Morphology and optical properties of films based on CVD graphene and nanostructured gold

E V Boyko and D V Smovzh
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. In the work presented, the polymer-graphene-gold composites obtained by the methods of chemical vapor deposition and pulsed laser ablation (PLA) are studied. The morphological and optical properties of the given samples are studied in detail. It is shown that with an increase in the number of laser pulses in the PLA method, the metal coating transforms from separate small gold particles to a continuous cover with the presence of large nanoparticles. It is shown that a change in the gold film thickness influences significantly the efficiency of plasmon attenuation of a signal: with an increase in the average mass thickness, the effect increases and reaches its maximal value at film thickness of 6 nm. It is shown that the most intense plasmon absorption occurs in the wavelength range from 550 to 750 nm. A further increase in the thickness of metal coating decreases sample transparency in the studied range and does not affect the intensity of plasmon absorption and scattering.

1. Introduction

Due to their unique properties [1, 2, 3], gold nanoparticles are used in various areas of human activity: medicine, pharmaceutical chemistry, food industry, engineering, etc. They are used when producing optical sensors, biomedical devices, anticancer drugs, cosmetics, and protective coatings for various equipment [4, 5]. Nanoscale particles of noble metals are the unique structures that not only affect the physicochemical properties of various systems, but also demonstrate interesting physical phenomena. The phenomenon of surface plasmon resonance (SPR) deserves special attention [6]. The essence of this phenomenon is the occurrence of collective oscillations of conduction electrons due to incident electromagnetic radiation. Such surface plasmons have a number of interesting properties: their brightness is very high, so light scattered from individual nanoparticles can be detected using simple optical systems; they have a peak in the spectra of light reflected at a certain wavelength, depending on the size, shape and material of the particles; gold nanoparticles (Au) scatter light effectively in the visible range. However, in some cases, metallic nanostructures alone may not be enough: their sensitivity can be enhanced by integration with other materials. Therefore, from this point of view, the composites based on gold and graphene nanoparticles are of a particular interest.

Graphene, attracted great attention of researchers in such fields as physics, chemistry and materials science, demonstrates exceptional physical properties and chemical resistance [7]. Due to its unique two-dimensional crystal structure, graphene can act as a catalyst carrier. Usually, metallic nanoparticles deposited on the graphene surface exhibit increased catalytic activity as a result of good
dispersion of nanoparticles over the entire graphene surface and high mobility of discharge carriers at the graphene-metal interface [8,9]. Together with catalysis, graphene is widely used in creation of optoelectronic devices [10]. Plasmon properties of graphene can be easily changed by doping, exposure to external electric fields or temperature changes. By itself, graphene is quite transparent: absorption in the visible range is 2.3%. It is shown in [11], [12] that combining graphene with other materials, such as nanoparticles of noble metals, is a promising and reliable approach to increasing the absorption of visible light in graphene-based photodetectors. The coefficient of radiation absorption increases dramatically in the GHz - THz ranges [13]. Thus, in the graphene-based optoelectronic devices, the frequencies of surface plasmon resonance can be used in both the visible and gigahertz ranges. This has several advantages over conventional optoelectronic devices.

The growing interest in the system of graphene/noble metal nanoparticles is caused by their enormous potential in various industries: solar energy, catalysis, medicine, etc. Thus, the purpose of this work is to study the properties of these composites, in particular, AuNPs/Graphene.

2. Experiment

Graphene was synthesized in a thermal reactor using the method of chemical vapor deposition on a copper catalytic substrate. The synthesis temperature was 1075°C, while the copper substrate was in the Ar/H₂/CH₄ gas mixture under the atmospheric pressure. After the synthesis stage, the graphene coating was certified using a T64000 Horiba Jobin Yvon Raman spectrometer; the wavelength of exciting radiation was 514.5 nm.

After successful certification of samples, graphene was transferred to polyethylene terephthalate/ethylene-vinyl acetate (PET/EVA) polymer. At this stage, the method of mechanical transfer, based on thermal pressing, was used. The PET/EVA polymer coating was deposited on a copper substrate with graphene at the temperature of 190°C. The resulting samples were mechanically stabilized during copper foil separation to minimize deformation of the graphene layer. A more detailed description of the graphene transfer process is presented in [14].

The polymer graphene composites obtained as a result of transfer stage were coated with gold nanoparticles using the laser ablation method with various numbers of pulses: 500 - 6000 pulses. (ILTI 407b Nd: YAG laser radiation with the wavelength of 532 nm; pulse duration was 9 ns).

Using scanning electron microscopy, the morphology of the obtained samples was analyzed. In addition, their optical properties were investigated: the spectra of radiation attenuation in the range from 200 nm to 1100 nm were obtained using the SF-2000 spectrophotometer.

