Optical properties of polymer-graphene composites coated with gold and silver alloy nanoparticles

E V Boyko¹,², I A Kostogrud¹ and D V Smovzh¹,²

¹ Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia
² Novosibirsk State University, Novosibirsk, Russia

E-mail: renboyko@gmail.com

Abstract. The plasmon resonance phenomenon occurring in the system of graphene-polymer-nanoparticles of an alloy of gold and silver is investigated. The possibility of controlling the attenuation of the intensity of electromagnetic radiation passing through the sample by changing the composition and thickness of the deposited coating is shown. For the investigated gold and silver alloy nanoparticles, the highest degree of radiation attenuation falls on the wavelength range from 400 to 600 nm. It was shown that by changing the composition of the nanoparticles (changing the ratio of gold and silver in the alloy), it is possible to achieve the maximum selective light attenuation by more than 2.5 times in the 500 nm region. In the 700 nm region, light attenuation by not more than 2 times is achieved. It was revealed that the use of films with different metal ratios allows us to shift the position of plasmon absorption in the entire visible wavelength range.

1. Introduction

The number of studies devoted to the study of composites based on graphene materials and silver and gold nanoparticles is growing every year [1, 2]. There are various methods for producing such composites: the growth of metal nanostructures directly on graphene, the transfer of graphene to an array of previously deposited metal nanoparticles, or the functionalization of the surface of samples with graphene by metal nanoparticles [3–6]. In addition, graphene derivatives, such as graphene oxide [7, 8], also can be used to obtain hybrid nanostructures with plasmonic properties.

Plasmonic composite nanomaterials demonstrate various new optical properties, for instance, modulation of the optical response, local amplification of electromagnetic fields, etc. [9–12]. In addition, there are studies in which the possibility of enhancement nonlinear optical properties [13], as well as changing the optical response by applying an external electric field [14], was demonstrated.

Composite materials containing noble metal nanoparticles and graphene derivatives can also be used in various photocatalytic reactions in the visible radiation range [15]. The combination of surface plasmon resonance phenomenon and optimal electrical conductivity of graphene-metal composites can be used to amplify the photoelectric effect in graphene/metal nanoparticle systems, which opens up the possibility of creating photodetectors with an adjustable response in the visible and infrared ranges of electromagnetic radiation [16, 17].

This work is devoted to the study of the optical properties of graphene-metal nanoparticles of gold and silver alloy composites deposited using pulsed laser ablation.
2. Methods
Graphene was synthesized by chemical vapor deposition on a copper catalyst substrate. After the synthesis step, the obtained samples were analyzed with a Raman spectrometer T64000 Horiba Jobin Yvon with an excitation radiation wavelength of 514.5 nm.

Graphene was transferred onto a polymer surface (PET/EVA) using mechanical transfer method, described in [18]. Then, the substrates coated with graphene layers were functionalized using Au and Ag alloy nanoparticles in order to change locally the optical properties of the samples. The metal deposition process was performed by the method of Pulse Laser Ablation (ILA) in accordance with the scheme shown in figure 1. A target made of silver, gold or their alloy (metal purity of 99.99%) was installed in a special holder (not shown in figure 1.) and placed in a vacuum chamber. The chamber was a quartz tube with a diameter of 45 mm and a length of 700 mm. The end flange of the chamber, mounted opposite the target holder, had an input square (25 mm side) quartz window with a high transmittance for visible radiation. The second flange (blank flange) was equipped with a quick removal system to replace the target holder in the chamber. The system was evacuated using an ANEST IWATA ISP-250C SV oil-free foreline pump with a capacity of 250 L×min^{-1}, which made it possible to reach a maximum vacuum of 1 Pa. In all experiments, after reaching the maximum vacuum, the pump was cut off from the chamber using a shut-off valve, and then the chamber was filled with argon using the mass flow rate regulator RRG-10. Next, the shutoff valve was opened and argon was continuously pumped at low flow rates. The pressure in the chamber was maintained near a value of 60 Pa.

![Figure 1. Scheme of the experiment on functionalization of graphene layers by nanostructured films of silver, gold and their alloy by the ILA method.](image)

We used Nd: YAG laser radiation ILTI 407b (wavelength of 1064 nm, pulse duration of 9 ns). The second harmonic of radiation was focused on the target (wavelength of 532 nm, pulse duration of 7 ns). The number of laser pulses was 4000. Various modes of metal deposition on a graphene surface were used: sequential sputtering by alternately sputtering targets of pure silver and gold and simultaneous sputtering of targets from AgAu and AgAu_{4} alloys.

In the obtained composites, the optical properties were studied using an SF-2000 spectrophotometer, and absorption spectra were obtained in the range from 200 nm to 1100 nm.

