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Preparation of Transparent Conducting Films from CVD Graphene by Lamination and Their Characterization

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Abstract—In this work we use the method of direct transfer of graphene grown by chemical vapor deposition (CVD) onto a transparent polymer substrate for obtaining a transparent conducting (TC) film. In order to implement this, we use a standard laminator and a film for lamination. A copper foil with the CVD graphene is glued by the laminator to the polymer film. After copper etching, a TC film with improved electrical and optical characteristics is obtained.

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INTRODUCTION

As is known, transparent conductors (TCs) are widely applied in various photoelectric devices, such as liquid crystal displays, organic light-emitting diodes, sensor panels, and solar cells. They are a thin conductor layer with less than 100 nm thickness deposited onto a transparent substrate from glass or polymer. Metal oxides, conducting polymers, composites of carbon nanotubes, and graphene are used as conductors. At present, the main material for manufacturing TCs is indium tin oxide (ITO), which possesses high transparency and low surface resistance. However, ITO has two substantial disadvantages: high cost and fragility. Therefore, significant efforts are made to manufacture TC films based on carbon nanomaterials. One of the directions for obtaining TCs is the use of carbon nanotubes [1, 2]. The preparation of thin films from a polymer composite which includes carbon nanotubes made it possible to obtain a transmission coefficient of 70% and surface resistance of 90 kOhm/□ [3]. These parameters are insufficient for competition with ITO; therefore, various technologies are proposed for preparing TCs from carbon nanotubes with improved parameters of transparency and conductance [4]. TC films based on graphene were obtained in [5]. The process of film preparation was rather complicated. A suspension of graphene oxide was obtained from graphite by chemical oxidation and centrifugation. Then, the graphene suspension was obtained by chemical reduction with the application of hydrazine. The graphene suspension was converted into a film on a filtering membrane and transferred onto a quartz substrate. These samples were annealed for removing oxygen and impurity residuals. The graphene films possessed a surface resistance less than 2 kOhm/□ and a transparency exceeding 80% at a wavelength of 550 nm. These properties are considered quite sufficient for many applications, such as TC films for sensor panels. A similar method for preparing graphene films without the use of graphene oxide was proposed in [6]. The graphene suspension was obtained by the electrochemical delamination of graphite in aqueous solutions of inorganic salts. Single-layer graphene sheets had a high hole mobility of 310 $cm^2/(V\ s)$ and a surface resistance of 1.96 kOhm/□, which are better than analogous indicators for a chemically reduced graphene. The graphene films that had been obtained were transferred onto a transparent flexible substrate of polyethylene terephthalate (PET) by vacuum filtering and dry transfer. The graphene films on PET with a thickness of 6 and 16 nm had a transparency of 91 and 80% and a surface resistance of 24.2 and 7.56 kOhm/□, respectively. The high resistance of thin-film device can be attributed to the interstitial resistance between graphene flakes. Despite the progress achieved in the preparation of TC films from graphene suspensions, their electrical parameters, evidently, will be worse than those of solid graphene films grown by CVD. As is known, CVD onto metal substrates such as Cu makes it possible to obtain a graphene of a large area and high quality [7]. The main difficulties for the serial production of transparent films from CVD graphene are the quality of the graphene film and multistep processes of transfer onto various substrates. The existing methods of transferring the graphene films grown by CVD onto various insulating substrates are diverse and require a lot of operations [8]. The electrical properties of the transferred films strongly depend on the substrate material, the reagents, and the transfer method [8]; therefore,

Fig. 1. (Color online) Lamination of a copper foil with CVD graphene.

Fig. 2. (Color online) Film for the lamination with the transferred CVD graphene.

the task of searching for new modes and methods of graphene film transfer onto insulating substrates remains topical. Such a method, which simplifies the process of CVD graphene transfer onto polymer substrates, can be the method of lamination [10, 11]. In this method a copper foil with the deposited CVD graphene is simply glued to the polymer under the action of temperature and pressure [10].

EXPERIMENT AND DISCUSSION

Graphene films were synthesized using CVD. Copper foil of two types was used as the catalyzing metal substrates: a roll copper foil for technical purposes with a thickness of 0.030 ± 0.003 mm, a copper content of 99.98%, and an oxygen content of 0.01% (GOST 5638-75) and an Alfa Aesar copper foil of special purity with a thickness of 25 μm and a copper content of 99.999%. We used a gaseous methane with a purity of 99.99% as a source of carbon.

In order to smooth the surface relief of copper foil (GOST 5638-75), we used electrochemical polishing. The copper foil was immersed into a solution of the following composition: 200 mL of water and 0.5 g of sodium persulfate; a direct voltage of 12 V was applied. The foil served as a cathode and the Pt/Ir wire as an anode; the time of treatment amounted to 2–10 min depending on the copper foil size. After polishing, the foil was dried in a nitrogen flow.

