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Optimized graphene transfer: Influence of polymethylmethacrylate (PMMA) layer concentration and baking time on graphene final performance

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ABSTRACT

The influence of transfer parameters on the final structure, morphology and electrical properties of graphene were investigated in this work. Optical microscopy and atomic force microscopy (AFM) images showed that a double layer of PMMA can enhance or degrade graphene quality depending on its concentration. When properly diluted (15% in anisole, resulting in a PMMA layer of 1.35%) the transfer technique using double layer PMMA produces high quality graphene with fewer PMMA residues, non-cracked surface and sheet resistance around 247 ohm/square. We also investigated the influence of different baking times and temperature, and observed that the increase in baking time can degrade graphene quality thus leaving higher amounts of PMMA residues. Several works regarding graphene transfer are reported in the literature, but PMMA-based transfer processes still present challenges in yielding a clean and high quality graphene.

1. Introduction

Many techniques have been developed to prepare high quality graphene, which is in turn crucial to exploit in the upper limit its unique electrical, mechanical and thermal properties that leads a wide range of high performance applications [1–3].

Regarding growth methods, chemical vapor deposition (CVD) appears as a prominent technique since it allows the growing of uniform single layer graphene with high quality suitable to industrial applications [4,5].

In the CVD process, the first step is the annealing of the metal substrate (in a hydrogen/argon atmosphere) in order to increase the grain size of the metal catalyst, providing

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more uniform deposition. The second step takes place with the graphene growth, with the injection of carbonaceous gas precursors, followed by the cooling down step. CVD growth in copper is simple and straightforward, which makes the high quality graphene growth quite affordable. Thin copper sheets are inexpensive and can be etched by chemicals, such as $FeCl_3$, which facilitates the transfer process. In addition, copper has low carbon solubility and thus even at high temperatures graphene forms at the surface with negligible carbon dissolution into the bulk, which enables a self-terminating monolayer growth [4,6,7]. All these characteristics make the CVD growth using copper as catalytic substrate an attractive process for monolayer graphene growth [6,7]. The graphene quality can vary depending on the copper quality [8,9] and a cleaned copper surface is crucial for growing high quality graphene monolayers. In this work we followed the cleaning procedure reported by Kim et al. [9]. Commercial Ni etchant (based on nitric acid) or nitric acid is an easy and reproducible way of cleaning the copper foil, allowing high quality CVD graphene growth.

The main drawback of using CVD graphene is the transfer process from the metal to the target substrate. It is imperative that graphene quality remains preserved during transfer, otherwise the material can become unfeasible for practical applications [10].

Several techniques can be used to transfer CVD graphene, among them the polymer supportive layer-based transfer, usually poly(methyl methacrylate) (PMMA) is widely reported [10–13]. In this technique, first PMMA is spin coated on graphene/metal substrate surface, followed by the metal etching. PMMA/graphene stack is scooped onto a target substrate, followed by PMMA/graphene baking step in order to improve graphene-substrate adhesion. In the last step the supportive layer is etched away by annealing or dissolution in acetone [10,14]. This fast low-cost method can produce high quality graphene, but has some drawbacks related to the presence of PMMA residues whose total removal is still challenging. PMMA residues on graphene surface can induce p-doping effect and act as centers of carrier scattering, decreasing carrier mobility and leading to a low-quality graphene [14–16]. Due to the strong interaction between the PMMA and the graphene layer, the etching process can introduce structural discontinuities such as tearing and cracks which are not desirable [10,17].

Previously, Li et al. reported an improved transfer process by adding a second layer of PMMA. A much lower density of cracks and tears, along with excellent optical transmission and electrical conductivity of graphene films were observed [12]. Pirkle et al. reported improved electrical properties in graphene containing fewer residues. By AFM and Raman analysis fewer amounts of residues were observed when samples are treated by acetone and annealing process [15]. More recently, Jeong et al. used UV radiation to degrade PMMA chemical structure, thus reducing the intermolecular interactions between the polymer and the graphene. Consequently, PMMA etching was facilitated and the graphene layer showed better properties [18].

