Annual report for the second year PhD.

"Effect of the synthetic rubbers on the properties of CVD graphene."

By- Ayush Tyagi
PhD Student in Nanoscience
Scuola Normale Superiore (NEST) Pisa.

Supervisor- Dr. Camilla Coletti
IIT@NEST, Pisa.

Project-1

“Electrical and morphological properties enhancement of CVD graphene by removing PMMA residues from graphene.”

Graphene, a distinct two-dimensional material, has shown its potential in numerous fundamental and technological applications because of its intriguing properties such as high electrical and thermal conductivity [1,2]. Device fabrication based on 2D materials such as graphene requires polymethyl methacrylate (PMMA) to be used during conventional transfer and lithography process [3-4], which leads to the degradation in electrical properties of graphene as these residues act as external scattering centers for charge carriers [5]. Here, in this work we present a new way to enhance morphological and electrical properties of chemical vapor deposited (CVD) graphene by adopting a two-step cleaning technique.

RESULTS AND DISCUSSION.

AFM Characterization of PMMA residues on CVD graphene.

Typical height profiles of graphene per size 10×10 μm^2 on Si/SiO_2 are measured using AFM as shown in Fig. 1. (a) and 1. (b). Fig. 1. (a) shows the morphology of graphene with PMMA residues on its surface obtained by AFM in which PMMA is removed using conventional acetone method for couple of hours for the lift-off during device fabrication process. The surface of graphene in Fig. 1. (a) is covered by dense and amorphous PMMA residues as previously reported [6]. It is notably can be seen that the residues are primarily located on the graphene surface compare to the silicon substrate, which further reveals that graphene has more strong adhesion to the polymers even though it is assumed to be chemically inert [7]. All the PMMA residuals shows nonuniform distribution on the surface of graphene. The root-mean-square roughness, R_{RMS}, value right after the device fabrication is obtained about 4.5 nm. The PMMA residues are agglomerated on graphene surface with height distribution, Z_{mean}, which is between 25-30 nm as shown in Fig. 1. (c). Similarly, the topographic images were taken after cleaning graphene with remover for 3 min as a second step cleaning shown in Fig. 1. (b), which clearly concludes towards super clean graphene with $\geq$ 90% PMMA particles are detached.