3. Results and discussion
Figure 2 shows the transmission spectra of samples coated with a film of an alloy of gold and silver deposited upon irradiation of the target with 4000 pulses. The spectra were measured at various points along the vertical axis of the sample, starting from the edge and moving toward the center of deposition in increments of 1.2 mm. To measure the thickness of the films sprayed in different zones, calibration experiments were carried out with sputtering on quartz glass.

The transmission spectra of PET/EVA-graphene films coated with nanoparticles of various compositions are presented in figure 2. An increase in the concentration of gold in the film leads to a shift in the absorption peak to the IR region. In addition to a shift to the IR spectral region, an increase
in the gold concentration is accompanied by a broadening of the absorption peak. So for pure gold the region of the most effective absorption (550-800 nm) [19] is almost two times wider than that of silver [20]. It can be seen from the spectra in figure 2 that by varying the composition of the sprayed coatings and the spraying method, it is possible to shift the position of plasmon absorption in the entire optical wavelength range.
Figure 2. Absorption spectra of radiation of a polymer-graphene composite functionalized with nanoparticles: A) upon sequential irradiation of a silver target, then a gold target (2000 pulses in each case); B) similar to point “A” but with the reverse sequence of deposition of C) AgAu alloy (silver/gold) at a ratio of 1:4 (number of pulses – 4000); D) AgAu alloy at a ratio of 1:1 (number of pulses – 4000).

With an increase in the thickness of the metal film, the interference response of the film becomes less pronounced, which is probably due to the high value of the imaginary part of the refractive index.
of the metal. As the coating thickness increases, the plasmon absorption peak becomes more pronounced and shifts slightly toward the IR region. Upon reaching a coating thickness of 6-7 nm (the thickness of the metal coating from the periphery to the center of the sample varies linearly and is observed at a distance of 6.0 mm from the periphery), the position and depth of the plasmon peak stabilize. It is assumed that the attenuation of transmitted electromagnetic radiation at a small thickness of the metal film is associated with the phenomenon of plasmon absorption on small metal nanoparticles. For the indicated thickness, the transmittance of the samples in the plasmon resonance region is close to 24% (for AgAu 1:1), 23% (for AgAu 1:4), 28% (for Ag + Au), and 25% (for Au + Ag). With a further increase in the thickness of the metal coating and an increase in the number of coarse fraction nanoparticles (from 100 nm), the attenuation of the signal is enhanced due to plasmon scattering on these particles; in this case, the transmittance of the sample drops to 17% (for AgAu 1:1), 14% (for AgAu 1:4), 18% (for Ag + Au) and 14% (for Au + Ag). Thus, using nanoparticles made of an alloy of gold and silver, it is possible to achieve the maximum selective attenuation of light by more than 2.5 times in the region of 500 nm, while for 700 nm the attenuation decreases by no more than 2 times. When using gold and silver alloy nanoparticles, the region of the most effective plasmon absorption falls on the wavelength range of 400-600 nm, and the signal is attenuated by a maximum of 3 times in this wavelength range, which is associated with plasmon absorption and scattering.

Figure 3. Comparison of the transmission spectra of the optical signal with films of various compositions and without metal deposition.

Figure 3 shows a comparison of the transmission spectra of an optical signal transmitted through a polymer-graphene composite coated with films of various compositions. It can be seen from the spectra of pure silver and gold coatings that the maximum signal attenuation occurs in the wavelength range of 380–500 nm and 550–800 nm, respectively. For films with nanoparticles of a metal alloy with different stoichiometry, the optical signal is similar in shape to the signal for coating with silver nanoparticles.
An admixture of gold in the film in the case of successive deposition of nanoparticles, in both cases, leads to the appearance of an additional minimum in the region of 500–600 nm, while the signal attenuation related to gold particles in the region of 550–800 nm is not observed. The sequence of deposition of nanoparticles affects only the transparency of the samples; when silver is deposited after gold, the light transmission coefficient decreases, which can be explained by a higher reflectance of silver in the visible range of light. In the case of sputtering of an AgAu alloy of different stoichiometry, the signal is characterized by one minimum (plasmon resonance) shifted to the transition region between the positions of the plasmon resonances of gold and silver nanoparticles. In this case, a change in the stoichiometry of the composition by four times weakly shifts the position of the resonance of the alloy towards the IR region.

From the presented data, it can be concluded that an insignificant addition of silver in gold nanoparticles leads to a significant shift of the plasmon resonance frequency to the ultraviolet region. In all cases, no plasmon absorption peaks associated with gold nanoparticles are observed. During sequential sputtering, plasmon resonances of silver nanoparticles and an AgAu alloy with stoichiometry close to 1:1 are observed. When sputtering nanoparticles from alloys, only the signal for plasmon resonance of alloy nanoparticles is observed. Therefore, in the coating deposition technology used in the case of using a target made of a gold-silver alloy, the stoichiometry of the coating nanoparticles corresponds to the stoichiometry of the sprayed target. Otherwise, a second plasmon absorption peak corresponding to a different stoichiometry would appear in the transmission spectra. In the case of alternate deposition of metals on the surface of graphene, the formation of nanoparticles of metal alloy occurs. Interpolating the obtained experimental data, it can be assumed that the use of alloys with a higher gold content will lead to more effective attenuation of the signal in the wavelength range of 380–800 nm.