In this work we studied the influence of each parameter regarding the PMMA transfer technique. The discussion is centered on the evaluation of how the concentration of the second layer of PMMA affects transfer results. The influence of baking time and temperature of PMMA/graphene/SiO_2/Si stack in order to enhance graphene/substrate contact was also evaluated. This work aims to identify the influence of each step of PMMA-based transfer in graphene morphology, structure and electrical properties thus proposing an optimization of the graphene transfer process.

2. Experimental

2.1. Graphene growth

Graphene monolayers were synthesized through chemical vapor deposition (CVD) and copper foil (purchased from Alfa Aesar) was used as catalytic substrate. The graphene growth follows four stages: (1) Ramping up the temperature, (2) Substrate Annealing, (3) Graphene growth, (4) cooling down process. In the first step, the copper foil substrate was purged with 9 sccm of hydrogen flow, followed by ramping up the furnace temperature to 1000 °C for 20 min. After the temperature reached 1000 °C, the H_2 environment was maintained for 30 min to reduce the native copper oxide on copper foil surface. The growth step was carried out flowing 50 sccm of hydrogen and 20 sccm of methane for 30 min at the same temperature. The cooling down step was made by opening the furnace (fast cooling down). During the cooling down step was flowed the same gas composition as growth stage.

2.2. Transfer process of graphene films

2.2.1. Regular transfer

Graphene monolayers were transferred using the PMMA-based technique (PMMA, MicroChem 950 A9 – (9% in anisole) – 950,000 molecular weight). The as-received PMMA was diluted an addition 50% in anisole – which resulted in a 4.5% PMMA layer and was spin-coated on the graphene film at 2500 rpm for 1.5 min. After coating, the sample was annealed at 80 °C for 15 min. In order to etch the copper foil, the graphene/PMMA film was immersed in copper etchant (Trancene CE100) for 15 min. The suspended films were transferred to deionized water (2 times of 20 min each) followed by Hydrochloric acid – 10% (1 time of 10 min) and then deionized water (3 times of 20 min each) to remove any residual copper etchant. The target substrate (SiO_2/Si) was cleaned using the following procedure: First the target substrate was sonicated during 20 min in acetone, followed by immersion in boiling isopropyl alcohol (IPA) during 30 min. After this procedure, the target substrate was cleaned with isopropyl alcohol in ambient temperature and dried using a nitrogen gun. Subsequently, the graphene/PMMA films were transferred onto SiO_2/Si substrates. PMMA drying was made following 3 steps. The first one was made using a nitrogen gun for some seconds to improve the contact between PMMA/graphene/substrate and also to decrease the amount of water, followed by baking at 80 °C for 5 min and a second baking step at 130 °C for 20 min. The PMMA layer was removed using different methods:

1-immersion in acetone for 20 min.
2-immersion in acetone for 2 h.
3-immersion in acetone for 20 min followed by 2 h of annealing at 500 °C, using gas flow of 700 sccm of hydrogen and 400 sccm of argon.

2.2.2. *Number of PMMA layers*

The transfer was made as described in Section 2.2.1 until the PMMA etching step. Instead of removing the PMMA layer from the SiO_2/Si substrate, a second layer of PMMA was added using a pipette. For this second layer we used PMMA with additional dilutions of 15% or 50% in anisole, from the as-received PMMA A9, which resulted in 1.35% and 4.5% PMMA layer, respectively. The polymer cure was made at room temperature during 30 min. The removal of the double-PMMA layer was carried out by soaking the samples in acetone for 20 min followed by 2 h of annealing at 500 °C with gas flow of 700 sccm of hydrogen and 400 sccm of argon.

2.2.3. *Baking time*

Prior to this step, the transfer was made as described in Section 2.2.1, using one layer of PMMA 4.5%. In order to evaluate the influence of baking time of the PMMA layer the followed variations were made:

(a) 5 min at 80 °C.
(b) 5 min at 80 °C + 20 min at 130 °C.
(c) 5 min at 80 °C + 40 min at 130 °C.

The PMMA layer was removed by soaking in acetone for 20 min, followed by annealing at 500 °C for 2 h with gas flow of 700 sccm of hydrogen and 400 sccm of argon.