The prepared samples were placed on a quartz boat into the central part of a quartz tube of a Nabertherm 80/750/11 furnace. The process of deposition was carried out according to the standard scheme by filling the working tube with a mixture of argon and hydrogen, heating to the required temperature, annealing for the purification of copper foil surface, deposition of carbon, and cooling. A series of experiments has shown that the optimal conditions for the growth of graphene films on a copper substrate are the preliminary annealing of the foil at a temperature of 1000–1040°C for 30–40 min in a flow of argon and hydrogen mixture at a rate of 100 cm^3/min, methane delivery at a rate of 10 cm^3/min for 5–10 min, and the subsequent cooling to room temperature for 16–18 h.

In our work we have studied a simple mode of transferring the graphene film grown on a copper foil from a gaseous phase onto a standard film for lamination using a laminator. The essence of the method is that the copper foil with the grown graphene is placed at the laminator input between a paper and polymer film (Fig. 1).

The pressure and temperature of the laminator rolls glue the polymer film to the copper foil with graphene. A sample of the required shape and size is cut from the resulting polymer/graphene/copper foil structure, copper is etched out, and then the sample of CVD graphene on polymer is rinsed and dried and the procedure of transferring is accomplished. The film for lamination is multilayered and contains three layers. The first layer is from polyethylene terephthalate (PET); it serves as the basis and provides the film with hardness and elasticity. The second layer is from polyethylene (PE); it serves as a connecting link and a kind of "pad" by lamination. The third layer is a polymer

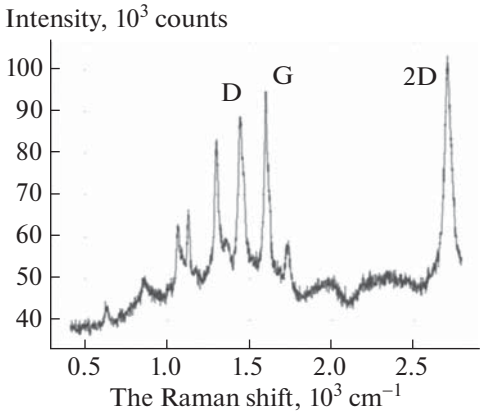

Fig. 3. Raman spectrum of the transferred CVD graphene.

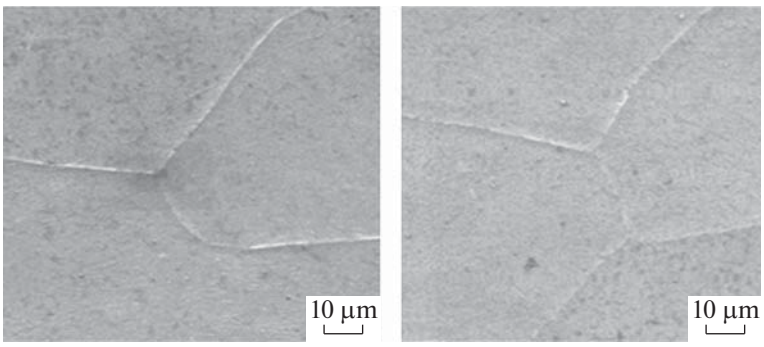

Fig. 4. Image of graphene film transferred by lamination obtained using a JEOL 7800 F scanning electron microscope.

"glue" from low-melting (95–120°C) polymer and possesses adhesion properties. The authors used a standard film with a thickness of 125 and 175 μm. An FGK–120 laminator with a temperature controller was used for lamination. The quality of transfer depends on the lamination temperature. Films of different thickness and composition require the selection of optimal lamination mode. The temperature should be such that no air bubbles could be formed between the foil and film and the surface resistance of the graphene film after etching should be minimal. In order to etch the copper foil, we used an iron chloride solution and a solution of citric acid in 3% hydrogen peroxide. The result of etching the film with copper foil in citric acid is shown in Fig. 2.

In order to estimate the transfer quality, we have obtained the Raman spectrum of CVD graphene on a polymer film (Fig. 3). The peaks of CVD graphene are rather clearly seen against the background of the peaks from polymer material. Peak 2D is comparable to or higher than peak G. This means that the transferred graphene film contains one or two graphene layers. As can be seen from the spectrum (peak D), the defects of the graphene film are insignificant. The measurements were carried out on an Integra Spectra measuring complex (NT-MDT Company, Russia). By carrying out the measurements of the Raman spectra, we used a 100× lens with numerical aperture NA = 0.7 and a solid laser with a wavelength of exciting radiation of λ = 532 nm and a power of ~3.5 mW in the beam with a diameter less than 1 μm. We have chosen the mode of spectra collection with a time of signal accumulation of 50 s. By carrying out the measurements of spectra, we used the 600/600 diffraction grating of a Solar TII spectrometer.

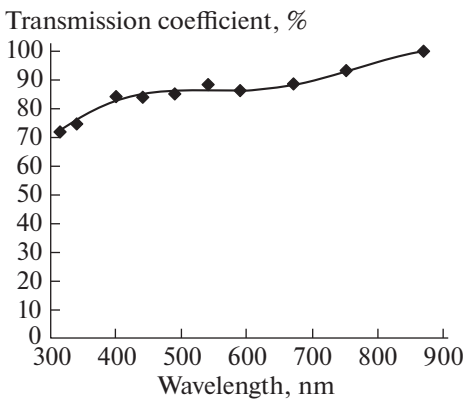

Fig. 5. Wavelength dependence of transparency of the CVD graphene on a film for lamination.