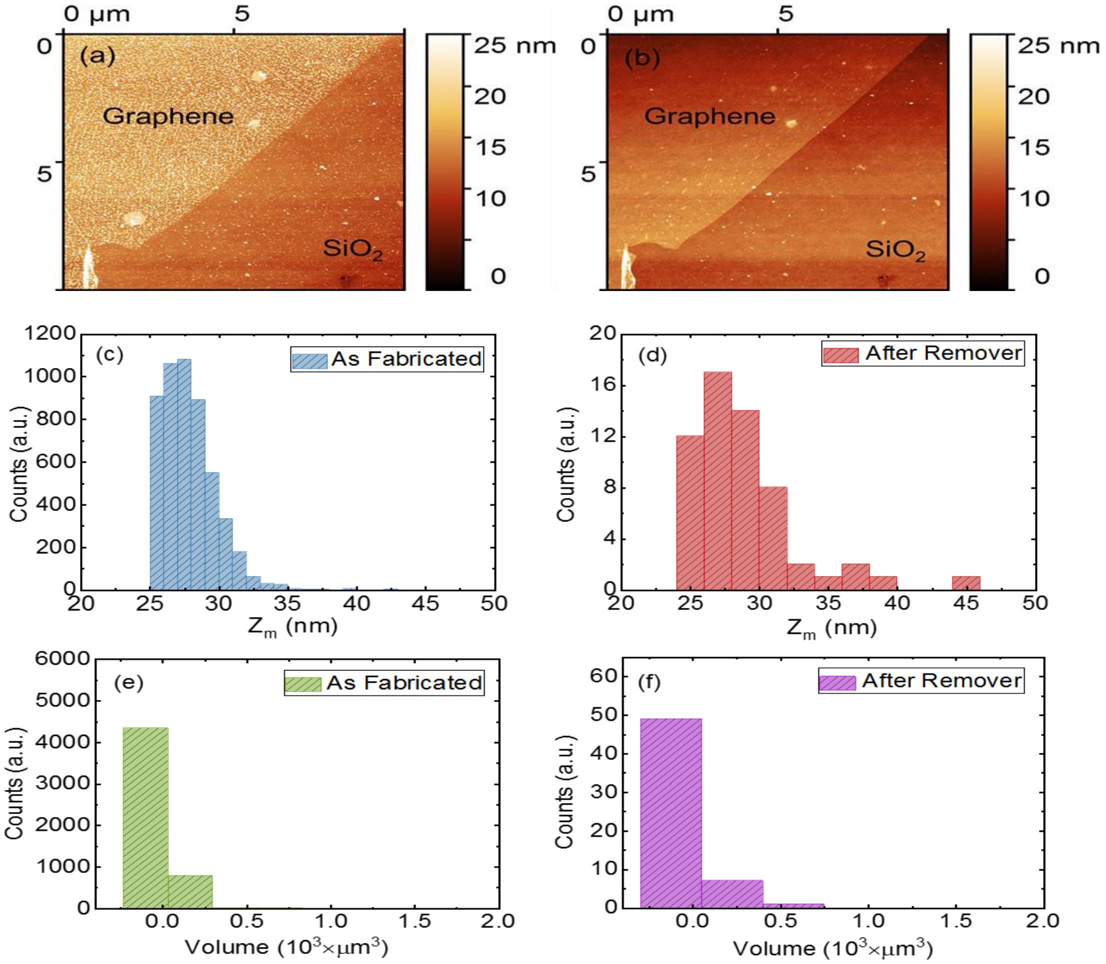


Fig. 1. (a), (b) AFM image of the border of single crystal CVD graphene after device fabrication and after cleaning with remover. (c)-(f) Mean heights and volume of PMMA residues calculated before and after remover cleaning.

Raman characterization of graphene before and after cleaning with Remover.

A typical Raman spectrum of graphene after device fabrication and after cleaning with remover was measured by using a laser of wavelength (λ) of 532 nm to elucidate structural and doping characteristics. Fig.2. (a)-(d) represent the Raman correlation data observed on CVD graphene before and after cleaning process, which depends on both doping [8–9] and strain [10]. In particularly, Fig.2. (a) shows the positions (ω_G, ω_{2D}) of G and 2D-peak of graphene transferred on Si/SiO_2 cleaned with acetone for couple of hours with average values 1583.2 cm^{-1} and 2673.7 cm^{-1}, Fig.2. (b) represent the intensity ratio of 2D and G-peaks (I2D/IG) was plotted with an average value of 3 and Fig. 2. (c), (d) shows the values of FWHM of G-peak and area ratio of the peaks (A(2D)/A(2D)) were observed with an average value of 11 cm^{-1}, which confirms that graphene is slightly p-doped compare to the neutral graphene. The reason for the unintentional doping could be the oxygen (O_2) and water (H_2O) molecules adsorbed at the graphene surface due to the exposure of CVD graphene to the air [5,11]. Afterward, the graphene on Si/SiO$_2$ was treated with the remover for 3 min which surprisingly revealed that the unintentional doping was reduced. The reason for this reduction in doping is assumed to be the dissolution of PMMA residues by remover.

