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Improved polymer residuals removing after the graphene transfer to enhance sensors performance

L.A. Barsukov¹ ✉, N.P. Nekrasov¹, A.V. Romashkin¹,

I.I. Bobrinetskiy¹, D.D. Levin¹, V.K. Nevolin¹

¹ National Research University of Electronic Technology, Moscow, Russia

✉ leonty.barsukov@gmail.com

Abstract. Graphene transfer using polymers as a supporting layer makes sensors with exceptional yield and few defects. It is still an issue to make scalable and versatile high-purity graphene transfer method. Current-voltage characteristic slope and hence the sensitivity of the graphene-based devices are limited by the residual polymer left after the transfer process that forms local defects and trapped states quenching charge transfer. Due to the strong interactions between polymer and graphene, residual removal remains an important problem to solve. In this work graphene on Cu foil was covered using spin-coating of poly(methyl methacrylate) (PMMA) with different molecular masses and the addition of a low volatile additive. The film obtained was transferred onto Si/SiO₂ substrates. In order to remove PMMA residues multiple cleaning techniques with different solvents were used and compared to each other; new methods were developed. The quality of the purified graphene was studied by analyzing AFM, Raman, fluorescence spectroscopy data. The structure was <1 nm thick with a 2D to G peak ratio, of ~ 5.

Keywords: graphene transfer, polymer removal, sensor, polymethylmethacrylate

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Повышение эффективности удаления остаточного полимера после переноса графена для повышения чувствительности сенсоров

Л.А. Барсуков¹ ✉, Н.П. Некрасов¹, А.В. Ромашкин¹,

И.И. Бобринецкий¹, Д.Д. Левин¹, В.К. Неволин¹

¹ Национальный исследовательский университет «МИЭТ», Москва, Россия

✉ leonty.barsukov@gmail.com

Аннотация. При переносе графена с использованием полиметилметакрилата удается формировать высокочувствительные сенсоры на основе графена с высокой воспроизводимостью геометрических параметров канала на микроуровне и малой дефектностью. Однако, удаление остаточного полимера остаётся актуальной проблемой. Было осуществлен перенос графена с использованием ПММА с различной молекулярной массой на Si/SiO₂ подложки. Для удаления слоя ПММА сравнивались различные методики с применением широко используемых растворителей. При использовании наиболее



эффективной методики очистки, толщина перенесённого графена с остаточным ПММА составила менее 1 нм, а соотношение 2D/G составило ~ 5 . С помощью разработанных методик удаления остаточного ПММА может быть обеспечено увеличение чувствительности для недорогих многоразовых сенсоров на основе графена.

Ключевые слова: перенос графена, сенсор, удаление полимера, полиметилметакрилат

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Introduction

Graphene transfer with the use of poly(methyl methacrylate) (PMMA) is the base method to manufacture devices based on graphene [1, 2], which is initially synthesized on Cu foil by chemical vapour deposition (CVD) and has an acceptable quality of the graphene. However, after graphene is transferred to a substrate, it usually contains PMMA residuals, which greatly decreases the effective sensibility of the work area. Therefore, the current-voltage slope and, hence, device performance depend on the quantity of residual PMMA left [3]. Apart from covering the surface and making it impossible to modify it, PMMA residuals also cause defects formation and trap-like behavior states on it. Despite the efficiency of the solvents, a thin layer of PMMA clusters stays coupled with the graphene as that is more energetically favorable than being removed by the solvent. Removing this residual layer is an important problem to solve, thus a special cleaning technique using two or more different solvents [3] and two-stage cleaning is to be developed [4] since the standard PMMA solvents (acetone, ethyl acetate, trichloroethylene etc. [5]) do not provide a sufficient degree of graphene purity. The quality of pristine graphene can be estimated by the 2D to G peaks ratio at Raman spectra, hence the effectiveness of the rinsing method applied evaluates this ratio and reaches $\sim 2-5$ at best [3, 4]. The high fluorescence of pristine and rinsed graphene is an effect of interactions between graphene, residuals and solvent molecules that can be used to evaluate the number of residuals on the surface [6-8]. However, its relation to the analysis of the graphene cleaning quality is not studied enough. Thus, it is required to develop efficient methods for the residual polymer removal after the main PMMA layer is removed with standard solvents, as well as study the performance of such methods using atomic force microscopy (AFM), fluorescence and Raman spectroscopy altogether.

