The dependence of the graphene electrical resistance on mechanical deformation

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Abstract. In this work, the piezoresistive properties of polymer-graphene composites were investigated. The electrical resistance of these samples ranged from 693 to 1277 Ohm/sq for single-layer graphene coating, and from 477 to 1096 Ohm/sq for multilayer coating. It was shown that with a tensile strain of 4%, the maximum gauge factor was 100. For bending with a radius of curvature of 70 mm, which corresponds to a stretch of 0.75%, the maximum gauge factor was 34. It is shown that samples with a single-layer graphene coating are more resistant to deformation processes – their electrical resistance changes less than in samples with a multilayer graphene coating. Such a phenomenon can be associated with an increased concentration of defects and imperfections in graphene structures, which, in the case of a multilayer coating, leads to lower strength of the entire structure and much more destructive consequences in tension. A multilayer coating can have a heterogeneous structure: individual multilayer islands can be connected by single-layer sections. The gap between the latter leads to a significant drop in the electrical resistance of the entire sample.

1. Introduction

Over the past decades, sensors based on the piezoresistive phenomenon have become widespread. This phenomenon determines the degree of change in the electrical resistance of the material in which it occurs due to mechanical stress [1]. The phenomenon of piezoresistivity is the basis of many types of sensors, such as gyroscopes, scales, pressure and acceleration sensors, dynamometers, torque sensors, etc. [2]. Due to significant progress in the field of nanotechnology and the ubiquitous process of miniaturization of all devices, the transition to small sensors with high sensitivity is inevitable. Among the materials used as a sensitive element of such sensors, the most common are allotropic carbon modifications: for instance, carbon nanotubes, carbon nanofibres, graphene, etc. These materials turned out to be extremely attractive as candidates for the creation of piezoresistors, as evidenced by the growing number of studies in this field [3–8]. For instance, piezoresistive sensors based on single-walled carbon nanotubes (SWNTs) were investigated by Stampfer et al. [9], and it was shown theoretically and experimentally that ballistically conducting SWNTs exhibit nonlinear piezoresistive sensitivities of up to 1500 (applied strain was equal to 1%). At the same time, the gauge factor of silicon is one order of magnitude lower and is about 200 [10]. However, graphene is the most interesting material in terms of application as the piezoresistor’s main component. This material is currently one of the most widely studied carbon materials because of its excellent mechanical and electrical properties, and special two-dimensional architecture, which gives an advantage over other carbon materials (for instance, CNTs). Given that graphene is one of the most durable materials (~ 1
TPa), graphene-based sensors can withstand more significant mechanical deformations compared to other existing materials.

Every year, several works are devoted to the study of the phenomenon of piezoresistivity in graphene-related materials [11–15]. For example, in the work [16] the mulberry paper-based graphene strain sensor with a gauge factor of 3.82 was demonstrated. In the work [17], the authors obtained a sample with a gauge factor of about 6.1 based on graphene grown by a CVD method on a copper substrate, followed by transfer to a Si/SiO$_2$ substrate. However, at the same time in the work [11], the gauge factor of the graphene monolayer, obtained by the same CVD method and then transferred to the polymer substrate from polydimethylsiloxane (PDMS), was 151. In the work [18], where the authors used multilayer graphene as the basis of deformation sensors, a gauge factor of 300 units was achieved.

A significant number of studies in this area confirm the importance and relevance of using graphene as the basis for piezoresistive (strain gauge) sensors; however, disparate data on strain sensitivity coefficients indicate that an unambiguous technique for creating graphene-based strain gauges has not yet been developed. This work is devoted to the study of the strain sensing properties of graphene materials obtained using the chemical vapor deposition (CVD) method.

2. Methods
Graphene was synthesized using a chemical vapor deposition (CVD) method on the surface of a copper catalyst substrate. Two types of samples were prepared – with multilayer and single-layer graphene coatings. The graphene-coated samples were analyzed using Raman spectroscopy on a T64000 Raman spectrometer manufactured by Horiba Jobin Yvon, with an excitation radiation wavelength of 514.5 nm. Pictures of the copper foil surface coated with graphene were taken using an Olympus BX51M optical microscope.

Graphene was transferred onto a PET/EVA polymer surface (polyethylene terephthalate/ethylene vinyl acetate) by heat pressing of copper-graphene samples with a PET/EVA polymer followed by chemical etching of a copper substrate in a 30% solution of nitric acid (HNO$_3$).

In the obtained polymer-graphene composites, the piezoresistive properties of graphene materials under various types of deformation were investigated. For this purpose, the Handpi HLA/HLB test bench was used.

The sensitivity (gauge factor) at a given deformation was measured as the ratio of the absolute value of the difference in electrical resistance before and after deformation to the electrical resistance before deformation:

$$T = \left| \frac{R_{\text{before}} - R_{\text{after}}}{R_{\text{before}}} \right| \times 100\%$$

here $R_{\text{before}}$ and $R_{\text{after}}$ are electrical resistances of the sample before and after deformation, respectively, $\varepsilon$ is the elongation of the sample.

3. Results and discussion
Samples with single-layer and multi-layer graphene coatings were used in the work, which is confirmed by Raman spectroscopy data taken from the samples immediately after the synthesis stage.
Figure 1. A) The Raman spectra of a single-layer and multilayer graphene coating are indicated by black and red lines, respectively. B) Optical microscopy of a single-layer graphene coating on a copper substrate and its Raman spectra, taken at two points (1 and 2) of the surface after the graphene synthesis stage.

