

# The main sources of graphene damage at transfer from copper to PET/EVA polymer

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## ARTICLE INFO

### Keywords:

Graphene  
CVD  
Transfer  
Polymer  
PET/EVA  
PMMA

## ABSTRACT

The defects formed at transfer of graphene layers from a copper substrate using a PET/EVA thermoplastic were analyzed. It is shown that the damages of graphene layer occur at the stage of thermal sintering of samples and mechanical separation of copper. A method for stabilizing the copper foil and polymer substrate, which makes it possible to minimize the mechanical defects at sample separation, is proposed. The transfer process for the PET/EVA system was optimized by the sintering temperature. The PET/EVA-graphene composites with the resistance of 1.5–8 kΩ/□ were obtained using single-layer and few-layer CVD graphene at transfer.

## 1. Introduction

Since the moment of the first graphene obtaining, many studies aimed at its exceptional mechanical, electrical and thermal properties have been carried out by means of detachment of highly oriented pyrolytic graphite (HOPG) [1]. Thus, it was found out that graphene possesses high mobility of charge carriers, superconductivity under certain conditions, high optical transparency and mechanical strength [2–5]. The method of chemical vapor deposition (CVD) on the metal surface is most suitable for industrial manufacturing of graphene samples with large areas due to its low cost, efficiency and high quality [6–8]. The main difficulty in the use of graphene, when creating flexible touch displays, photoelectric devices, organic light-emitting diodes, photodetectors, etc., is its transfer from the metal substrate, where its growth occurred, to the target substrate [9]. There are many technologies for graphene transferring, including the two main ones: chemical and mechanical methods [10–13]. Often, the chemical transfer process involves the use of a polymer as a temporary graphene carrier, followed by copper etching in acid (for example, HNO<sub>3</sub>), drying and polymer removing by acetone or other solvents [14–17]. In the mechanical method, copper is removed by its detachment from the polymer surface [18,19]. Various polymers can be used in these methods: polymethyl methacrylate (PMMA), polydimethylsiloxane (PDMS), heat-insulating tape, polycarbonate (poly (biphenol-A carbonate)), polyethylene terephthalate/ethylene vinyl acetate (PET/EVA), etc. [20,21]. It is extremely important that the quality of graphene does not become worse during the transfer; otherwise, the range of material applicability for

the practical use is narrowed. Chemical etching of the metal substrate, in comparison with mechanical separation, has a more gentle effect on graphene. However, for practical introduction of graphene, it is necessary to develop the transfer methods with preservation of the copper substrate for its reuse [22]. This will significantly reduce the cost of production of transparent electrodes.

In the case of mechanical separation of copper, adhesion of the graphene layer to the polymer matrix, stronger than to copper, is required. This is achieved by ensuring the contact of polymer with copper substrate coated with graphene over the entire area [23], including the formation of chemical polymer-graphene bonds [24]. The uniform mechanical stresses, which depend on the copper thickness, polymer substrate thickness [23], and mechanism of breaking force application, are equally important for transfer.

The present work deals with the development of the methods for mechanical transfer of graphene to polymers. The spin-coating and hot-pressing methods using PMMA (polymethyl methacrylate) and PET/EVA (polyethylene terephthalate/ethylene vinyl acetate) polymers, respectively, were used to apply the polymer to graphene. The copper substrate was removed by mechanical separation and chemical etching in nitric (HNO<sub>3</sub>) acid. To characterize the resulting polymer-graphene composites, their electrical resistance was measured. The main goal of this study is to compare the above methods of single-layer and few-layer graphene transfer and identify the types of defects that arise during mechanical transfer. The dependence of electrical resistance of transferred graphene was also studied as a function of the sintering temperature of the PET/EVA/Graphene structure.

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<https://doi.org/10.1016/j.matchemphys.2018.08.001>

Received 2 April 2018; Received in revised form 13 July 2018; Accepted 1 August 2018