Materials and Methods

In this work we used CVD-grown graphene (Graphenea, Spain) on Cu foil. PMMA with different molecular mass – 495 kDa (MicroChem, USA) with 2-phenyl ethanol (2PE) additive, as well as 350 kDa 2% solutions in anisole (Sigma-Aldrich, USA), was used to form the supporting layer required for transfer. PMMA was spin-coated onto graphene at 2.5 krpm and annealed at 80 °C after. In order to remove polymer residuals film was rinsed in different solvents: acetone, trichloroethylene (TCE), isopropanol (IPA), butyl acetate (BA), tetrahydrofuran (THF) (Komponent-Reaktiv, Russia), for about half an hour at ~ 50 °C to increase the dissolution rate. The quality of graphene was investigated using AFM (Solver-Pro, NT-MDT, Russia) for graphene transferred on Si/SiO₂ and Raman spectroscopy with background fluorescence intensity analysis (Centaur U HR, 532 nm laser, Nano Scan Technology, Russia) for graphene on Cu foil (without transfer, but with all processes of deposition and removing PMMA).

Results and Discussion

AFM images obtained (Fig. 1) show that the residual layer is whole, with small craters in different areas, that can also be identified as pores due to the probe's large curvature radius. Rinsing in acetone left a lot of PMMA residuals [1] with a total height of graphene with PMMA layer ~ 4 nm (Fig. 1, *c*). Sample re-rinsed with the mixture of commonly used solvents THF:BA, 6:4 decreased the size of individual PMMA clusters between clean areas of graphene, left after the first rinsing (Fig. 1, *d*). Since THF and BA are similar in properties to the solvents used in another work [4] this mixture can effectively remove polymer residual from graphene.

Rinsing with THF:BA mixture forms clean areas of graphene between residual PMMA clusters, while the best PMMA solvent – trichloroethylene [5] leaves the thin but continuous layer of PMMA residuals. Therefore, the near-surface layer removal has a weak dependence on polymer solubility and is determined by the interaction of polymer molecules with graphene. Solvents such as THF, especially in combination with the small non-solvent molecule, can provide a better polymer removal rate [9], which is why in our work we have switched from using THF:BA or IPA:H₂O [3], to the THF:H₂O.