The recorded spectra contain D, G, and 2D bands characteristic of graphite structures. The characteristic FWHM of the 2D band for single-layer graphene is about 30 cm\(^{-1}\). With an increase in the number of layers of graphene coating, the FWHM of the 2D band increases. Thus, for all samples after synthesis on copper, the FWHM of the 2D line and the intensity ratio \(I_{2D}/I_G\) were measured; the condition at which FWHM is equal to about 30 cm\(^{-1}\), and the ratio \(I_{2D}/I_G > 1\) corresponds to single-layer graphene; while multilayer graphene is characterized by the condition at which FWHM is more than 40 cm\(^{-1}\), and the ratio \(I_{2D}/I_G < 1\).

Figure 2 shows the electrical resistances of the obtained polymer-graphene composites.
Figure 2. The initial electrical resistance of the obtained polymer-graphene composites.

As a result of the synthesis and transfer procedures, polymer graphene composites were obtained, whose electrical resistance varied from 693 to 1277 Ohm/sq for single-layer graphene coating and from 477 to 1096 Ohm/sq – for multilayer coating.

Figure 3. Scheme of deformation of polymer-graphene samples.

To study the piezoresistive properties of the obtained composites, the samples were stretched by 1, 2, 3, and 4% according to the scheme shown in Fig. 3. Stretches of more than 4% led to irreversible deformation of the PET/EVA polymer substrate. The results are presented in Figure 4.
At a 1% elongation of the sample, the electrical resistance for both types of graphene coatings (single-layer and multilayer) changed only slightly. However, further tension led to a gradual increase in the electrical resistance of the samples. It is worth noting that the increase in resistance for a multilayer coating is faster, in comparison with samples coated with a single layer of graphene. This may be due to an increased concentration of defects and imperfections in graphene structures, which, in the case of a multilayer coating leads to lower strength of the entire structure and much more destructive consequences in tension. A multilayer coating can have a heterogeneous structure: individual multilayer islands can be connected by single-layer sections. The gap between the latter leads to a significant drop in the electrical resistance of the entire sample.

In the case of a single-layer graphene coating, the structure is more uniform and with fewer defects and more resistant to deformation: when the sample is stretched by 3%, the gauge factor is ~ 1 and ~ 8 for a single-layer and multi-layer coating, respectively.
For multiple stretchings, the results of which are shown in Fig. 5, samples with a multilayer graphene coating demonstrate good repeatability (compared to a single-layer coating) with a gradual increase in the total electrical resistance, which is a consequence of the gradual destruction of bonds inside graphene layers. The initial electrical resistance of the samples is noticeably lower (Figure 5, cycle # 0) in comparison with the subsequent values of that at the undeformed state. This is due to the consequences of the process of installing the sample in the test bench: there is slight damage to the graphene layer in the places where the clamps are attached to the sample (Figure 3).

Samples with a multilayer graphene coating showed a greater gauge factor, and, with each tensile cycle, the total electrical resistance gradually increased. With a tension of 4%, the coefficient of strain sensitivity reached 100 (Figure 5).

Tests of the sensitivity of composites at various bending radii (20, 50, 70, and 100 mm) were also conducted. However, for these tests, the initial structure of graphene/polymer samples was modified to increase the strain sensitivity coefficient, the overall safety of the graphene coating, and, as a consequence, the repeatability of the results. As a result, the following structure was tested:

![Figure 6. Dual samples (labeled # 1 and # 2) of polymer graphene composites.](image)

With this configuration, it was possible to achieve higher values of gauge factors (in comparison with the bending of the samples of the initial configuration), Figure 7.
Figure 7. A) The averaged measurement results, and B) the results of cyclic measurements of the electrical resistance of samples in bending with different radii of curvature. (the zero cycle is the initial resistance of the composite, each subsequent even cycle is the bending of the sample).

Also, as in the case of tension, initially, the samples have lower electrical resistance, but after preparing the samples for testing, due to deformations, a slight decrease in the conductivity of the samples occurs. With a sample thickness of 0.5 mm, bends with radii of curvature of 100, 70, 50, and 20 mm correspond to sample elongation of 0.5, 0.75, 1, and 2.5%.

In the case of using dual samples, a decrease in the electrical resistance during bending occurs, which can be explained by the pressing of graphene layers against each other, leading to the better electrical conductivity of the entire sample. However, with a gradual decrease in the curvature radius of the bend, a smooth increase in the electrical resistance of the entire composite in the undeformed state occurs due to damage to the graphene structure. The highest gauge factor was 34 units when bending with a radius of curvature of 70 mm.

Conclusion
As a result of this work, the piezoelectric properties of polymer-graphene composites were investigated. The electrical resistance of these samples ranged from 693 to 1277 Ohm/sq for single-layer graphene coating, and from 477 to 1096 Ohm/sq for multilayer coating.

It is shown that, under tension, specimens with a single-layer graphene coating are more resistant to deformation processes – their electrical resistance changes less compared to that of the samples with a multilayer graphene coating.

It was shown that with a tensile strain of 4% the gauge factor was 100. For bending, the maximum coefficient of sensitivity was 34 for bending with a radius of curvature of 70 mm, which corresponds to a tensile strain of 0.75%. This difference can be explained by the different contributions of two competing processes – on the one hand, ruptures and damage to graphene structures under both types of deformation, and on the other hand, a more dense arrangement of graphene layers under bending conditions (as a result of using dual samples), which leads to an increase in the electrical conductivity of the sample.
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