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Optimization of nanostructures based on Au, Ag, Au–Ag nanoparticles formed by thermal evaporation in vacuum for SERS applications

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ABSTRACT

SERS substrate containing SERS-active array of Ag, Au and $Ag_{50}Au_{50}$ nanoparticles with normal size distribution, a mirror layer and a separating SiO₂ layer was optimized. A layer of amorphous carbon was used as the object of study. It is shown that such a structure enhances the Raman signal both due to the localized surface plasmon resonance and due to interference. The average size of nanoparticles, the reflection coefficient of mirror layer, and the thickness of SiO₂ layer influence the amplification of the Raman signal. To provide amplification the thickness of SiO₂ layer should be calculated for the appropriate wavelength in order to get constructive interference. It is revealed that additional amplification of the Raman signal occurs if the mirror layer as well as the array of particles is made of plasmon metal and thickness of separating SiO₂ layer is quite small (up to 30 nm).

1. Introduction

Nanoparticles of some metals due to the presence of strong localized surface plasmon resonance (LSPR) can act as antennas for transferring energy of electromagnetic waves [1,2]. This property makes it promising to use arrays of such particles for photovoltaics [3,4], photodetection [5–7], photocatalysis [8–10] and medicine [11,12].

Another well-known application of such plasmon metal nanostructures is Surface-Enhanced Raman Spectroscopy (SERS) [13,14]. There are two extreme approaches to the formation of SERS-substrates. The first approach involves the use of photolithography techniques [15–17]. This method is the most precise one. It allows formation of highly ordered surface nanoobjects with certain identical dimensions and certain distances between them. Naturally, such structures have high SERS and the best reproducibility of measurement results. The only drawback of such SERS-substrates is high manufacturing laboriousness and, inevitably, high cost. The second approach is to form the nanoparticles from solutions by chemical methods [18–21]. This is the simplest and cheapest method. It allows controlling particle size well enough. However, the transfer of these particles to the surface of a solid to form an array is poorly reproducible. Often particles are uncontrollably randomly accumulated in agglomerates [22,23], which makes it impossible to reproduce the results of measurements on such surfaces.

Arrays of nanoparticles on the surface can be formed by the method of thermal evaporation in vacuum [24,25]. The particles in such arrays are of different sizes, but their size distribution is Gaussian. The average particle size is well controlled and reproduced [26]. The distance between the particles is also well reproduced, but its variation is limited, because it correlates with the particle size. This method occupies an intermediate position in comparison with two methods mentioned above. It is significantly cheaper and less labor-consuming compared to the lithographic method, and is more precise and reproducible than the chemical one.

In this paper we analyze the main factors that cause the amplification of the Raman signal when using SERS structure with an array of particles with normal size distribution, which makes it possible to optimize SERS substrate.

2. Experiment

The design of the planar SERS-structure optimized in this paper is schematically presented in Fig. 1. Such a construction is well known [27–29]. It consists of several functional layers. The main layer is the

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Fig. 1. Schematic diagram of the optimized planar SERS-structure (1 – substrate; 2 – mirror layer; 3 – layer of insulator; 4 – SERS-active layer).

SERS-active one. In our case it is represented by a self-organized array of metallic nanoparticles having normal size distribution. In addition, the structural elements are a mirror layer and an intermediate layer of optically transparent material. The thickness of metal films used as reflecting layers in this study was 100 nm for all structures. The parameters of the remaining layers varied depending on the factor studied.

Single-crystal silicon wafers were used as substrates. When preparing the samples, the substrates were washed standardly in a Caro solution H_2SO_4 : H_2O_2 (1:1), then washed in deionized water and dried in isopropyl alcohol vapor. Subsequently, a reflecting metal layer and a separating optically transparent SiO₂ layer were sequentially deposited on the substrate by electron beam deposition in a single vacuum cycle at room temperature of the substrate. The deposition rate of the layers was ~1 Å/c. Then, an array of plasmon nanoparticles with a given average size was formed by vacuum-thermal evaporation of small portions of matter and subsequent low-temperature vacuum annealing. Modes of formation of nanoparticle array with a given average size are described in detail in [24,25].

A 20 nm thick film of amorphous carbon was used as an object of study. It was chosen because it is well investigated [30], practically transparent at a specified thickness, and perfectly reproduced. Films of amorphous carbon were deposited by magnetron sputtering of a graphite target in Ar ambient at working gas pressure of $4,5 \times 10^{-2}$ Torr. For all vacuum processes the residual pressure value was not higher than 5×10^{-6} Torr.

