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## Integration of CVD graphene in gaseous electron multipliers for high energy physics experiments

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**ABSTRACT:** To enhance the performance of micro-patterned gaseous detectors (MPGDs) to meet the challenging requirements of future high energy physics (HEP) experiments, two-dimensional (2D) materials are attractive candidates to address the back flow of positive ions, which affects detector performance by distorting electric field lines. In this context, graphene is promising to work as selective filter for ion back flow suppression, being transparent to electrons while at the same time blocking ions. Also, graphene membranes can physically separate drift and amplification regions of the detectors, offering additional flexibility in the choice of gas mixtures and allowing independent optimizations of detector sensitivity and electron multiplication processes. Here we present an approach to integrate graphene grown via chemical vapor deposition (CVD) on gaseous electron multiplier (GEM) prototypes via a wet transfer procedure in order to suspend graphene over thousands of holes with 60  $\mu\text{m}$  diameter and overcome the challenges encountered due to process

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steps involving liquids, mostly related with the capillary effects during drying and evaporation of them. In order to overcome the risk of damaging the membrane and decreasing the yield of suspended 2D material membranes, critical point dryer (CPD) and inverted floating method (IFM) procedures are investigated. In addition to the necessity to cover the full holes in the active area, polymeric residuals have to be minimized in order to evaluate the graphene transparency at the electron energies (i.e.,  $< 15$  eV) typically obtained in the operating conditions, measurements in these energy ranges are still not deeply investigated.

**KEYWORDS:** Micropattern gaseous detectors (MSGC, GEM, THGEM, RETHGEM, MHSP, MICROPIC, MICROMEGAS, InGrid, etc); Gaseous detectors; Materials for gaseous detectors

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## 1 Introduction

In the last decade, graphene has shown its potential in numerous technological applications because of its many useful properties such as mechanical strength, electrical and thermal conductivity, as well as atom impermeability. Thanks to the progress made in the field of scalable graphene synthesis via CVD, wafer-scale graphene is now accessible and can be integrated for different applications ranging from photonics to optoelectronics and sensing [1]. It may also be promising in HEP detectors to enhance the performance of MPGDs, solving some operational issues such as the back flow of the ions, preventing the distortion of the field line and adding more flexibility in the choice of gaseous mixture improving stability and electron amplification during the operation [2, 3].

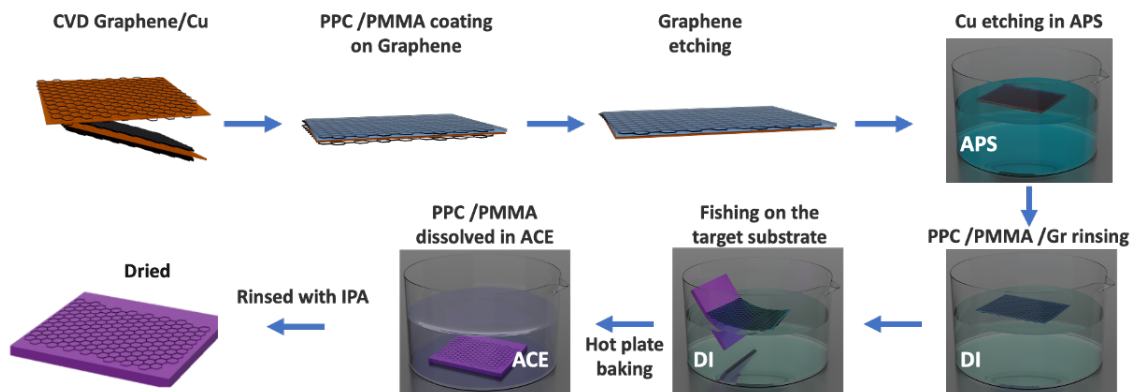
The requirements of the application rely on the possibility to suspend graphene covering thousands of holes with tens of micrometers of diameter, satisfying the transparency to low energy electrons (i.e.  $< 15$  eV) and the low permeation to gases. Since graphene is formed by strong  $sp^2$  covalent carbon-carbon bonds, it exhibits the largest Young's modulus in nature close to  $1$  TPa [4]. However, this is the case when single grains with no defects (i.e. carbon vacancies, grain boundaries) are taken into consideration; when dealing with CVD polycrystalline graphene, on the other hand, randomly distributed grains with topological defects are typically present. In particular, the presence of these defects impairs the effective mechanical, electrical and thermal properties of graphene in the devices and reduces its mechanical strength introducing weak points in the material [5].

