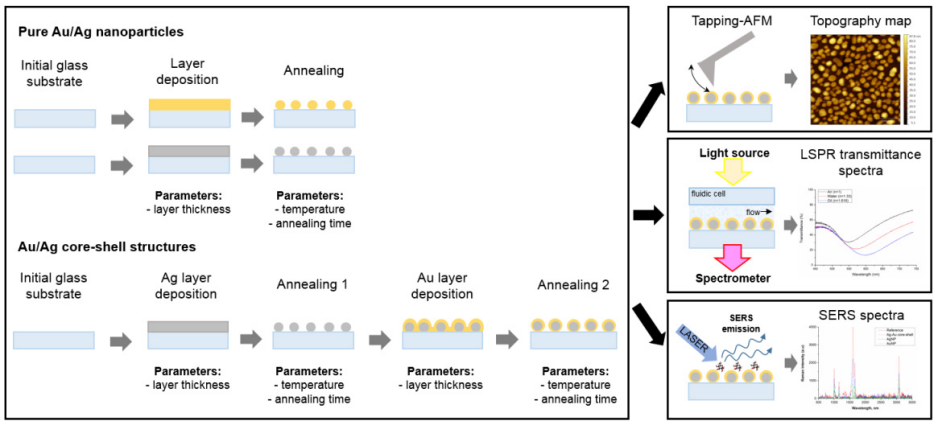

Fig. 1. Comprehensive illustration of the nanoparticle preparation technologies (layer deposition with sputtering, thermal annealing) and the characterization methods (tapping-mode AFM, transmittance-mode spectrophotometry and SERS).

3. Results and Discussion

The LSPR bulk refractive index sensitivity of the prepared samples was measured by optical spectrophotometry, by changing the medium above the nanoparticles between air ($n = 1$) and water ($n = 1.33$) respectively. Fig. 2 summarizes the results in terms of absorbance peak shift for all of the investigated samples, while Fig. 3 presets the LSPR transmittance curves for samples #4 and #7 (which had the highest sensitivity) in air and water. Two important things transpire from the results: 1) by increasing the deposited thin film layer thickness and thus the resulting nanoisland size the refractive index sensitivity increases; 2) by increasing the annealing time the sensitivity for a given initial layer thickness decreases.

The connection between the obtained results and the nanoisland morphologies can be understood by studying the AFM topography images presented in Fig 5. It is known that decreasing the distance/gap between two nanoparticles leads to a significantly increased near field between the particles due to plasmon coupling effects [5]. Since this strong field enhancement can be related to plasmon tunneling through the gap, a way to increase the coupling and thus the sensitivity of the nanoparticle arrangement is to 1) maximize the surface coverage of nanoislands (increase the surface ratio of covered/non covered areas); 2) maximize the surface area of the nanoisland, through which they face each other; 3) minimize the gap between the particles. The AFM images of Fig. 5 confirm this connection between the morphology and the obtained sensitivities. It can be seen for both pure Au and Ag/Au particles that longer annealing times lead to more defined particles (due to Ostwald-ripening) which leads to increased gap sizes and thus smaller refractive index sensitivities. Besides the discussed results, a more detailed investigation of the technological parameters and their connection to the LSPR sensitivities will be presented in the full paper.

Sample ID	Type	Layer thickness [nm]	Annealing time [h]
#1	Au	10	0.5
#2	Au	10	2
#3	Au	10	4
#4	Au	14	0.5
#5	Au	14	2
#6	Au	14	4
#7	Ag/Au	6/14	0.25/0.5
#8	Ag/Au	6/14	½
#9	Ag/Au	6/14	2/4

Table 1: Technological parameters of the deposition and thermal annealing to generate nanoislands on glass substrates (annealing temperature was 550 ºC in all cases).

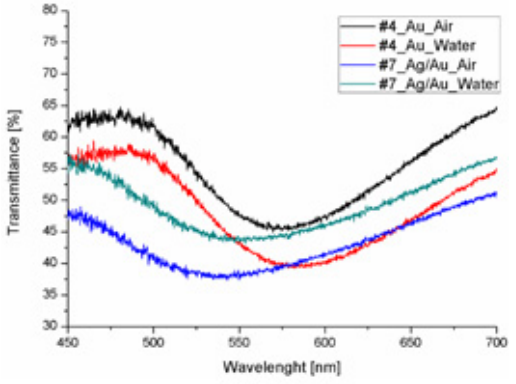

Fig. 3. LSPR transmittance shift of samples #4 and #7 measured in air (n=1) and water (n=1.33), respectively.