The investigation of the formed SERS structures was carried out using Raman spectrometer LabRAM HR Evolution (Horiba production).



The samples were measured at room temperature at laser wavelengths of 488, 514, and 633 nm. Laser power did not exceed the maximum by more than 10%. Raman spectrometer was calibrated by recording the Raman peak of a silicon wafer at 520 cm^{-1} . In micro-Raman spectrometer the laser beam was focused onto the amorphous carbon layer using a high numerical aperture objective lens ($100 \times$). Acquisition time used for recording spectra was 10 s for each point.

Typically, to characterize the gain of SERS structure, the absolute gain is calculated [31]. In our work we have used relative gain factor EF for the convenience of presenting the results, because it differs significantly for different materials. Relative EF was determined as the ratio $I_{\rm G}/I_{\rm max}$. In this ratio $I_{\rm G}$ is Raman signal intensity for the G-spectral line of the amorphous carbon film (~1580 cm⁻¹) averaged over the surface of the sample and normalized to the pumping power of each SERS structure, and $I_{\rm max}$ is the maximum achieved $I_{\rm G}$ value in the studied series of samples.

Measurements of transmission spectra of the samples were carried out in the wavelength range of 350–900 nm using SF-2000 spectrometer.

The composition and geometric parameters of nanoparticle arrays were studied using transmission electron microscope FEI Technai G^2 20 S-Twin equipped with an attachment for X-ray energy-dispersive microanalysis EDAX. Samples for TEM were prepared in several stages. At the initial stage 20 nm thick layer of amorphous carbon was deposited on a single crystal of KCl salt. After that, arrays of nanoparticles were formed there. At the final stage of fabrication the samples were immersed in deionized water to dissolve KCl. A thin film of amorphous carbon floated to the surface and was caught on a standard copper grid for TEM. The analysis of the obtained images made it possible to establish particle density per surface unit and average particle size of the resulting arrays.

3. Results and discussion

On the one hand, an increase in the sensitivity of the SERS structure under consideration can be achieved by increasing the efficiency of pumping energy of an incident electromagnetic wave by amplifying the field near the surface of plasmon nanoparticles. In this regard, a localized plasmon resonance is known to be of great importance [32].

Fig. 2 shows the experimental transmission spectrum of an array of

Fig. 2. The transmission spectrum of the array of Au nanoparticles with an average size of ~40 nm covered with a 20 nm a-C film. Corresponding diagrams of the approximate plasmon absorption of this array are shown by dashed columns. Colour columns show the relative gain EF of the particle array on a gold layer with 20 nm thick intermediate SiO₂ layer for Raman scattering using laser wavelengths of 488, 514, and 633 nm. λ_L is laser wavelength; λ_R is the corresponding wavelength of Raman shift G-line of 1580 cm⁻¹ for an amorphous carbon film.

gold nanoparticles with an average size of 40 nm covered with a layer of amorphous carbon. As it can be seen the transmission minimum, i.e., obviously, the absorption maximum associated with plasmon resonance occurs at wavelength of ~600 nm. It should be noted that this effect is valid in a certain wavelength range. The diagram superimposed on the transmission spectrum shows correlation between the relative gain of SERS structure based on the specified array of gold particles and the gold mirror layer, which are separated by a 20 nm SiO₂ layer. When using incident laser radiation wavelength of 633 nm closest to LSPR position we see the largest plasmon absorption and we have the greatest amplification of the Raman signal. Conversely, a wavelength of 488 nm is at the edge of the plasmon, and the absorption magnitude is small. Therefore, we can expect that we observe the weakest Raman signal amplification at this wavelength.

Thus, the position of the peak of the localized plasmon resonance really needs to be "tuned" in accordance with the wavelength of incident laser radiation. This can be done by selecting material and optimizing the size of plasmon nanoparticles in the array of SERS-active layer.

On the other hand, an increase in the sensitivity of SERS structure can be achieved by increasing the efficiency of using an incident light wave. We may consider the described design of the planar SERS structure as a kind of Fabry-Perot interferometer and increase the reflection coefficient of the mirror layer by optimizing the thickness of the optically transparent spacer layer.

3.1. Influence of the average size of Ag and Au nanoparticles in the array

An important feature of metal nanoparticle arrays formed by vacuum-thermal evaporation is the relationship between the prevailing particle size and surface density of particles [24,25]. TEM studies show that particles practically do not touch each other, and the distance between the particles in such arrays is commensurable with particle size: at an average particle size of 7 nm the mean particle-to-particle spacing is 7 nm(Fig. 3 a), and at 25 nm–25 nm (Fig. 3 b).