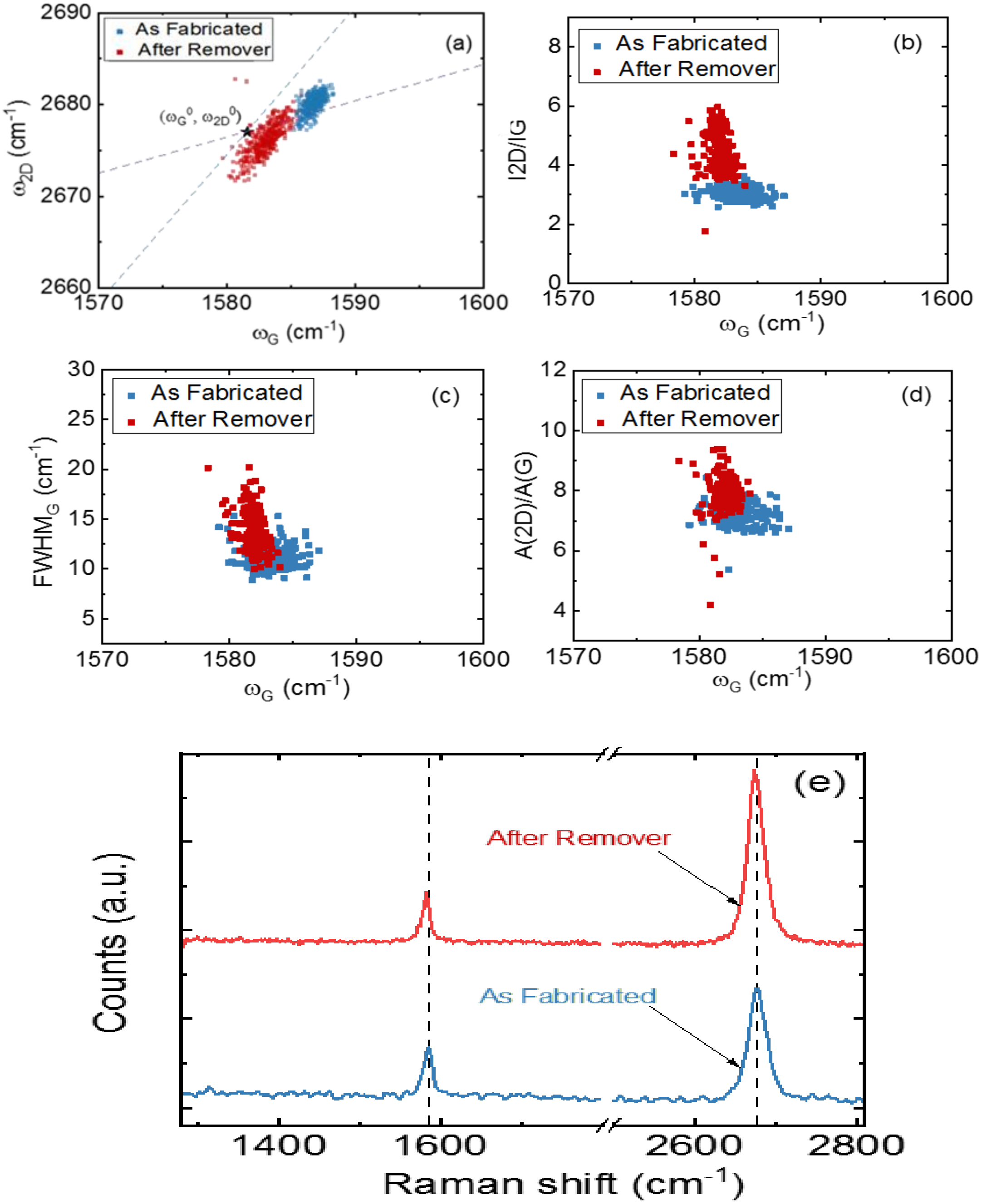


Fig.2. (a) Representing 2D vs G-peak positions after fabrication and after cleaned with remover. (b) I2D/IG ratio with respect to the position of G-peak. (c), (d) FWHM of G-peak versus its

position and area ratio of both the peaks and (e) Raman shift of uncleaned and cleaned graphene at wavelength (λ) = 532 nm.

Electrical characterization of CVD graphene.

The electrical properties were investigated by measuring mobility which was extracted before and after cleaning with remover in ambient conditions. As shown in the Fig.3. (d) the mobility values (μ) of graphene were measured before and after washing with remover. The mobility values were about~ 2502 cm^{2}V^{-1}s^{-1} and~ 2235 cm^{2}V^{-1}s^{-1} for electrons and holes respectively. The mobility values are low right after the transfer and there can be two reasons for that, (1) due to the PMMA residues attached to the graphene and (2) because of the O_2 and moisture present in the air [11,12,13]. While after cleaning for 3 minutes with remover mobility became almost twice for electrons and holes with values about~4600 cm^{2}V^{-1}s^{-1} and~4386 cm^{2}V^{-1}s^{-1} while in some case it was even around 10000 cm^{2}V^{-1}s^{-1} which is higher as previously reported [5,6]. The reason behind the increment in the mobility of graphene could be considered as the removal of the contamination, caused by the PMMA residues as well as due to the oxygen (O_2) and water (H_2O) molecules [11,12].