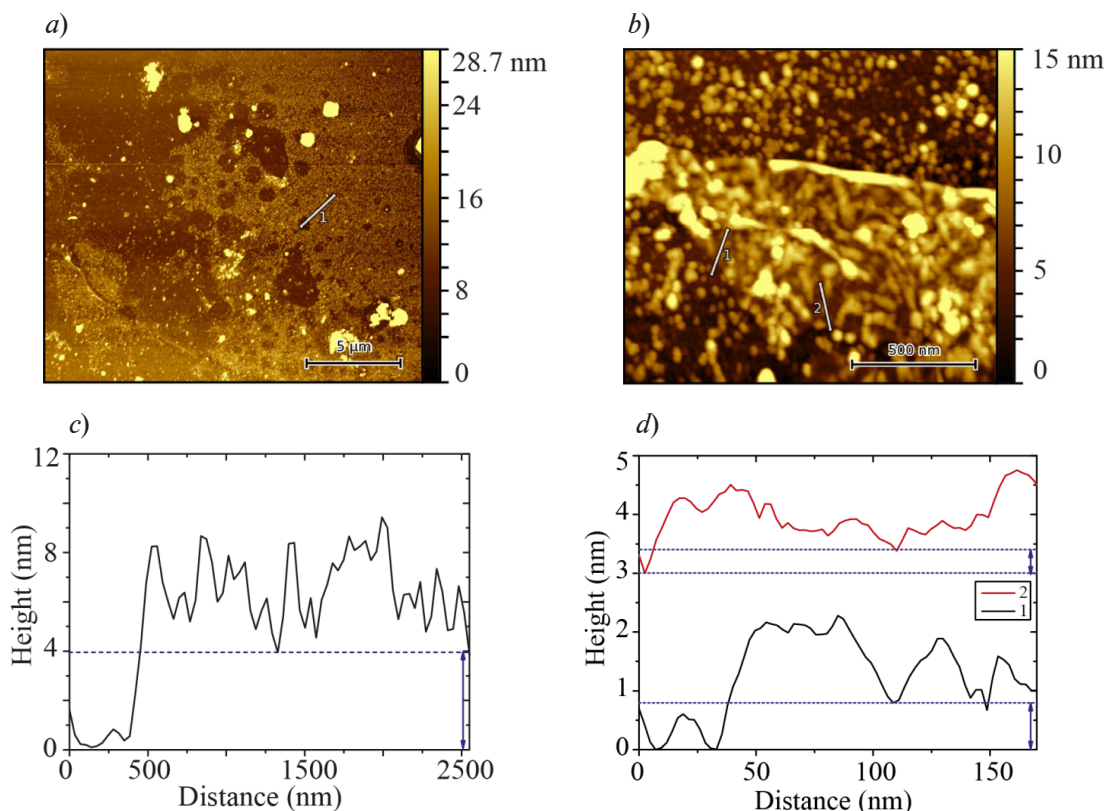


Fig. 1. AFM data of the 495 kDa PMMA on graphene rinsed with acetone (*a*, *c*), THF:BA (*b*, *d*)

AFM data does not provide sufficient information to estimate the number of defects in the crystal structure of graphene. However, Raman and fluorescence spectra show a strong correlation between residuals left and 2D peak width, position and 2D to G peak intensity ratio, which allows us to estimate the quality and purity of rinsed graphene. AFM data has shown that the 495 kDa PMMA sample cleaned with acetone average thickness of polymer residuals is larger than the 350 kDa one rinsed the same way, but Raman spectra 2D/G ratio is bigger for the 495 kDa one, proving that it is cleaner than for 350 kDa one. Hence, 350 kDa PMMA has formed the continuous layer with less clean graphene areas.

Intensive fluorescence was observed on the samples with graphene on the Cu foil (Fig. 2, *a*, *b*) [6], which can be an effect of interaction between graphene and residuals or impurities on its surface causing fluorescence similar to graphene quantum dots [7] with more than 20 nm sizes [8],

which can be formed between residual molecules at graphene. The spectra of the point with the least amount of graphene in the laser spot (looking the same as no graphene areas in the optics) show less fluorescence, proving that it is caused by interactions between graphene and other molecules. Moreover, fluorescence decreased for the samples with PMMA 350 kDa layer formed, and increased for the 495 kDa PMMA with 2PE ones, compared to the initial graphene. Using 495 kDa PMMA with 2PE additive forms non-homogeneous graphene regions with either more 2PE or PMMA. That is similar to the fluorescence signal from graphene regions with polymer molecules separated by the clean areas or vice versa. Trichloroethylene cleaned samples and the uncleaned ones full-covered with PMMA have almost the same fluorescence, especially for PMMA with smaller molecular weight, indicating that the residuals are not entirely removed, which can also be proved by the 2D to G ratio (Fig. 2, *c, d*). Both 495 kDa PMMA with 2PE additive and 350 kDa PMMA samples were rinsed with THF:water, which has led to fluorescence increase (Fig. 2, *a, b*), showing that this treatment still leaves residual molecules on the surface. Nonetheless, this particular re-rinsing procedure allows us to dramatically decrease the number of residuals left, resulting in larger 2D to G peaks ratios ~ 5 (Fig. 2, *c, d*), which is the high value [4]. Thus, most of the graphene is cleaned, but it still has nanoscale areas separated by residual molecules that are not entirely removed, hence the quality of the graphene obtained can be improved even further.

