Plasmon resonance in CVD graphene-silver nanoparticle composites

E V Boyko and I A Kostogrud
Kutateladze Institute of Thermophysics SB RAS, Lavrentiev ave. 1, Novosibirsk, Russia
Novosibirsk State University, Pirogov str. 1, Novosibirsk, Russia
E-mail: renboyko@gmail.com

Abstract. Investigation results on the morphology and optical properties of polymer-graphene composites with silver nanoparticles deposited by pulsed laser ablation are presented. Graphene was obtained by the CVD method and transferred to PET/EVA polymer through thermal pressing. It has been established that with an increase in the thickness of deposited silver film, a transition from bimodal distribution of particles to formation of elongated rectangular nanostructures is observed. A similar phenomenon can be explained by accumulation of deposited silver particles along the boundaries of adjacent graphene crystallites. It is experimentally shown that the degree of plasmon absorption depends strongly on the mass-average thickness of the deposited metal coating and size of nanoparticles. Deepening of the peak of plasmon absorption simultaneously with a general decrease in sample transparency occurs when the film thickness is changed up to 6 nm. A further increase in thickness does not affect the intensity of plasmon absorption and scattering, but leads to a general decrease in transparency of the polymer-graphene-silver composite. It is shown that the highest degree of radiation attenuation is in the wavelength range from 400 to 600 nm.

1. Introduction
Due to such properties as good chemical stability, exceptional optical properties, high biocompatibility, solubility in water, etc [1], silver nanoparticles (Ag) are recognized as an excellent material for immunological methods of analysis; photothermal therapy of cancer cells, and creation of photovoltaic devices, based on the phenomenon of surface plasmon resonance (SPR). This phenomenon occurs due to collective oscillations of electron gas caused by its interaction with electromagnetic radiation [2]. According to the results of [3, 4], the geometrical parameters of silver nanoparticles (their shape and size) can have a significant impact on the resonant properties of devices. The authors of [5] showed that an increase in the size of nanoparticles intensifies plasmon resonance and, therefore, improves the sensitivity of SPR-based devices. In addition, the chemical stability of nanoparticles also affects the characteristics of devices greatly [6, 7]. Integration of metal nanostructures with two-dimensional (2D) materials attracted the attention of researchers in connection with the possibility of enhancing the resonant properties of such hybrid structures [8].

One of the most striking examples of 2D materials is graphene. This material is one of the allotropic modifications of carbon and has a number of interesting properties: impermeability for a variety of gases, significant thermal conductivity, high mobility of charge carriers, strength [9, 10]. In addition, it has universal optical transparency from the visible to infrared ranges of radiation due to its special electronic structure [11]. Graphene is widely used, especially as electrochemical and bioelectrochemical sensors [12], while metal graphene-based nanocomposites are finding an increasing number of practical applications [13]. The inclusion of silver nanoparticles in graphene allows obtaining the composites with antibacterial properties [14]. Nanoparticles of silver and other noble metals deposited on graphene can be used in the food industry to detect various prohibited food additives and toxins [15]. Moreover, the composites of silver and graphene can be used as the components in fuel cells [16], as well as electrochemical sensors [17]. A large surface areas as well as unique optical and plasmon properties make graphene a suitable candidate to be used as a component, when making the plasmon devices [18]. However, the properties of such systems are little studied, so the research in this area is required.
2. Experiment
Graphene was synthesized in a thermal reactor using the method of chemical vapor deposition on a copper catalytic substrate at the temperature of 1075°C in the Ar/H2/CH4 gas mixture under the atmospheric pressure. After the synthesis stage, the samples were certified by the Raman spectroscopy using a T64000 Horiba/JobinYvon Raman spectrometer; the wavelength of exciting radiation was 514.5 nm.

Graphene was transferred to the polymer surface (PET/EVA) using the mechanical method. PET (polyethylene terephthalate) played as a frame, while EVA (ethylene vinyl acetate) acted as a binder between graphene and PET. A PET/EVA polymer sheet was deposited at a temperature of 190°C on a copper substrate with synthesized graphene. The polymer coating was separated from the copper foil mechanically, while the samples were mechanically stabilized to minimize graphene deformation. Next, silver nanoparticles were deposited by pulsed laser ablation. The number of laser pulses was varied from 1000 to 6000. At this stage, second harmonic radiation of the Nd: YAG ILTI 407b laser with a wavelength of 532 nm and pulse duration of 9 ns was used. Ablation was carried out in the atmosphere of background argon under the pressure of 60 Pa.

The polymer-graphene-silver composites obtained were studied by scanning electron microscopy using an SF-2000 spectrophotometer. As a result, data on the surface morphology were obtained, and the optical properties were studied in detail: radiation transmission spectra were obtained in the range from 200 nm to 1100 nm.

3. Results and discussion
To characterize the thickness of the sprayed metal coating, a film was deposited on the quartz substrate of 18×12 mm. This coating was analyzed at various points using an SF-2000 spectrophotometer. The sample was shifted relative to the inlet window of the spectrophotometer using a coordinate mechanism with a step of 1.2 mm (the movement error was 0.01 mm). According to the transmission spectra obtained, the thickness distribution along the sample was determined (Fig. 1).

Data obtained through the SEM analysis are presented in Fig. 2.
Figure 2. SEM photos (A - D) of the polymer-graphene composite surface functionalized with silver nanoparticles. Number of laser pulses - 6000. The photos are made at different points of the vertical axis of sample starting from A (sample edge) to D (deposition center).