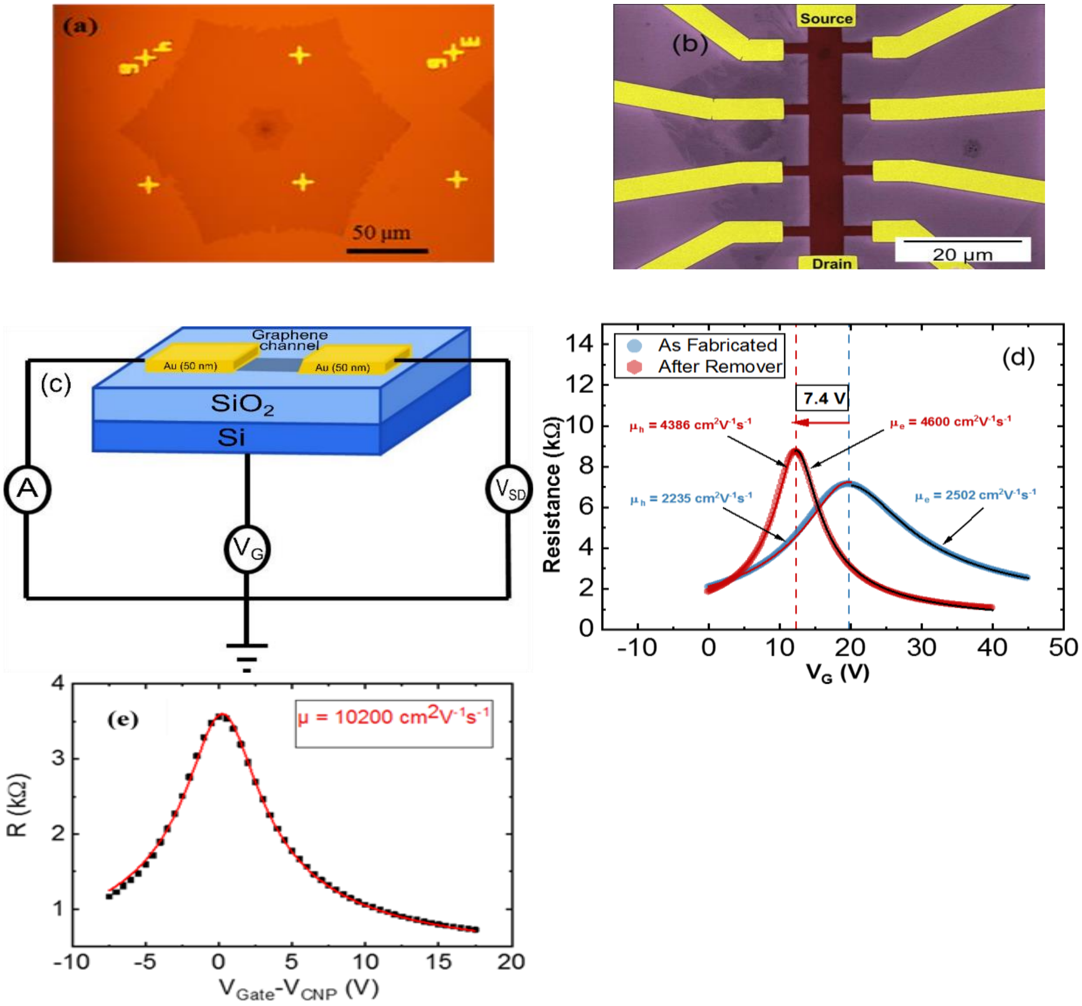


Fig.3. (a) Representing the optical image of CVD graphene single crystal transferred on Si/SiO_2 substrate, (b) shows the SEM image of Hall-bar structure, (c) schematic structure of back-gate graphene field effect transistor (FET) and (d), (e) resistance vs applied gate voltage respectively before and after cleaning with remover.

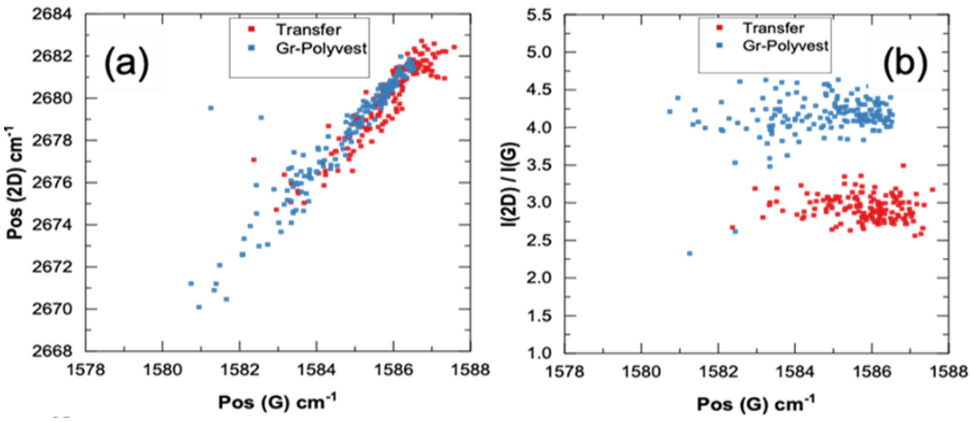
Project-2

"Effect of synthetic rubbers (polybutadiene and styrene butadiene) on the properties of CVD graphene."

Rubbers, having unmatchable viscoelastic properties, are important materials with immense applications in industries. Conventionally, rubbers are too fragile to fulfill the requirements for many applications. But by using particular filler materials the strength could be increased several times. Different types of fillers have been used till now such as carbon black, silica, carbon nanotubes etc. [14]. Graphene has attracted enormous attention in the field of rubber composites for its excellent potential for improving overall rubber performance [15]. It refers to a sp^2 hybridized C-atoms sheet. Graphene is a two-dimensional gapless material. It is a semimetal with remarkably high charge carrier mobility, excellent thermal conductivity, extraordinary mechanical flexibility and ultrahigh chemical stability, which comes because of the unique structure and geometry of graphene. These features make graphene promising candidate for rubber composites as a filler [16].

RESULTS AND DISCUSSION.

Raman characterization of polymer deposited on graphene.