To study the effect of this factor we prepared two series of samples with different average particle size. In the first series the SERS-active layer was made of Ag nanoparticles, and in the second series it was made of Au nanoparticles. In both cases Ag was used as a mirror layer. The thickness of the SiO₂ layer for all samples was 20 nm.

The transmission spectra of the fabricated nanoparticle arrays showed that depending on the average size the position of the

transmission minimum of LSPR varies in the range 405–425 nm for Ag and 525–560 nm for Au.

Fig. 4 shows the results of SERS spectroscopy for all samples. According to Fig. 4 for all wavelengths used the maximum amplification of the Raman scattering signal is observed at an optimal average particle size. In addition, when the wavelength of the exciting radiation increases a certain shift of this optimum toward a larger particle size is observed. This result for nanoparticle array with a normal size distribution on the whole confirms the results obtained by different groups of authors for SERS structures formed by photolithography in which all metal particles have the same size and strict periodicity [33,34].

The change in the optimum particle size is a result of displacement of the position of the G-spectral line at 1580 cm^{-1} relative to the positions of LSPR maxima at different wavelengths of exciting radiation. When the average particle size in the array increases, the maximum position of LSPR shifts toward the long waves [35]. Therefore, increase of the laser wavelength leads to the enlargement of optimal size of array particles.

However, we draw your attention to Fig. 4. It shows the dependences of the relative gain on average particle size. All three relationships are represented on a single graph. When the laser wavelength is removed from LSPR position, intensity of the Raman signal reduces by three orders of magnitude for Ag, and by an order of magnitude for Au.

3.2. Influence of material in Ag-Au system

The material of nanoparticles affects the position of the localized surface plasmon resonance maximum to even a greater extent than the particle size. A change in the average particle size from 7 to 60 nm allows us to vary the position of LSPR in the range of \sim 50 nm. While changing smoothly the composition of Ag–Au alloy nanoparticles from Ag to Au, it can be varied within \sim 120 nm.

Ag_{0.5}Au_{0.5} alloyed nanoparticle array efficiency determination was carried out on SERS structures with an average size of Ag–Au particle \sim 25 nm, a mirror layer of Ag and 20 nm thick SiO₂ layer. An Ag–Au alloyed nanoparticle array was formed by successive thermal evaporation and condensation of small weight portions of Au and Ag onto a cold substrate and subsequent low-temperature annealing in vacuum in accordance with [36].

The main results of SERS spectroscopy of the prepared samples are presented in Table 1. For comparison the table also shows the



Fig. 3. TEM images of Au nanoparticle arrays with an average size of 7 nm (a) and 25 nm (b) formed by the vacuum-thermal evaporation method followed by vacuum annealing at 350 °C for 30 min.



Fig. 4. Dependences of relative gain factors on average particle size for G-spectral band at 1580 cm^{-1} of amorphous carbon thin film for different laser wavelengths. SERS structures with Ag mirror layer, a separating layer of SiO₂ and an array of silver (a) and gold (b) nanoparticles were used.

Table 1

Experimental values of Raman signal intensities of G-spectral band of an amorphous carbon film for investigated samples.

Material of the particles	Laser wavelength, nm					
	488	514	633			
	Raman intensity, relative units					
Ag Ag _{0,5} Au _{0,5} Au	$\begin{array}{l} 2.5\times 10^{7} \\ 9.7\times 10^{3} \\ 2.7\times 10^{4} \end{array}$	$7.3 imes 10^5$ $1.6 imes 10^4$ $2.1 imes 10^4$	$\begin{array}{c} 3.6 \times 10^{4} \\ 7,8 \times 10^{3} \\ 3,7 \times 10^{4} \end{array}$			

intensities for similar SERS substrates on the basis of arrays of silver and gold nanoparticles ($d_{avg} = 25 \text{ nm}$).

It can be seen that the intensity maximum shifts to the long-wave region after the shift of the plasmon resonance position. The maximum value of Raman signal intensity for SERS structures based on self-or-ganized Ag_{0.5}Au_{0.5} alloy nanoparticle array falls to the wavelength of the exciting radiation of 514 nm and is in the interval between Ag and Au, and correlates with the position of the localized surface plasmon resonance for this array ($\lambda_{LSPR} \sim 550$ nm).