3. Results and discussion

To determine the characteristic thickness of deposited metal coatings, a gold film was deposited on the surface of a fused quartz substrate of 18 × 12 mm. The number of laser pulses was 5000. The sample was analyzed at various points using the SF-2000 spectrophotometer. The sample was shifted relative to the inlet window of spectrophotometer with a step of 1.2 mm using a coordinate mechanism; the positioning accuracy was 0.01 mm. An area of 1 mm was separated by the entrance slit of spectrophotometer. It was found that when the sample was displaced along the horizontal direction, the optical properties remained almost unchanged.

The transmission spectra taken at various points along the vertical axis of sample are shown in Fig. 1. The film thickness was determined by scanning electron microscopy.
Upon further deposition, it was taken into account that the thickness of films is directly proportional to the number of laser pulses.

Data obtained as a result of SEM analysis, as well as spectra of radiation transmission are presented in Figs. 2 and 3. The SEM photographs and spectra were taken at different points along the normal to the sample edge from the center of gold deposition. It was experimentally shown that the mass concentration of deposited gold decreases linearly in the direction from the sample edge to the center of deposition.

**Figure 1.** Transmission spectra of the gold film on a quartz substrate at various points of the vertical axis with a step of 1.2 mm.

**Figure 2.** SEM photos (A - C) of the polymer-graphene composite surface functionalized with gold nanoparticles upon target radiation with 6000 pulses and transmission spectra (D).
Dependence of the density of nanoparticle deposition when moving from the sample edge to the center of deposition is clearly visible in the photographs presented (it is minimal in Fig. 2a and Fig. 3a and rises to Fig. 2c and Fig. 3c, respectively). The character of a particle size change, while moving towards the deposition center, is different for different modes of deposition. When the substrate is functionalized with 6000 pulses, in the region of low mass concentration of deposition, an island structure with a large fill factor is formed; the characteristic size of individual islands varies greatly, reaching 300-400 nm. Closer to the deposition center, the islands are replaced by large nanoparticles with a size of about 200 nm. Directly in the very center of deposition, the large particles become the dominant fraction with the same characteristic size (200 nm). With the deposition mode of 1000 laser pulses, there is a transition from separately lying gold nanoparticles with an average size not exceeding 20 nm to a continuous coating. The difference in the morphology of deposited films in the areas with different mass concentrations of deposition and during deposition with a different number of laser pulses suggests that the metal film structure is determined by the processes of nanoparticle coagulation on the surface. In all cases, the nanoparticles with a size of about 20 nm are observed on the deposited surfaces. Their formation can occur during condensation of vapors of the sprayed material in a jet, which is formed during ablation of the material; when hitting the surface, the mobility of particles is sufficient to form the larger nanoparticles and continuous coating.

The transmission spectra in the wavelength range from ultraviolet to infrared radiation with different amounts of laser pulses (1000 and 6000) are shown in Figs. 2d and 3d. The measurements were carried out at several points corresponding to different mass thicknesses of deposited metal coating. The region of most effective plasmon absorption is in the 550-750 nm wavelength range. The plasmon absorption efficiency of the samples presented increases with increasing mass concentration of deposition and reaches a maximum when the average mass thickness of the film is 6 nm. At that, with an increase in deposition thickness, general weakening of the optical signal, corresponding to data obtained on a quartz substrate, occurs, Fig. 1a. The observed signal attenuation
at low mass concentrations of deposition can be associated with plasmon absorption on the gold nanoparticles, an increase in the coating thickness, and an increase in the fraction of large nanoparticles of more than 100 nm; in the sprayed film signal attenuation increases due to plasmon scattering on nanoparticles. When the mass-average film thickness is 6 nm, the optical properties of the film stabilize. Thus, in the resulting graphen-polymer-gold composites, the maximum signal attenuation by the factor of 3 was achieved due to plasmon absorption and scattering in the range of wavelengths 550-750. These structures can be used to make the optical filters or systems that have selective absorption in the above wavelength range.

Conclusions
The system of gold nanoparticles and graphene, synthesized by chemical vapor deposition on a copper catalyst substrate, was investigated. The morphological and optical properties of samples were analyzed in detail. It is shown that with an increase in the number of laser pulses, a metal coating is transferred from separately lying small gold particles to a continuous cover with large nanoparticles. The study of the optical properties of the system showed that the plasmon absorption peak depends on the degree of sample coverage with gold nanoparticles. With an increase in the thickness of the gold film, the efficiency of plasmon attenuation of a signal increases and reaches the maximum value when the average mass thickness of the film is 6 nm. With a further increase in the coating thickness, the intensity of plasmon absorption and scattering does not change, while the sample transparency in the studied range decreases. It is shown that the most intense plasmon absorption occurs in the wavelength range from 550 to 750 nm.

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