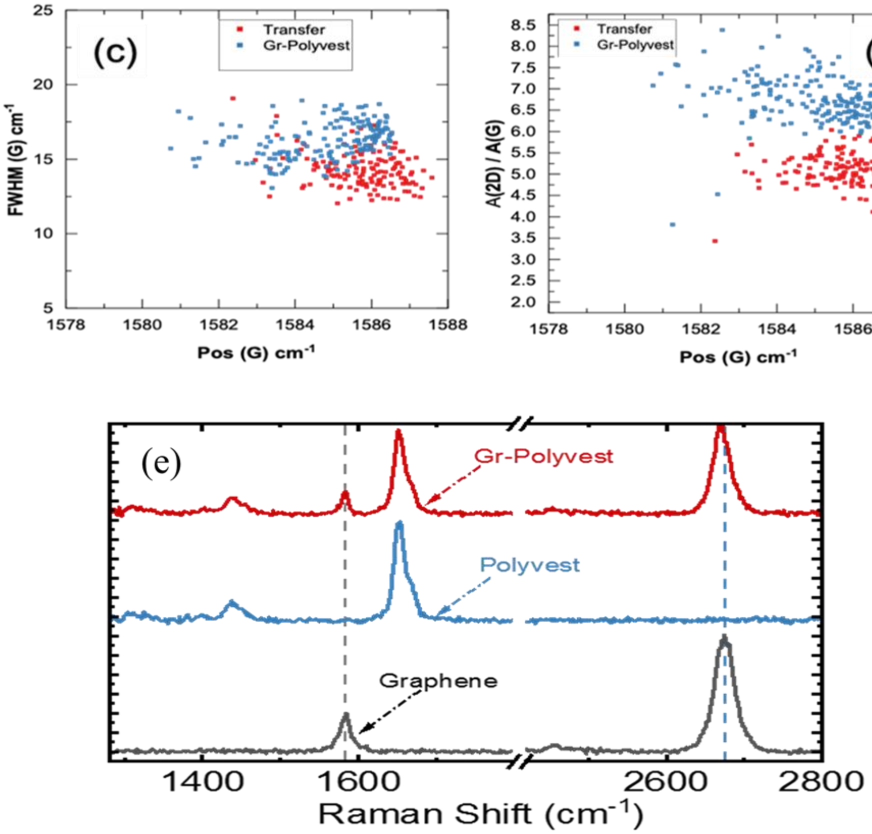
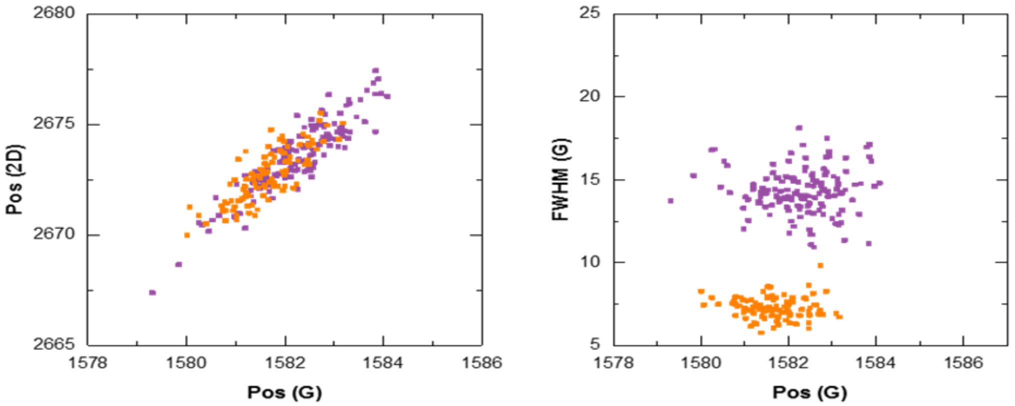


Fig.1. (a) Representing 2D vs G-peak positions of graphene and graphene/polyvest. (b) I2D/IG ratio with respect to the position of G-peak. (c), (d) FWHM of G-peak versus its position and area ratio of both the peaks and (e) Raman shift of graphene and graphene/polyvest at wavelength (λ) = 532 nm.

In the fig. comparison between graphene and graphene/Polyvest is shown. It can be seen clearly that CVD grown graphene has high quality without any defect. The Raman spectra of Polyvest and graphene/Polyvest was measured as well. It can be seen clearly that there is a slight red shift in both 2D and G-peak positions, FWHM of G-peak has shown increment while the ratios I(2D)/I(G) and A(2D)/A(G) both are increased as well, which confirms that the graphene became neutral after depositing polymer [17]. It could work as a dielectric material for different graphene electronic devices and at the same time open up a new approach to understand the rubber/graphene interactions for tire applications. Similar results were obtained for graphene/SBR samples which are shown in Fig.2.