The studies on a scanning electron microscope show an imprint of domains of the copper foil on the graphene film transferred onto the polymer (Fig. 4).

The optical properties of the graphene film on a polymer substrate were studied by a KFK–MP photocolorimeter with a spectral range of 315–980 nm, a transmission coefficient of 10–100, and an error of the transmission coefficient of 1. The results of the optical studies of CVD graphene on a laminate are presented in Fig. 5.

As can be seen from Fig. 5, the film transparency in the visible spectral range (400–700 nm) amounts to 85–90%. In the IR spectral range the transparency of the film will increase.

The electrical characteristics of the TC graphene film obtained by lamination were studied using a Hall Effect Measurement System device in a four-probe scheme. The results of these studies and the measurements of the optical transmission coefficient for various samples are presented in the table. The electrical parameters of the TC graphene film obtained by the above method exceed those of the TC films obtained from graphene nanotubes and graphene suspensions.

The simplest field transistor structure, which is shown in Fig. 6, was built from the CVD graphene transferred onto a polymer film by lamination. The gate insulator was represented by a graphene oxide film with a thickness of 1 μm, which was superimposed in a wet state onto a strip of polymer film with the CVD graphene. After drying, the source, drain, and gate electrodes were deposited by silver paste onto this structure (Fig. 6).

Electrical characteristics and optical transmission coefficient of graphene films

Sample	Surface resistance, kOhm/□	Mobility, $cm^2/V\,s$	Transparency, %, $\lambda = 400–700$ nm
1	0.650	1160	85–90
2	1.060	850	82–85
3	1.170	780	81–85
4	2.880	1100	80–87
5	2.490	400	76–77

The length and width of the transistor channel are $L = W = 2.5$ mm and the gate capacitance is $C_G = 55$ pF. The dependence of the drain current on the gate voltage is shown in Fig. 7.

The average slope $S = 3.9 \times 10^{-3}$ mA/V of the I–V characteristic of this field transistor graphene structure is somewhat larger than that of a similar transistor on a polymer film [9]. The mobility of carriers was calculated from the gate characteristic according to the following well-known formula for the field transistor [8].

$$\mu = \frac{L}{C_G V_{DS} W}\frac{\Delta I_{DS}}{\Delta V_G} \approx 910\frac{\text{cm}^2}{\text{V s}},$$

where C_G is the gate capacitance per unit area, V_{DS} is the source–drain voltage, V_G is the gate voltage, and I_{DS} is the source–drain current. It can be seen from this formula and the table that a good agreement is achieved between the mobilities obtained by the measurements of the Hall effect and the characteristics of the transistor structure. The gate leakage current from the graphene oxid varied from 10 nA to 1 μA depending on the ambient humidity and the gate voltage.

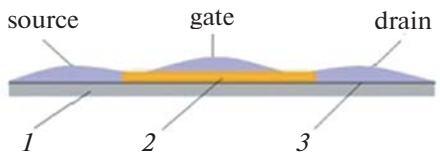

Fig. 6. (Color online) Transistor structure consisting of CVD graphene on a film for lamination: polymer film (*1*), 1 μm thick graphene oxide film (*2*), and CVD graphene film (*3*).

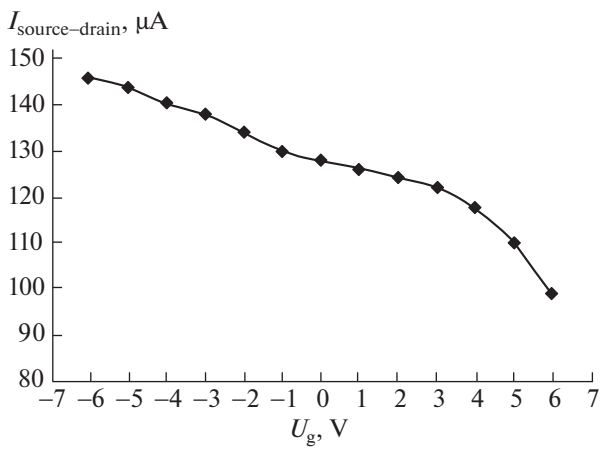

Fig. 7. Dependence of the source–drain current on the gate voltage.

CONCLUSIONS

A simple method of CVD graphene transfer onto a transparent polymer film by lamination has been applied and studied. TC graphene film has been obtained which possesses improved optical and electrical parameters when compared to those of TC films from graphene nanotubes and graphene suspensions. The method of transfer using a laminator is simple and can find wide applications in the optoelectronics, in particular, in the manufacture of sensor screens and by developing various graphene sensors and biosensors based on graphene two-terminal devices and transistor structures.

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