Furthermore, during the fabrication, the membranes are frequently ruptured mainly because of the surface tension of the liquid acting on the membrane during the drying procedure, consequently, limiting the size of the aperture to few tens of micrometers as well as the yield of covered holes. Different possibilities to lower the tension of the liquid on the membrane have been proposed, the two most promising techniques are the use of (i) CPD [6] and the (ii) IFM [7]. In the first method, after the polymer removal in acetone, the sample is dried in a CPD to reduce as much as possible the surface tension of the liquid acting on the suspended membrane; in the second, the poly(methyl methacrylate) (PMMA) removal is performed without dipping the sample into any solvent, but by keeping the PMMA side of the sample floating on the surface of an acetone bath avoiding, in this case, the tensions of the solvent trapped in the holes by capillarity.

Graphene has been transferred on GEM foils with the use of CPD, however, the presence of defects (i.e. small apertures/cracks in the suspended membrane) and residuals, i.e., adsorbates, metallic and polymeric particles negatively affects the performance of the devices, showing a low electron transparency [3]. In this work, we present the optimization of graphene transfer on GEM foils with larger diameter using a wet transfer approach. We optimize the yield rates to suspend graphene by investigating the use of CPD and IFM and reduce the polymeric residuals to improve the detector performances.

## 2 Methods

The devices fabrication is performed by transferring polycrystalline graphene, synthesized via CVD in an Aixtron black magic reactor on  $4 \times 4 \text{ cm}^2$  electropolished Cu-foils (25  $\mu\text{m}$  thick, Alfa Aesar, purity 99.8 %) following the recipe reported in [8] on top of custom made GEMs foils. Standard GEMs foils are composed by 50  $\mu\text{m}$  thick Kapton foil with 5  $\mu\text{m}$  Cu coated on both sides, holes with 70  $\mu\text{m}$  diameters are photolithographed in a hexagonal lattice geometry with a pitch of 140  $\mu\text{m}$ . The hole density, the surface roughness and the metallic coating have been optimized in order to favour the best adhesion and relaxation of the membrane on the substrate to reach the optimal coverage. Hole diameter of 60  $\mu\text{m}$  with a pitch of 280  $\mu\text{m}$  and an Au coating have been selected. Figure 1 shows the adopted procedure of the wet transfer [9], the graphene is coated with PMMA (AR-P 672.045, Allresist) and 15 % poly(propylene) carbonate (PPC) dissolved in Anisole (Sigma-Aldrich) to increase its rigidity [10]. After the etching of graphene from the back side via reactive ion etching (RIE), the copper is etched in an ammonium persulfate (APS, Sigma-Aldrich) solution (0.1 M concentration) overnight. The PPC/PMMA/graphene stack is rinsed three times in de-ionized (DI) water and left floating overnight in DI water to reduce the residuals left by the etchant solution. While floating on the water, the membrane is then transferred on the GEM foil. After the wet transfer procedure, the substrate is left drying overnight in a clean and dry environment to evaporate the water between the graphene and the substrate. In order to improve its adhesion with the substrate the device

