

STUDY OF THE INFLUENCE OF SOLVENT ON TRANSMISSION QUALITY GRAPHENE

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Abstract

The standard methods of transferring graphene onto semiconductor substrates apply acetone to solve the layer of polymethyl methacrylate (PMMA) on the surface of graphene layer at the end of '*wet transfer process*'. During this process, however, impurities on the order of nanometres get entrapped and have a subsequent negative effect on the practical utilization of graphene in the field of optoelectronics. To optimize the wet transfer of graphene using PMMA as a supporting polymer, several solvents were compared in terms of resulting contamination. The solvents subjected to the research included: acetone, chloroform, dimethyl succinate (DMG), and n-ethyl pyrrolidone (NEP). The lowest graphene contamination at the end of transfer process was achieved with NEP solvent, which was studied using atomic force microscopy.

Keywords: Graphene, graphene transfer, solvents, PMMA, AFM

1. INTRODUCTION

Graphene was discovered in 2004 [1], and has unambiguously proven its distinct potential of utilization in many applications and in a variety of industries. Its unique mechanical properties have found their use in the research of resistant layers, coatings and composite materials [2]. In the field of optoelectronics, the research is focused on solar cells [3], organic photodiodes [4], infrared sensors [5] and elastic touchscreens [6]. Proper functioning of the aforesaid devices depends on the entire quality of graphene. It is primarily given by the selected process of graphene transfer onto the chosen substrate. The manner of transfer affects the extent of damage of the transferred layer as well as the contamination of the graphene surface. '*Wet transfer*' is the most frequently applied transfer process in the literature [7], which uses polymethyl methacrylate (PMMA) as a mechanical support for the transfer of graphene, see **Figure 1**.



Figure 1 Schematic illustration of wet transfer of graphene

The mechanical support made of PMMA prevents from getting the layer damaged during the graphene transfer onto the target substrate. At the end of the *'wet process'* this PMMA supporting layer is solved in acetone.



Unfortunately, acetone is not able to solve the supporting layer completely. The residues of unsolved PMMA tend subsequently toward forming a nanometric contamination on the graphene surface that negatively affects electrical properties of the layer transferred. To remove the aforesaid contamination, several approaches were proposed, including mechanical removal using atomic force microscopy (AFM) probe tip or thermal decomposition [8-9]. The method of reducing the contamination by means of AFM probe tip enables to remove such contamination only locally and is rather time-consuming. Thermal decomposition is able to remove PMMA residues from a large area, but its disadvantage consists in high energy and process performance. The high process temperature (over 300 °C) is another disadvantage that could damage thermally sensitive materials, which eliminates the application of this procedure in the development of organic semiconductors. When compared to the procedures as above, the use of solvents to reduce the graphene contamination is more advantageous in terms of time, process and energy, and can also be implemented at the room temperature. Within this study, four solvents, including acetone, chloroform, dimethyl succinate (DMG) and n-ethyl pyrrolidone (NEP), were used to reduce the unsolved PMMA layer. Total effect of a solvent on the residual contamination at the end of wet transfer was evaluated using AFM measurements and optical microscopy.

2. EXPERIMENTAL

2.1. Transfer of graphene on the target sample

The graphene for our experiment was grown using chemical vapour decomposition (CVD) [10]. Copper foil with a size of 40x40 mm and a thickness of 25 µm was used as a catalyst for graphene growth and placed in the CVD reactor. In the course of graphene decomposition methane was used as a source of carbon. To achieve the decomposition of methane on the surface of the copper catalyst to individual atoms of hydrogen, the reactor was heated to 1 000 °C for a period of 30 minutes. With this time period elapsed, the reactor was gradually cooled down to the room temperature, which was accompanied by the formation of graphene. PMMA by Microchem with various molecular mass was then applied by spin coating onto the graphene prepared as described and placed on the copper foil. The first layer, as well as the other two layers of PMMA, was solved in anisole and had a molecular mass of 50K. The second and the third layers showed a molecular mass of 450 K and 950 K, respectively. The application of PMMA layer structured like that and featuring low molecular mass ensures a low contamination of graphene with sufficient mechanical resistance that is necessary for transfer. For all layers, the same parameters of spin coating were used. Revolutions per minute were set to 4 000 and took 30 seconds. The layer was allowed to cure at 180 °C for a period of 90 seconds. Since graphene got released on both sides of the copper foil during CVD process, it was necessary to remove imperfect graphene layers from underneath the copper foil. If this layer is removed insufficiently, it will make the etching of copper difficult. To remove the layer, oxygen plasma with an output of 50W was used and exerted its effect on the sample for a period of one minute. For the further procedure of wet transfer, the size of CVD graphene was modified to 5x5 mm using a pair of scissors. Here, ammonium persulfate by Sigma Aldrich with a purity of 99.99 % was used to solve copper. The samples coated with graphene with PMMA layer had a size of 10x10 mm and were made by cutting the silicon substrate with 270 nm silicon oxide using wire electrical discharge machining (WEDM) method [11-14]. The sample was immersed in each of four solvents (acetone chloroform, DMG and NEP) for a period of one hour. With this time period elapsed, any solvent in excess was removed from the sample using a stream of gaseous nitrogen with a purity of 99.99 %. The solvents used within this work featured a semiconductor purity.