We found out that during re-rinsing with THF:water at 50 °C, the copper foil is a catalyst for the reaction between THF and water [10], resulting in Cu_2O formation [11]. Cu oxidation is characterized by Raman peaks in the spectra (from 534 to 540 nm, Fig 2, *a, b*). Oxidation has affected the reduction of the fluorescence suppression characteristic of the original metal surface.

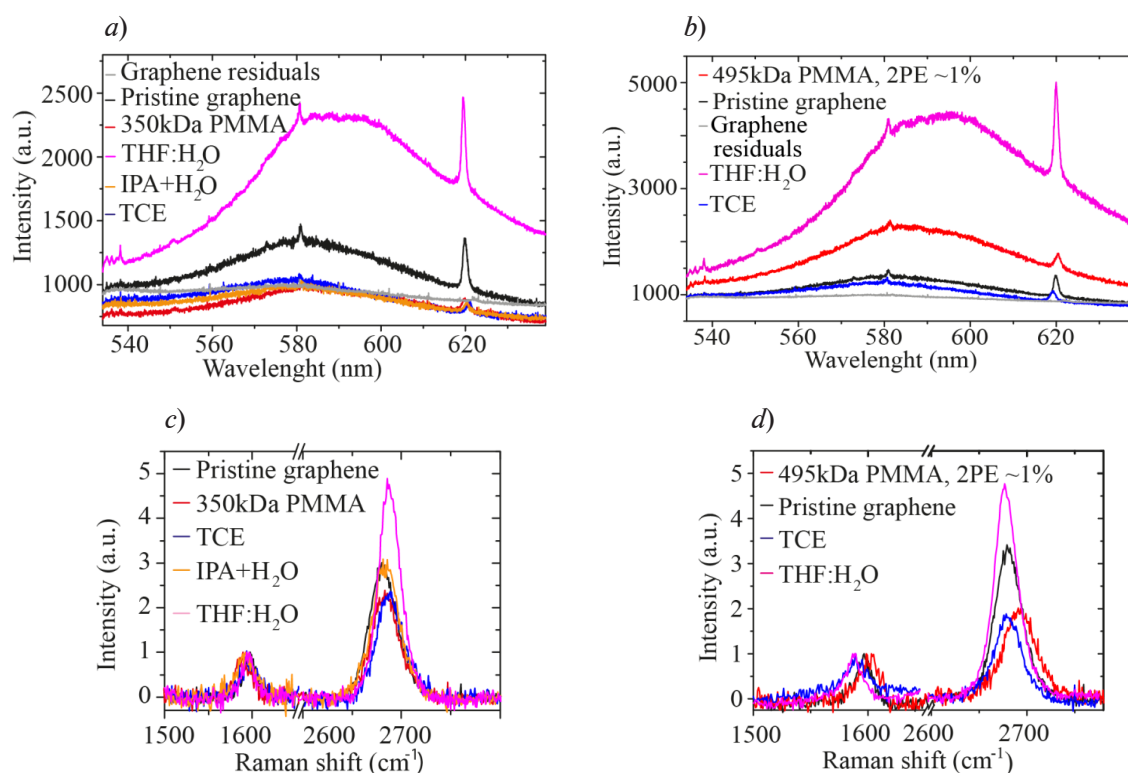


Fig. 2. Fluorescence (*a, b*) and Raman spectra (*c, d*) of the graphene with different treatment

Mechanical stress or changes in electronic structure in graphene with PMMA film deposited and removed are well characterized by 2D peak position (Fig. 3, *a*). Exfoliated graphene on a substrate, that has no residuals, has the 2D peak at $\sim 2686 \text{ cm}^{-1}$ [12]. The changes in the 2D peak position (Fig. 3, *a*) and in the 2D/G ratio (Fig. 3, *b*) compared to reference data for the deposited PMMA and rinsed one with TCE indicate different mechanisms of interaction with graphene for 495 kDa PMMA containing 2PE and 350 kDa PMMA.