The photographs were made while moving from the sample edge to the deposition center (from A to D) with a step of 2.5 mm. A change in the size of silver nanoparticles with displacement from the sample edge is well traced: they enlarge, keeping the bimodal distribution characteristic of the laser synthesis of nanoparticles [19, 20]. The diameter of small nanoparticles does not exceed 20 nm, while the characteristic size of large particles varies from 20 to 150 nm. In photo B you can see the beginning of formation of elongated rectangular nanostructures, whose size increases when approaching the center of silver deposition. At the very spot of deposition (photo D), the large fraction becomes dominant, while its lateral size is about 300 nm. The appearance of such threadlike structures can be caused by agglomeration of silver nanoparticles along the junctions of boundaries of individual graphene domains: the sprayed silver particles have a high mobility on the sample surface, which leads to formation of a continuous coating and particles of a large fraction.

The transmission spectra of silver films deposited at target radiation with 6000 pulses are presented in Fig. 3 (A); Fig. 3 (B) shows the attenuation spectrum of radiation transmitted through the sample. The measurements were carried out at various points along the vertical axis of the sample, starting from the edge and moving towards the center of deposition.
Figure 3. A) Transmission spectra of silver films deposited at target irradiation with 6000 pulses. The arrows indicate the direction of plasmon absorption peak displacement. B) Effectiveness of light attenuation after applying a silver film.

As the thickness of silver coating increases, the plasmon absorption peak becomes more pronounced and shifts towards IR waves [21]. Upon reaching a coating thickness of 6-7 nm, the position and depth of the plasmon peak stabilize. It is assumed that attenuation of transmitted radiation for a metal film with small thickness is associated with the phenomenon of plasmon absorption on small particles. For the specified thickness, transmittance of samples in the region of plasmon resonance is close to 20%. With a further increase in the silver coating thickness and number of silver nanoparticles of a large fraction (from 150 nm), signal attenuation is enhanced due to plasmon scattering on these particles; at that, sample transmittance drops to 5%. Thus, it was possible to achieve maximum selective attenuation of light by more than 7 times in the region of 450 nm, while for 700 nm, attenuation is reduced by no more than 2 times. It was revealed that with increasing thickness, the interference response of the film becomes less pronounced, which is probably caused by the high value of the imaginary part of the refractive index of metal. The resulting data set allows optimization of light attenuation selectivity and application when creating various photo filters.

Conclusions
As a result, the surface morphology of polymer-graphene samples obtained by chemical deposition from the gas phase, with silver nanoparticles deposited there by laser ablation, was investigated, and their optical properties were studied in detail. It is shown that with increasing film thickness, its morphology changes significantly: starting with bimodal distribution of particles at the sample periphery and ending with a large number of formed elongated rectangular nanostructures at the center of deposition. It is assumed that their formation is based on accumulation of sprayed nanoparticles along the boundaries of adjacent graphene domains.

It is shown that the intensity of plasmon absorption peak depends directly on the silver coating thickness and size of nanoparticles: the deepening of plasmon absorption peak simultaneously with overall decrease in sample transparency occurs when the film thickness changes to 6 nm. When the metal coating thickness is more than 6 nm, the depth of plasmon peak does not change, while total optical transmission of the sample continues decreasing. Thus, the possibility of controlling attenuation of the intensity of electromagnetic radiation passing through a sample is shown. The highest degree of radiation attenuation is in the wavelength range from 400 to 600 nm.

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References
[1] Daniel M C, Astruc D 2004 Chemical Reviews 104 293–346
[2] Richens J L, O’Shea P 2014 Biomedical Imaging
[3] Aden A L, Kerker M 1951 J. Appl. Phys. 22 1242–6
[4] Mie G 1908 Ann. Phys. 330 377–445
[5] Kumar M, Sandeep C S S, Kumar G, Mishra Y K, Phili R, Reddy G B 2014 Plasmonics 9 129–36
[6] Kumar M, Reddy G B 2010 Phys. E Low-Dimens. Syst. Nanostruct. 43 470–4
[7] Kumar M, Reddy G B 2016 Plasmonics 11 261–7
[8] Mohanty G, Sahoo B K, Akhtar J 2015 Opt. Quantum Electron 47 1911–8
[9] Novoselov K S, Geim A K, Morozov S V, D. Zhang J Y, Dubonos S V, Grigorieva I V, Firsov A A 2004 Science 306 666
[10] Lee C, Wei X, Kysar J W, Hone J 2008 Science 321 385
[11] Nair R R et al. 2008 Science 320 1308
[12] Chia J S Y, Tan M T T, Khiew P S, Chin J K, Siong C W 2015 Sens. Actuators B, 210 558–65
[13] Yola M L, Eren T, Atar N 2014 Electrochim. Acta 125 38–47
[14] Gu D, Chang X, Zhai X, Sun S, Li Z, Liu T, Dong L, Yin Y 2016 Ceram. Int. 42 9769–78
[15] Yola M L, Gupta V K, Atar N 2016 A Mater. Sci. Eng.: C 61 368–75
[16] Gupta V K, Yola M L, Atar N, Üstündağ Z, Solak A O 2014 J. Mol. Liq. 191 172–6
[17] Atar N, Yola M L, Eren T 2016 Appl. Surf. Sci. 362 315–22
[18] Wu Z et al 2013 IEEE Sensors J 13 (2) 777–82
[19] Starinskii S V, Shukhov Y G, Bulgakov V A 2016 Tech. Phys. Lett. 42 411–4 doi:10.1134/S1063785016040258.
[20] Starinskii S V, Shukhov Y G, Bulgakov A V 2017 Quantum Electron 47 343–6 doi:10.1070/QEL16253.
[21] Safonov A I, Sulyaeva S V, Timoshenko N I, Starinskiy S V 2016 Thin Solid Films 603 313–6 doi:10.1016/j.tsf.2016.02.030.