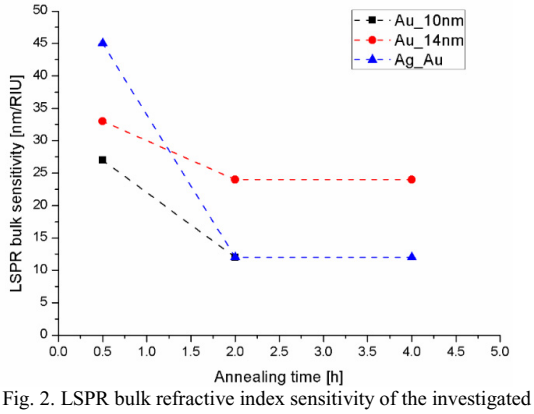

Fig. 2. LSPR bulk refractive index sensitivity of the investigated samples in function of the annealing time and layer thickness. Note: sample #3 is missing.

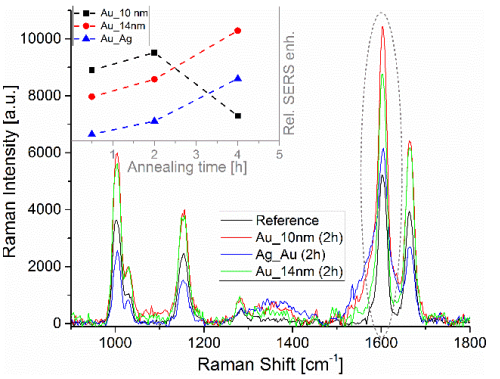

Fig. 4. SERS spectra of pure AuNP and Ag-Au core-shell nanostructures with the reference sample (benzophenon-izopropyl alcohol) in air.

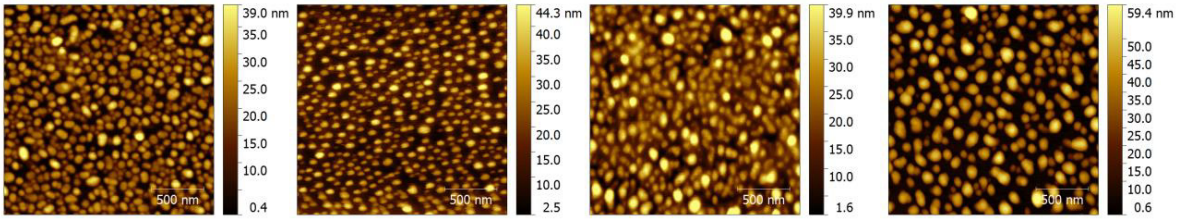

Fig. 5. 2x2 μm^2 tapping-mode AFM topography images of samples #4, #6, #7 and #9 respectively (from left to right).

Fig. 4 compares the some typical SERS spectra obtained with gold, silver and gold/silver composite nanoislands. While the highest observable increase in the intensity due to SERS is around 10x on the Figure, this comparison wih the reference spectrum does not reflect the exact SERS enhancement values. The enhancement occurs only in a close vicinity of the nanoislands, but there is a significant non-SERS contribution from other parts of the sample in both the SERS and the reference spectra, influencing the intensity ratios and their comparison. Therefore, the analysis was focused on the relative SERS enhancement factors of the different samples (inset in Fig. 4). The data indicate that thicker films result in lower SERS enhancement (at short annealing times) and the higher annealing time promotes it. SERS is highly sensitive to the relation of the excitation/Raman scattered wavelength regions to the plasmon resonance maximum of the nanoparticles, and the findings are in good agreement with the optical absorption data of the samples. With annealing the minimum of the optical absorption of the Au_10nm, Au_14nm and Au_Ag samples decreases from 564 nm to 546 nm, from 570 nm to 532 nm and from 544 to 517 nm, respectively. The closer the absorption minimum (the plasmon resonance maximum) to the 514 nm excitation wavelength, the better the SERS enhancement of the metallic nanoislands. Comparison with the AFM data shows that, in spite of the higher surface coverage of the untreated films the annealed ones perform better with SERS, so the most important criteria here is to match the plasmon resonance properties of the metallic nanoparticles with the excitation conditions.

4. Conclusions

The performance of thermally generated pure Au and Ag/Au core shell nanoislads for LSPR and SERS sensing applications was investigated. The morphology of the generated nanoisland arrangements was investigated with AFM and was compared to their sensing properties. We found that higher deposited layer thicknesses and shorter annealing times lead to higher LSPR bulk refractive index sensitivities which are strongly connected to the increased island sizes and smaller gap distances. Raman measurements confirm the SERS enhancement of the nanoislands and indicate that the plasmon resonance frequency are the main factor affecting the SERS efficiency.

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