It is well known that different materials of nanoparticles greatly differ in the possibility of amplifying the Raman signal, and the best one is silver [37]. From the values presented in Table 1 it can also be seen that for all three laser wavelengths SERS structures based on Ag_{0.5}Au_{0.5} alloyed nanoparticle arrays show a lower value of the Raman signal gain not only in comparison with SERS structures based on silver arrays, but even arrays of gold nanoparticles of a similar average size. Obviously, this result is quite natural. Gold and silver are mutually dissolving into each other in any proportions. Dissolution of the impurity in the metal (Au in Ag or Ag in Au) locally deforms crystal lattice and causes a periodicity violation in it, which is noticeably larger than a phonon. It leads to significant shortening the mean free path of electron and, as a result, to an increase in the electron scattering frequency, which manifests itself in an increase of alloy resistivity comparing with pure elements. According to the dependence of resistivity on the component composition of Ag-Au alloy for a bulk material the composition 50/50 at.% has resistivity of ~11.5 $\mu\Omega$ × cm, while resistivity for bulk Au corresponds to 2.44 $\mu\Omega$ × cm, and for bulk Ag is 1.47 $\mu\Omega$ × cm [38]. It is known from metallooptics [39] that the lower the resistivity of a metal, the greater the thickness of the skin layer, i.e. the deeper electromagnetic wave penetrates into the metal. This means that the greater the number of electrons will participate in polarization process and the higher their efficiency is, the greater will be the plasmon resonance value of the metal and the expected SERS effect. Nevertheless, we can

say that the amplification effect (albeit weaker) is also present in the array of Ag—Au alloy nanoparticles. This seems important, since record values of signal amplification are not always necessary, and in some cases, it is necessary that the Raman signal is not lost against the background of similar amplification of fluorescence. In this case, we must select a different laser wavelength and tune the localized plasmon resonance of SERS structure to it.

3.3. Mirror layer

To determine the effect of reflectivity of the mirror layer on the efficiency of SERS substrates we made several samples with mirror layers of different metals Ag, Au, Ni, Ti, and another option was the original Si substrate itself. The thickness of SiO₂ layer was 20 nm. As SERS-active layer, there was an array of gold nanoparticles with an average size of \sim 40 nm.

Measurements of Raman intensities were carried out at two wavelengths of the laser: 514 and 633 nm. Taking into account that SERSactive layer is an array of gold nanoparticles these wavelengths characterize two fundamentally different situations:

- 1. The wavelength of the laser is significantly shifted relative to the position of the localized surface plasmon resonance ($\lambda_{L2} = 514$ nm).
- 2. The wavelength of the exciting radiation ($\lambda_{L1} = 633 \text{ nm}$) is close to the position of the absorption plasmon peak maximum of gold nanoparticles array coated with a thin film of amorphous carbon ($\lambda_{LSPR} \sim 610 \text{ nm}$).

The reflection coefficients of metal films were measured using Leitz MPV-SP optical reflectometer. The obtained dependences are shown in Fig. 4.

Fig. 5 (a) shows that in the case of using laser with wavelength of 514 nm, a linear increase in the gain of the Raman signal with an increase in the reflection coefficient of the mirror layer is observed for investigated structures. For least-squares approximation, the correlation coefficient turns out to be equal to K = 0.969, which indicates a high probability of such a dependence. At the same time, for wavelength of 633 nm (Fig. 5 b), the approximation over all 5 experimental points gives low correlation coefficient K = 0.499. As can be seen in Fig. 5 (b), this is due to strong fallout of the point for the gold mirror layer. If this experimental point is not taken into account, then the dependence again turns out to be close to linear approximation and gives correlation coefficient K = 0.963. The wavelength of 633 nm is close to the position of the plasmon resonance of gold (610 nm). This fact indicates that not only the reflection coefficient of gold contributes



Fig. 5. Dependences of the relative gain of planar SERS-structures on the basis of arrays of gold nanoparticles on the reflection coefficient of the mirror layer at laser wavelength of 514 nm (a) and 633 nm (b).

Table 2

Values of intensities of Raman signal from the amorphous carbon film obtained on SERS substrates based on gold and silver particle arrays.

SiO ₂ thickness, nm	Au			Ag	Ag		
	Laser wavelength, nm						
	488	514	633	488	514	633	
	Intensity of Raman signal, relative units						
10 20 66 170	$6,8 \times 10^{3}$ $8,5 \times 10^{3}$ $8,3 \times 10^{3}$ $2,0 \times 10^{3}$	$1,5 imes 10^4 \\ 1,8 imes 10^4 \\ 1,7 imes 10^4 \\ 0,2 imes 10^4$	$\begin{array}{c} 2{,}5\times10^{4}\\ 2{,}7\times10^{4}\\ 2{,}1\times10^{4}\\ 0{,}1\times10^{4} \end{array}$	$\begin{array}{c} 1,8 \times 10^{6} \\ 2,5 \times 10^{6} \\ 2,4 \times 10^{6} \\ 0,2 \times 10^{6} \end{array}$	$\begin{array}{c} 4,5\times 10^5 \\ 7,3\times 10^5 \\ 4,2\times 10^5 \\ 0,1\times 10^5 \end{array}$	$2,8 \times 10^4$ $3,4 \times 10^4$ $9,6 \times 10^4$ $0,3 \times 10^4$	