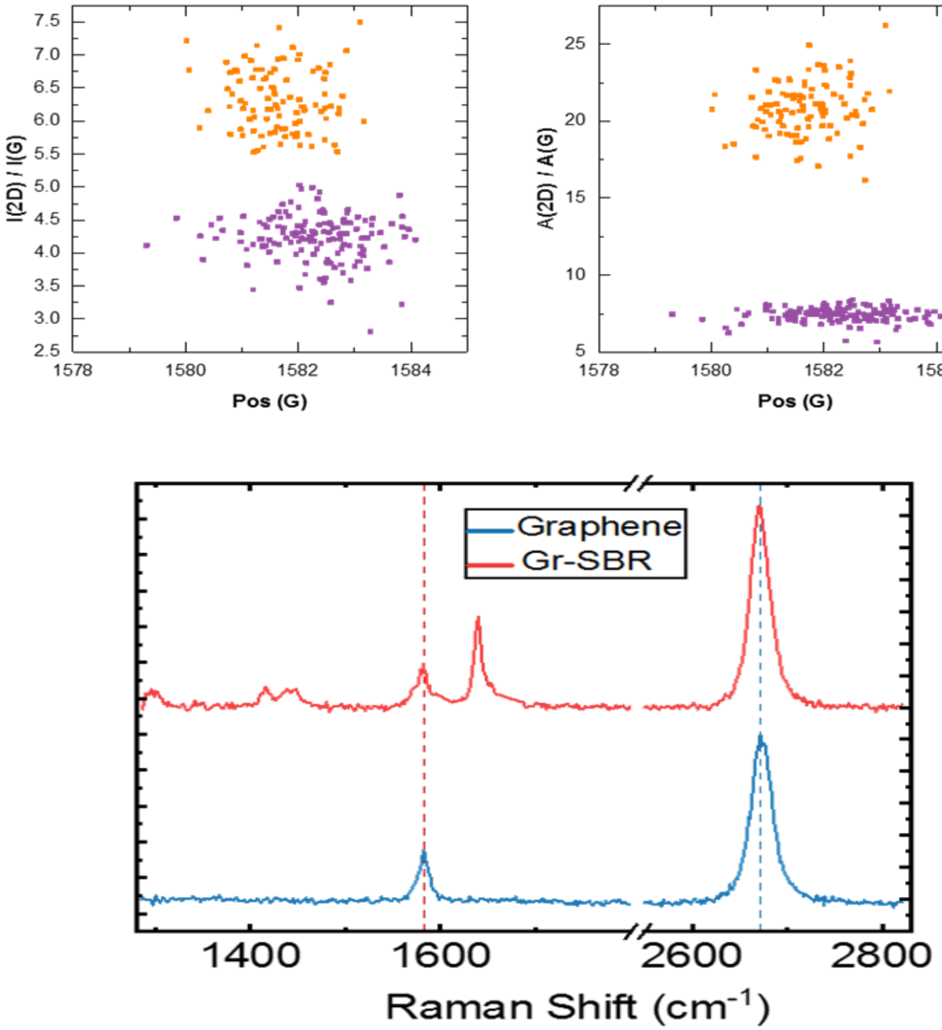
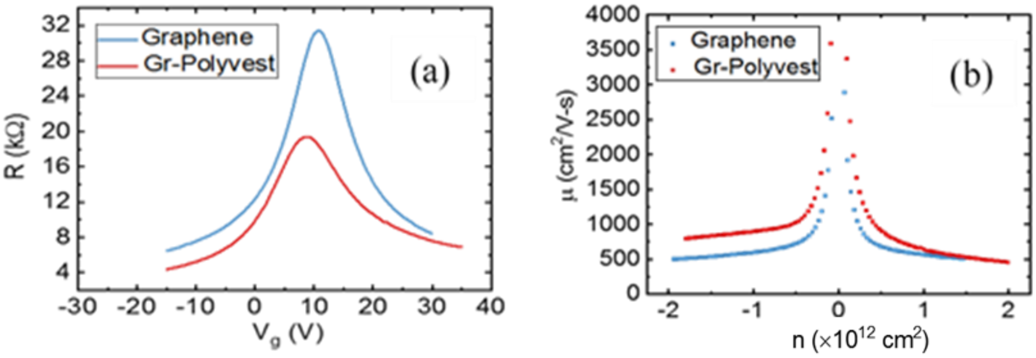


Fig.1. (a) Representing 2D vs G-peak positions of graphene and graphene/SBR. (b) FWHM of G-peak versus its position. (c), (d) I2D/IG ratio with respect to the position of G-peak and area ratio of both the peaks and (e) Raman shift of graphene and graphene/SBR at wavelength (λ) = 532 nm.

Electrical and AFM characterization of graphene/Rubber samples.