Thus, using a combination of the deposition of films of various compositions and thicknesses, photo filters can be obtained to control light transmission/absorption in different parts of the optical spectrum (figure 3). The obtained data set makes it possible to optimize the selectivity of the attenuation of light and use it when creating various optical filters.

Conclusions
It was shown that the intensity of the plasmon absorption peak depends directly on the thickness of the metal coating and the composition of nanoparticles: a deepening of the plasmon absorption peak with a simultaneous decrease in the transparency of the sample occurs with a change in the film thickness up to 6 nm. When the thickness of the metal coating is more than 6 nm, the depth of the plasmon peak does not change, while the total optical transmission of the sample continues to fall.

The possibility of controlling the attenuation of the intensity of electromagnetic radiation passing through the sample is shown. For the investigated gold and silver alloy nanoparticles, the highest degree of radiation attenuation falls on the wavelength range from 400 to 600 nm.

It is shown that by changing the composition of the nanoparticles (changing the ratio of gold and silver in the alloy), it is possible to achieve the maximum selective attenuation of light by more than 2.5 times in the region of 500 nm. In the 700 nm region, light attenuation by not more than 2 times is achieved.

It was revealed that the use of films with different metal ratios allows shifting the position of plasmon absorption in the entire optical wavelength range.

Acknowledgements
Experiments related to the creation of polymer-graphene-metal nanoparticle composites were financially supported by IT SB RAS (AAAA-A19-11906149008-3), experimental studies of the obtained composites optical properties were financially supported by Russian Foundation for Basic Research (Project No. 18-29-19099:18).
References

[1] Huang X, Qi X, Boey F and Zhang H 2012 Chem. Soc. Rev. 41 666

[2] Ferrari A C, Bonaccorso F, Fal’ko V, Novoselov et al. 2015 Nanoscale 7 4598

[3] Iyer G R S, Wang J, Wells G, Guruvenket S, Payne S, Bradley M and Borondics F 2014 ACS Nano 8 6353

[4] Echtermeyer T J, Nene P S, Trushin M, Gorbachev R V., Eidcn A L, Milana S, Sun Z, Schliemann J, Lidorikis E, Novoselov K S and Ferrari A C 2014 Nano Lett. 14 3733

[5] He F A, Fan J T, Song F, Zhang L M and Lai-Wa Chan H 2011 Nanoscale 3 1182

[6] Muszynski R, Seger B and Kamat P V. 2008 J. Phys. Chem. C 112 5263

[7] Nergiz S Z, Gandra N and Singamaneni S 2014 Carbon N. Y. 66 585

[8] Lan N T, Chi D T, Dinh N X, Hung N D, Lan H, Tuan P A, Thang L H, Trung N N, Hoa N Q, Huy T Q, Quy N Van, Duong T T, Phan V N and Le A T 2014 J. Alloys Compd. 615 843

[9] Wu J, Shi W and Chopra N 2014 Carbon N. Y. 68 708

[10] Hoggard A, Wang L Y, Ma L, Fang Y, You G, Olson J, Liu Z, Chang W S, Ajayan P M and Link S 2013 ACS Nano 7 11209

[11] Zaniecki A M, Schriver M, Gloria Lee J, Crommie M F and Zettl A 2013 Appl. Phys. Lett. 102 023108

[12] Zhu M, Chen P and Liu M 2011 ACS Nano 5 4529–36

[13] Kalanour B S, Bisht P B, Akbar Ali S, Baby T T and Ramaprabhu S 2012 J. Opt. Soc. Am. B 29 669

[14] Emani N K, Chung T F, Ni X, Kildishev A V., Chen Y P and Boltasseva A 2012 Nano Lett. 12 5202

[15] Li Y and Chopra N 2015 Phys. Chem. Chem. Phys. 17 12881

[16] Kim U J, Yoo S, Park Y, Shin M, Kim J, Jeong H, Baik C W, Roh Y G, Lee J, Im K, Son H, Hwang S, Lee C W and Park S 2015 ACS Photonics 2 506

[17] Fan G Q, Zhuo Q Q, Zhu J J, Xu Z Q, Cheng P P, Li Y Q, Sun X H, Lee S T and Tang J X 2012 J. Mater. Chem. 22 15614

[18] Kostogrud I A, Boyko E V. and Smovzh D V. 2018 Mater. Chem. Phys. 219 67

[19] Boyko E V and Smovzh D V 2019 J. Phys. Conf. Ser. 1359 12100

[20] Boyko E V and Kostogrud I A 2019 XXXV Sib. Thermophys. Semin. J. Phys. Conf. Ser. 1382 12150