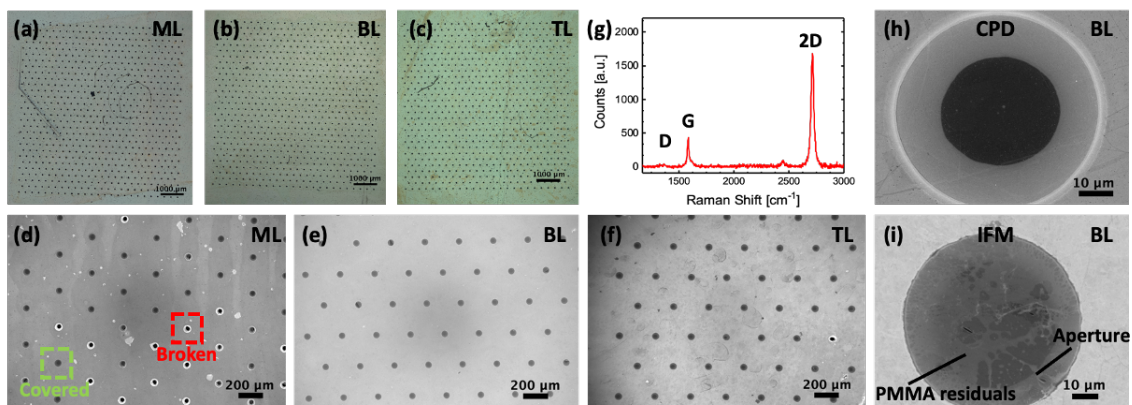


**Figure 1.** Schematic of CVD graphene wet transfer. CVD graphene is suspended using PMMA and PPC spin-coating, backside graphene etching, Cu foil etching in APS, rinsing, and wet-transfer onto the target device. Afterwards, the PPC/PMMA/graphene membrane is dried and baked, PPC/PMMA is removed (i) in ACE and then the sample dried with a CPD or (ii) via the IFM.

is heated with a hotplate at 105 °C for 4 hours. Finally, the PPC/PMMA is removed (i) in Acetone (ACE) for few hours, rinsed in isopropanol (IPA) and loaded in the CPD chamber filled with IPA in order to dry the membrane using liquid CO<sub>2</sub> in the supercritical phase to lower the tension of the liquid acting on the suspended material; (ii) with the inverted floating method, keeping the PPC/PMMA side of the sample floating on an ACE bath inside a beaker, avoiding also in this case, the tensions acting on the membrane of the liquid during the drying procedure. Monolayer (ML), bilayer (BL) and trilayer (TL) graphene transfers have been tested. The BL and TL preparation is performed following the schematic in figure 1 using as target substrate ML graphene on Cu, the procedure is repeated until the desired layer number is reached. Together with growth residuals, such as grain boundaries and metallic residuals [11], affecting the mechanical strength of the membrane, PMMA residuals are also left on the film by the solvents. An ulterior chemical step, to further remove PMMA residues left could be done, as reported by [10], treating the dried device with commercial remover AR-700-61 (Allresist) for three minutes, rinsed with DI water for 10 seconds and dried again in the CPD. After finalizing the transfer, the yield of the covered holes is estimated via scanning electron microscope (SEM) imaging. Raman spectroscopy is performed with a Renishaw InVia system equipped with a motorized stage for large-area mapping. The presence and the quality of the suspended graphene is characterized using a 473 nm laser with a spot size of approximately ~ 1 μm in diameter, a power of ~ 5 mW and an exposition time of 0.7 s [12]. In addition, graphene morphology is measured via an atomic force microscope (AFM, Dimension ICON-PT, Bruker). Topographic images are obtained in peak force Quantitative Nanoscale Mechanical (peak force QNM). Gwyddion software is used to process the AFM images, extract the surface profile and evaluate the surface roughness [13, 14].