Fig. 6. Calculated dependences of interference relative intensity on thickness of SiO₂ layer at laser wavelengths (a) 488 nm; (b) 514 nm; (c) 633 nm.

to the enhancement of the Raman signal. We can clearly state that in this case additional amplification of the Raman signal is due to the interaction of plasmons of the array of gold nanoparticles with the surface plasmon of the underlying mirror layer of gold.

3.4. Thickness of dielectric layer

To determine the intermediate dielectric layer thickness influence on the efficiency of planar SERS structures with a self-assembled nanoparticle array two series of samples were prepared with different thicknesses of SiO_2 : (1) based on gold and (2) based on silver. In this series the nanoparticles of SERS-active layer and the mirror film were made of the same metal. The average particle size in the array was 40 nm for gold, and 25 nm for silver. The refractive index of SiO_2 according to ellipsometry measurements was ~1.47.

Table 2 shows the values of Raman intensities of the spectral G-band of amorphous carbon thin film for these series of samples. The results of SERS spectroscopy as in the previous cases indicate that the maximum enhancement of light scattering for fabricated SERS structures based on both silver and gold is observed at the wavelengths of exciting radiation close to the position of plasmon resonance of structures.

Table 2 indicates that for all the samples when using laser wavelengths of 488, 514 and 633 nm the minimum value of the gain is observed at SiO_2 layer thickness of 170 nm, and the maximum value at



Fig. 7. Raman spectra of amorphous carbon thin film deposited on various SERS structures based on an array of Au nanoparticles with an average size of 40 nm using a laser with a wavelength of 633 nm.

20 nm (except Series 2 samples at $\lambda_L = 633$ nm). It should be noted that maximum values of Raman signal intensity fall on a structure with SiO₂ thickness of 20 nm.

If we superimpose the experimental values on the calculated dependence of relative intensity in the interference, it turns out that the experimental points for SiO₂ thicknesses of 66 and 170 nm fit perfectly on the calculated curve (Fig. 6) regardless of the nanoparticle material (Ag or Au). If laser with wavelength of 488 nm is used, the experimental point for thickness of 66 nm is close to the interference maximum, and for 170 nm - to the minimum (Fig. 6 a). In the case of laser with a longer wavelength of 633 nm, the experimental values become farther from the maximum and minimum of the interference, but, nevertheless, they are in strict accordance with the calculated curve (Fig. 6 b). At the same time, the points for SiO₂ layer thickness of 10 and 20 nm drop sharply for both laser wavelengths and both Ag and Au metals. These facts again indicate that additional amplification of the Raman signal is due to the interaction of the nanoparticle array plasmons with the mirror film surface plasmon. Studying the work of G. Lévêque and O.J.F. Martin where the LSPR position of a similar structure is simulated [28] we noticed that according to their calculations the maximal plasmon absorption is expected for the thickness of the separating dielectric layer of 20 nm, which in practice correlates with the amplification of the Raman signal.

Fig. 7 shows the results of SERS-structure optimization under consideration with an amorphous carbon film as an investigation object for comparison at different stages. It can be seen, G and D lines of the Raman shift are not visible when we are dealing with a pure film of amorphous carbon. Moreover, they cannot be distinguished from the background signal, even with increasing sensitivity. When using only an Au plasmon particle array, G- and D-lines of the Raman shift become noticeable. The largest signal gain for gold is achieved when we have gold nanoparticle array with an average size of 40 nm separated by 20 nm thick SiO₂ layer from the mirror layer of the same nature.

4. Conclusion

We have shown that SERS-substrate containing SERS-active array of

nanoparticles, the mirror layer and the optically transparent material layer that separates them should be "tuned" to the used wavelength of the exciting laser in order to achieve good amplification of the Raman signal. It is necessary to choose the optimal size of nanoparticles in the array. The mirror layer should have the highest possible reflection coefficient and/or should be made of plasmon material. When using a mirror layer of plasmon metal, the thickness of the optically transparent layer should be small (we think within 30 nm). Otherwise, we must select the thickness from the condition of constructive interference taking into account the refractive index of the material.

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