2.2. Measurement of residual contamination of graphene

At first, the graphene surface was examined with Axio optical microscope by ZEISS to detect the areas with a low concentration of surface contamination. The evaluation of residual contamination itself was made with an AFM microscope by Bruker in a semi-contact mode using a ScanAsyst-Air probe tip. The results obtained were further processed and analysed with Gwyddion program.



3. ACHIEVED RESULTS AND DISCUSSION

The microscopic contamination of graphene measured after one hour of exposure to the solvent was evaluated using optical microscopy, i.e. by comparing images in bright- and dark-field modes, which enabled to identify the areas with low and high contamination based on the comparison, see **Figure 2**.



Figure 2 Comparison of images of transferred graphene captured in: a) dark-field mode and b) bright-field mode

The brighter the area on the dark-field mode image, the larger the surface contamination. Dark areas identify the spots with minimum PMMA contamination. The information obtained by this comparison was used in the next step, i.e. for measuring the residual surface contamination using AFM in marked areas (violet and yellow squares), see **Figure 3**. Here, root-mean-square (RMS) of the roughness was evaluated; in this case it has a greater informative value than the arithmetic mean deviation of the profile (R_a). RMS parameter is defined by the relation according to ISO 4287-2 [15]:

$$RMS = \sqrt{\frac{1}{N} \sum_{n=1}^{N} r_n^2} \tag{1}$$

where *N* means a number of measurements, and *r* is a profile height value. **Figure 3a**), **c**), **d**) indicate that the solving of PMMA in acetone, DMG and NEP caused cracks in graphene. These probably resulted from the handling with the graphene layer during wet transfer. These cracks could caused problem during RMS evaluation when sharp torn edges could be put into account as PMMA residue.

The occurred white dots belong to areas with a high local contamination of graphene with nanometric PMMA residues. The lowest contamination value of only 1.7 nm was achieved with NEP, i.e. in the area marked with a yellow square as shown in **Figure 3d**).

When acetone was used as a solvent, the RMS parameter values complied with works by Michal Her [16], Yung-Chang Lin [17] and Ji Won Suk [18]. RMS evaluated over the entire surface of individual AFM scans shown in **Figure 3f**) has revealed that the lowest contamination for RMS, i.e. only 7.3 nm, was achieved with NEP. The highest value, i.e. 12.4 nm, was found in case of DMG, because its use caused a great number of white dots in form of PMMA on the graphene surface.





Figure 3 AFM measurements of graphene surface after one hour of exposure to the solvent with indicated areas of RMS measurement: a) acetone, b) chloroform, c) DMG, d) NEP, e) evaluated RMS for individual solvents

4. CONCLUSION

Having analysed the surfaces of samples prepared using the process of wet transfer of graphene onto silicon substrate with 270 nm SiO₂, the following conclusions were made:

- using light microscopy, areas with both lower and higher PMMA contamination were detected,
- on the examined surface of samples, AFM measurements were made, based on which the RMS was determined,
- in some areas, PMMA was not removed completely, which has resulted in the occurrence of spots with a high RMS value.

The evaluated RMS parameter values indicate that the lowest local as well as total levels of PMMA contamination were achieved with NEP solvent. Based on a local analysis, RMS value of only 1.7 nm and total value of 7.3 nm were evaluated. In addition, it is to conclude that similar RMS values were achieved with chloroform, but no cracks occurred in the graphene layer.

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