Available online 09 August 2018

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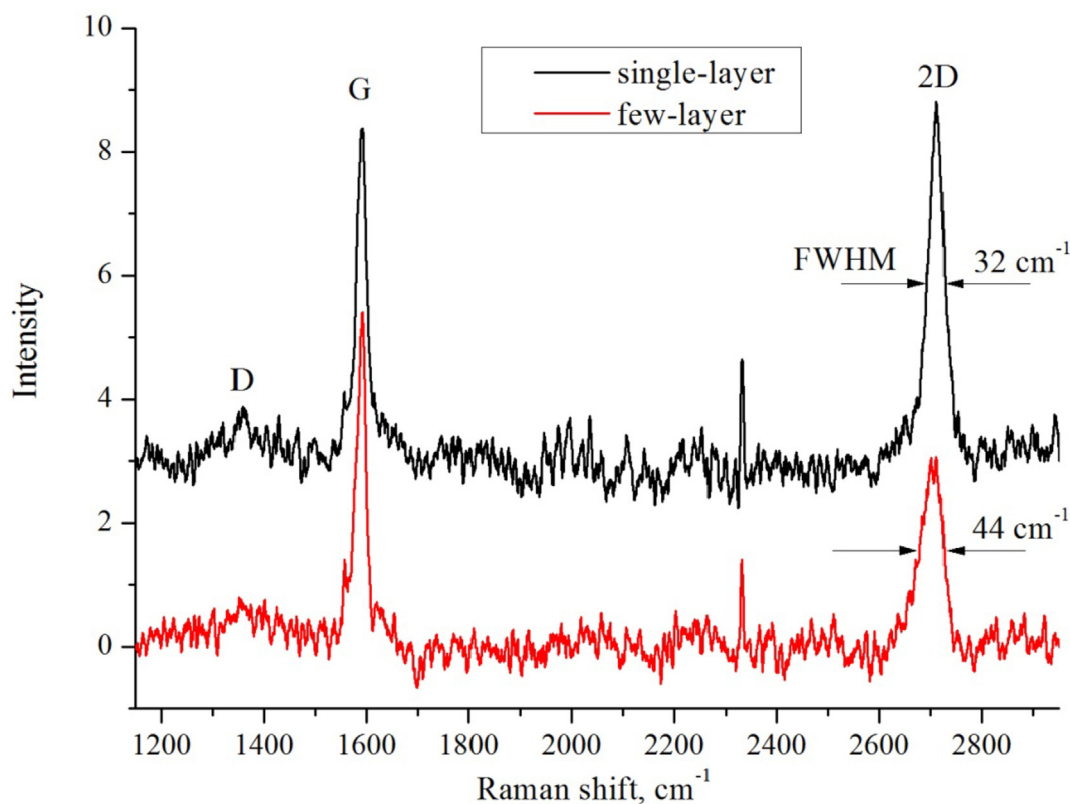


Fig. 1. The RS spectra of samples: single-layer; few-layer (1–3 layers).

## 2. Experiments

During this study, graphene was synthesized using the CVD method on a copper substrate, under the atmospheric pressure, using methane as a carbon precursor. The synthesis procedure is described in detail in Ref. [25]. Two types of graphene films with a continuous coating were synthesized: single-layer and few-layer (1–3 layers) ones. The quality of the obtained films was evaluated by Raman spectroscopy (RS) and optical microscopy. A T64000 Raman spectrometer produced by Horiba Jobin Yvon with a wavelength of exciting radiation of 514.5 nm was used for RS. Optical images were obtained with a Olympus BX51M optical microscope. The characteristic spectra of samples are shown in Fig. 1.

In experiments on graphene transfer, two types of polymers were used: PMMA and PET/EVA. To apply PMMA on a copper substrate coated with graphene, the Spin Coating method was used (centrifugation). PMMA polymer was dissolved in acetone with the ratio of 1–10 by weight. Before application, the solution was heated to the temperature close to the boiling point of acetone ( $\sim 56^\circ\text{C}$ ), and incubated for 30 min. This procedure is used to degas the solution and prevent formation of bubbles in the solidified polymer film. The resulting acetone-polymer solution was applied to a copper substrate, fixed on a platform rotating with the frequency of 1500 rpm. Under normal conditions, acetone was evaporated and a thin polymer PMMA film was formed on the surface. The resulting structure of PMMA-graphene-copper was adhered to a solid plate of glass or plexiglass by a double-sided adhesive tape to give the strength. Copper was removed by chemical etching in a 40% solution of nitric acid, followed by washing in distilled water (Gr/PMMA-chem.). The experiments on mechanically separation of the copper substrate from PMMA were also carried out, but in this case, graphene remained on the copper surface (Gr/PMMA-mech.).

The PET/EVA polymer was applied onto a copper substrate coated with graphene using the Hot-Press Machine method. In the

experiments, the PET/EVA polymer was presented as a solid lamination sheet with the thickness of 125  $\mu\text{m}$ , where PET plays a supporting role, and EVA is a hot-melt glue coating. The copper substrate with graphene was placed between two sheets of laminating film and pressed at the temperatures of 110, 150 and 190  $^\circ\text{C}$  for 10 min. The resulting PET/EVA/Graphene/Copper/Graphene/EVA/PET structure was cooled to the room temperature (Fig. 2). The polymer was mechanically removed from the side of the copper substrate, which was from below at the synthesis of graphene. Thus, the PET/EVA-graphene-copper structure was obtained. Then, copper was removed in three ways. In the first, copper was chemically etched in the 40% solution of nitric acid (Gr/PET/EVA-chem.). In the second, copper and polymer were mechanically split (Gr/PET/EVA-mech.). As compared with a thin PMMA polymer film, the PET/EVA lamination sheet is much stronger, but it is also subjected to stretching and bending. Therefore, in the third method, the samples were glued from both sides by a double-sided adhesive tape to the glass plates, to prevent bending and stretching of polymer and copper. After this stabilization, the PET/EVA-graphene-copper structure was mechanically separated (Gr/PET/EVA-mech.-stab.).

## 3. Results and discussion

The resistance of graphene-polymer films is determined by the parameters of the initial graphene structures, namely the size of graphene crystalline fragments and their defectiveness, as well as the effect of subsequent treatments associated with the transfer procedures. In the case of spin coating transfer, the mechanical deformations of samples are minimal; therefore, these polymer-graphene films can be considered as the reference with maximal conductivity for CVD graphene, synthesized under our conditions. Table 1 shows the results of measurements of resistance of the graphene-polymer films obtained by transferring single-layer and few-layer graphene to PMMA polymer. An attempt to separate mechanically the PMMA film and copper substrate

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