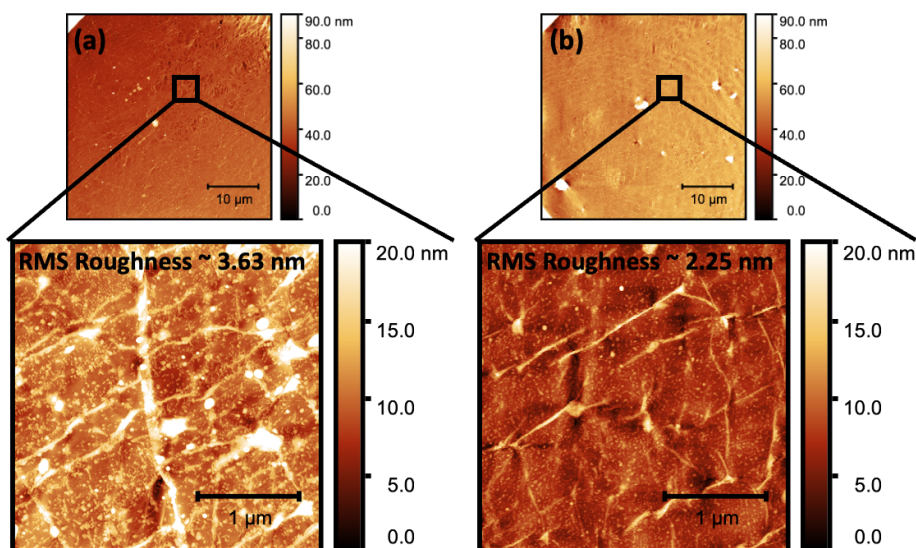
### 3 Results and discussion

GEMs foils with a pitch of 280 μm and additional Au coatings have been fabricated as target substrates to facilitate the adhesion of graphene during the transfer procedure. The adhesion on the substrates has been improved by treating the substrates before the transfer with remover AR-600-71 in order to make the surface more hydrophobic and, once transferred, reduce the trapped water at the substrate/graphene interface favouring the adhesion. The coverage yield has been evaluated via SEM imaging, images are taken across the active area of the sample in order to have a full overview of the sample. Both CPD and IFM approaches have been investigated. Typical SEM inspections can be seen in figure 2 after the transfer using a CPD. By looking at the different contrast intact and ruptured membranes can be distinguished as shown in figure 2(d) for a ML membrane where they are indicated in green and red, respectively. The ML graphene after the transfer exhibits a very poor coverage (around 10 %), due to the tension acting on the membrane during the drying and the presence of weak points randomly distributed in the material, i.e. grain boundaries. The strength of the membrane is increased by transferring BL and TL the yield is significantly improved reaching in both cases a 90 % coverage, as shown respectively in SEM images in figure 2(e) and (f). For additional structural characterization Raman spectroscopy on the suspended graphene has been used to confirm that the good quality of the graphene is kept after the transfer as indicated by the absence of disorder-induced D peak, see figure 2(g). CPD and IFM show compatible results in the final yield of the covered holes, however with the latter method the PMMA residuals left on the membranes are significantly higher, as can be appreciated in figure 2(h).



**Figure 2.** Optical and SEM images of GEM foils coated with graphene membranes with different thickness. (a,b, and c) Optical images of ML, BL and TL graphene on GEM foil after drying with a CPD, respectively. (d,e, and f) SEM images of samples mentioned in figure a, b and c. (g) Characteristic Raman spectrum of suspended graphene recorded with an excitation laser source at  $473\text{ nm}$  showing the characteristic peaks of graphene. (h and i) SEM images of a single hole covered with BL graphene using CPD and IFM, respectively.

The reduction of polymeric residual by treating the sample with remover has been confirmed by topographical images of the suspended membrane before and after the treatment. The topography has been evaluated by measuring the surface roughness in a  $3 \times 3\ \mu\text{m}^2$  area, as shown in figure 3. The comparison made for a BL yields a RMS roughness reduction by a factor of  $\sim 1.5$  after the treatment with the Remover.



**Figure 3.** AFM images showing the surface topography of the suspended membrane obtained via CPD. (a) AFM topography after the transfer. (b) AFM topography after the treatment with remover.

## 4 Conclusions

We presented the optimization of the wet transfer of CVD graphene on GEM foils. We showed that transferring ML graphene generally results in a poor yield of intact suspended membranes. However the yield can be increased by using BL and TL graphene (up to 90 %). Polymeric residuals left by the transfer procedure have also been lowered performing a remover treatment without significantly affecting the yield of the covered holes. The fabricated devices will be used to characterize the transparency of graphene to electrons in the low energy range, i.e. 5–50 eV, in an ultra high vacuum chamber. The electrons and ions transparency in gas will also be measured with a four GEMs stack configuration, placing graphene in the first GEM and using the triple GEM structure as an amplifier. In this configuration the lowest electrode of the last GEM will be connected to a preamplifier/amplifier/MCA, to record the spectra coming from the events, while the currents will be measured at anode, cathode and at the two electrodes of the first GEM. In this configuration the electron transparency will be defined as the ratio of the peak positions between the spectra of the events coming from the drift volumes after and before the first GEM, respectively. The ion transparency is defined as the ratio between the current at the cathode and the sum of the currents at the cathode and at the electrodes of the first GEM.

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