The electrical properties are confirming the results obtained by the Raman spectroscopy as the mobility is increased which confirms the doping reduction in graphene by depositing the polymers on the top of graphene. While the AFM image in Fig. 1. (e) showing the continuous distribution of polymer over graphene.



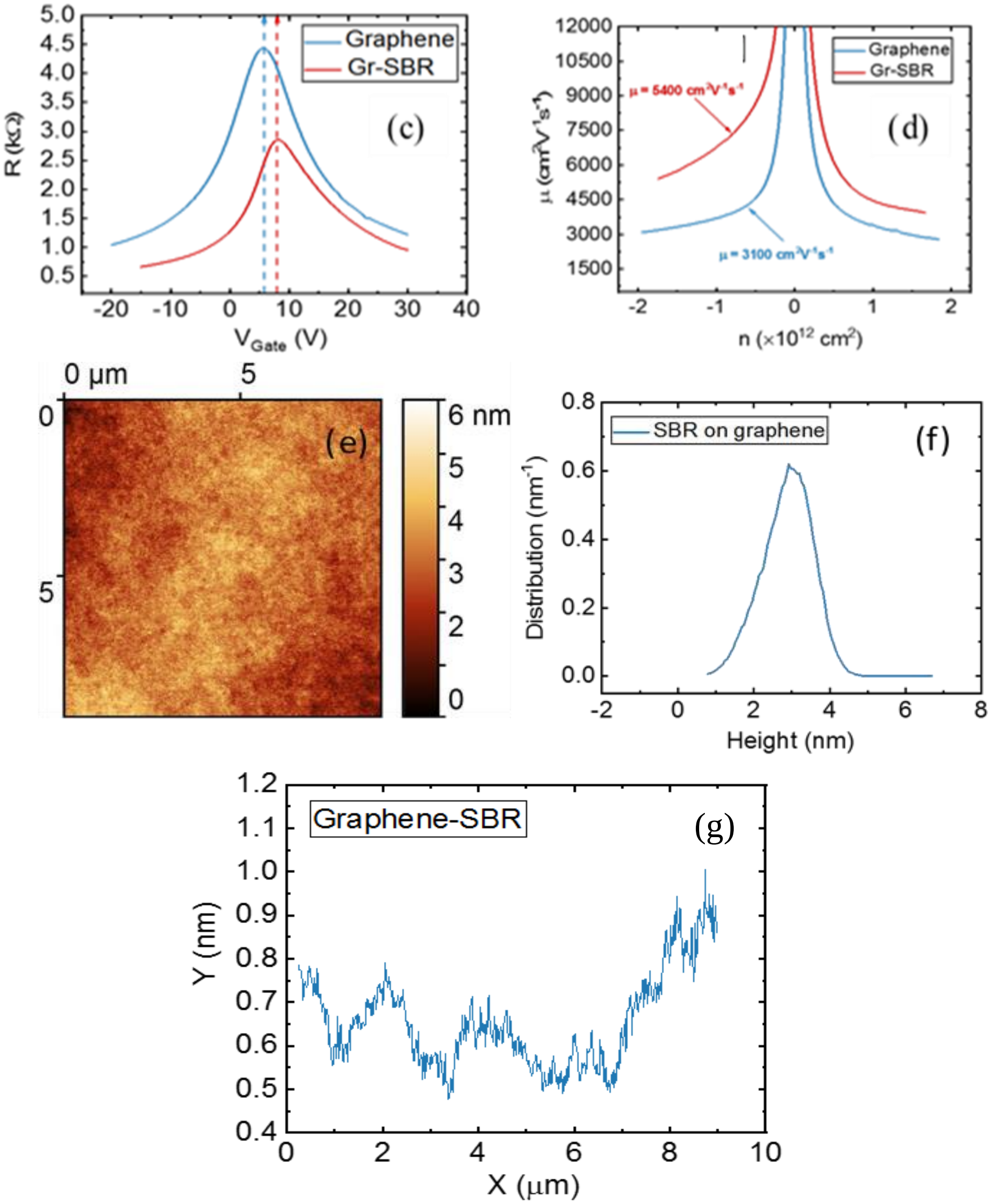


Fig.2. (a)-(d) Representing the resistance vs applied gate voltage and mobility vs carrier density in graphene/polyvest and graphene/SBR samples, (e)-(g) are showing the AFM image of rubber/graphene, height distribution and roughness values respectively.

Project-1

CONCLUSION

Here, we suggest an effective and rapid graphene cleaning method to reduce the PMMA residues available on the graphene surface after transfer and lithography process by using two-step cleaning method including remover and acetone without introducing any additional defect. Summarizing all the results together, we can conclude that this two-step cleaning technique is non-toxic, fast and potentially beneficial to improve the overall quality of CVD graphene. We are soon going to submit these results as our manuscript is ready.