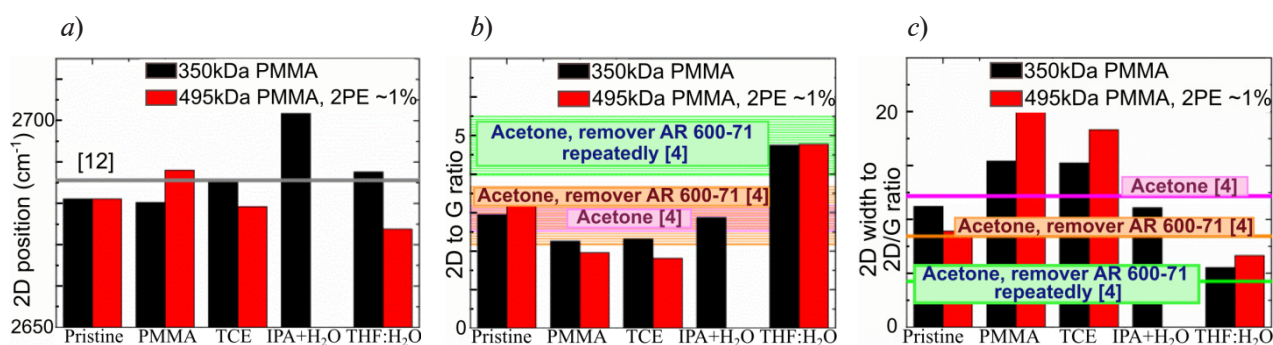


Fig. 3. Diagrams of the 2D peak position (a), 2D to G ratio (b), 2D width to intensity ratio (c)

This demonstrates the importance of the 2PE molecules remaining in the near-surface layer, which greatly affects the graphene properties. The significant improvement in the 2D/G ratio, as well as the narrowing of the 2D peak for samples rinsed with THF:water, in contrast to the behaviour of fluorescence, indicate the essential purity degree of the graphene. Due to the remaining shift of the 2D peak for the samples with the 2PE additive, it is evident that 2PE itself is still present after all purification procedures. The IPA:water treatment [3] provided an improvement over the TCE rinsing, but was less effective than THF:water.

Conclusion

New efficient method of PMMA residual removal from graphene was developed. This method includes post-processing in THF:water solution after traditional TCE washing. The main idea is to overcome the strong interaction between PMMA residuals and graphene by using specific solvent-non-solvent interactions with PMMA and removing all of them. Thus, high graphene purity was achieved, which is confirmed by the high-intensity ratio of the 2D/G peaks of about 5. However, these results can be further improved by removing the remaining molecules on the graphene, which is the goal of our further research. Clean graphene on the target substrate is a base for the further development of highly sensitive sensors of any sort able of detecting substances with extremely low molecule concentrations (~ 0.1 pM). This sensitivity can be improved by using the graphene channel purified with the proposed method. It allows us to make compact non-invasive reusable sensors able to detect diseases and viruses in outer body fluids like sweat and make gas sensors with improved sensitivity.

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THE AUTHORS

BARSUKOV Leonty A.

leonty.barsukov@gmail.com

ORCID: 0000-0002-4802-0014

NEKRASOV Nikita P.

8141147@gmail.com

ORCID: 0000-0003-1417-0177

ROMASHKIN Alexey V.

romaleval@gmail.com

ORCID: 0000-0002-0101-6122

BOBRINETSKIY Ivan I.

bobrinet@mail.ru

ORCID: 0000-0003-2380-2594

LEVIN Denis D.

skaldd@yandex.ru

ORCID: 0000-0002-8414-6191

NEVOLIN Vladimir K.

vkkn@miee.ru

ORCID: 0000-0003-4348-0377

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