Project-2

CONCLUSION AND FUTURE PERSPECTIVE

Here we represented the change in the properties of graphene by using polymers i.e., Polyvest (polybutadiene) and SBR (styrene butadiene) is investigated. These results are the important steps to understand the interaction between graphene and rubbers for the graphene tire applications. Furthermore, these two polymers could be the promising candidates as a polymeric dielectric material. In future we are trying to investigate the effect at nanoscale by combining the effect of graphene/rubbers/pyrroles to have an idea about the improvement in physicochemical properties of carbon allotropes i.e., graphene. Furthermore, we are investigating the effect of the different pyrroles on the properties of CVD graphene as they are the prime candidates to form strong adducts with rubber and graphene for graphene tire applications.

REFRENCES.

[1] Randviir E P, Brownson D A C and Banks C E 2014 A decade of graphene research: Production, applications and outlook *Mater. Today* **17** 426–32

[2] Novoselov K S, Fal’Ko V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 A roadmap for graphene *Nature* **490** 192–200

[3] Son B H, Kim H S, Jeong H, Park J Y, Lee S and Ahn Y H 2017 Electron beam induced removal of PMMA layer used for graphene transfer *Sci. Rep.* **7** 1–7

[4] Lin Y C, Lu C C, Yeh C H, Jin C, Suenaga K and Chiu P W 2012 Graphene annealing: How clean can it be? *Nano Lett.* **12** 414–9

[5] Pirkle A, Chan J, Venugopal A, Hinojos D, Magnuson C W, McDonnell S, Colombo L, Vogel E M, Ruoff R S and Wallace R M 2011 The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO2

Appl. Phys. Lett. **99** 2011–4

[6] Cunge G, Ferrah D, Petit-Etienne C, Davydova A, Okuno H, Kalita D, Bouchiat V and Renault O 2015 Dry efficient cleaning of poly-methyl-methacrylate residues from graphene with high-density H2 and H2-N2 plasmas *J. Appl. Phys.* **118** 123302

[7] Choi W, Seo Y S, Park J Y, Kim K B, Jung J, Lee N, Seo Y and Hong S 2015 Effect of annealing in Ar/H2 environment on chemical vapor deposition-grown graphene transferred with poly (Methyl Methacrylate) *IEEE Trans. Nanotechnol.* **14** 70–4

[8] Casiraghi C, Pisana S, Novoselov K S, Geim A K and Ferrari A C 2007 Raman fingerprint of charged impurities in graphene *Appl. Phys. Lett.* **91** 1–4

[9] Basko D M, Piscanec S and Ferrari A C 2009 Electron-electron interactions and doping dependence of the two-phonon Raman intensity in graphene *Phys. Rev. B* **80** 1–10

[10] Mohiuddin T M G, Lombardo A, Nair R R, Bonetti A, Savini G, Jalil R, Bonini N, Basko D M, Galiotis C, Marzari N, Novoselov K S, Geim A K and Ferrari A C 2009 Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Grüneisen parameters, and sample orientation *Phys. Rev. B - Condens. Matter Mater. Phys.* **79** 1–8

[11] Sojoudi H, Baltazar J, Henderson C and Graham S 2012 Impact of post-growth thermal annealing and environmental exposure on the unintentional doping of CVD graphene films *J. Vac. Sci. Technol. B, Nanotechnol. Microelectron. Mater. Process. Meas. Phenom.* **30** 041213

[12] Ryu S, Liu L, Berciaud S, Yu Y J, Liu H, Kim P, Flynn G W and Brus L E 2010 Atmospheric oxygen binding and hole doping in deformed graphene on a SiO2 substrate *Nano Lett.* **10** 4944–51

[13] Levesque P L, Sabri S S, Aguirre C M, Guillemette J, Siaj M, Desjardins P, Szkopek T and Martel R 2011 Probing charge transfer at surfaces using graphene transistors *Nano Lett.* **11** 132–7

[14] Yang, Z., Guo, B., & Zhang, L. (2017). Challenge of rubber/graphene composites aiming at real applications. Rubber Chemistry and Technology, 90(2), 225–237

[15] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. G. and A. A. F. (2016). Electric Field Effect in Atomically Thin Carbon Films. 306(5696), 666

[16] Galpaya, D., Wang, M., Liu, M., Motta, N., Waclawik, E., & Yan, C. (2012). Recent Advances in Fabrication and Characterization of Graphene-Polymer Nanocomposites. Graphene, 01(02), 30–49

[17] Das, A., Pisana, S., Chakraborty, B., Piscanec, S., Saha, S. K., Waghmare, U. V., Sood, A. K. (2008). Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. Nature Nanotechnology, 3(4), 210–215