Fig. 1 shows the schematic diagram of graphene transfer process by using PMMA-based technique for both regular and double layer transfer methodology.

3. Results and discussion

Graphene monolayers are really difficult to identify on SiO_2/Si substrate on higher optical microscopy magnification. To prove the uniform distribution of graphene across SiO_2/Si substrate, Raman spectroscopy and optical microscopy with lower magnification were performed. In Fig. 2 is possible to observe the difference between Raman spectra performed on graphene sample and on bare SiO_2/Si substrate. Raman spectrum performed on graphene sample shows the fingerprint modes D, G and 2D while no Raman signal is seen on bare SiO_2/Si substrate in the range of 1000–3800 cm^{-1}. Also in Fig. 2 is possible to observe that graphene monolayer is homogeneously distributed across the substrate with Raman spectra reproducible on different points across the sample (for these measurements were used graphene transferred using one layer PMMA etched by immersion in acetone followed by annealing). We ensure that graphene monolayers were well distributed across all samples studied in this work.

Graphene obtained using different techniques of PMMA etching were analyzed by optical microscopy in order to investigate the graphene films regarding uniformity and level of macroscopic impurities. It was observed that the worst result was obtained when acetone was used to remove the PMMA, for both 20 min and 2 h samples. The presence of PMMA residues, as well as dark spots attributed to copper residues on graphene surface are clearly seen on Fig. 3(a) and (b). The use of an annealing step to remove the PMMA layer improved graphene quality, but residues and cracks still remained, as shown in Fig. 3(c). A continuous film without macroscopic impurities was obtained only using a double-layer PMMA (see Fig. 3(d)).

Li et al. [12] reported a double-layer PMMA transfer and suggested that graphene quality improvement occurred because the deposition of a second layer makes the first one, attached to the graphene, to become more flexible. As

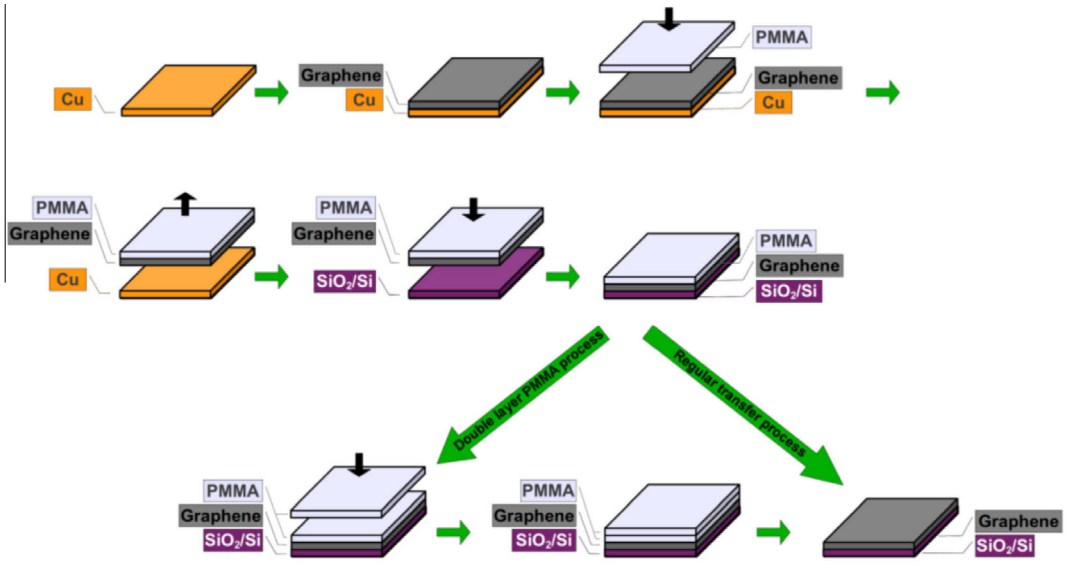

Fig. 1 – Schematic diagram of graphene transfer based on PMMA technique. (A color version of this figure can be viewed online.)

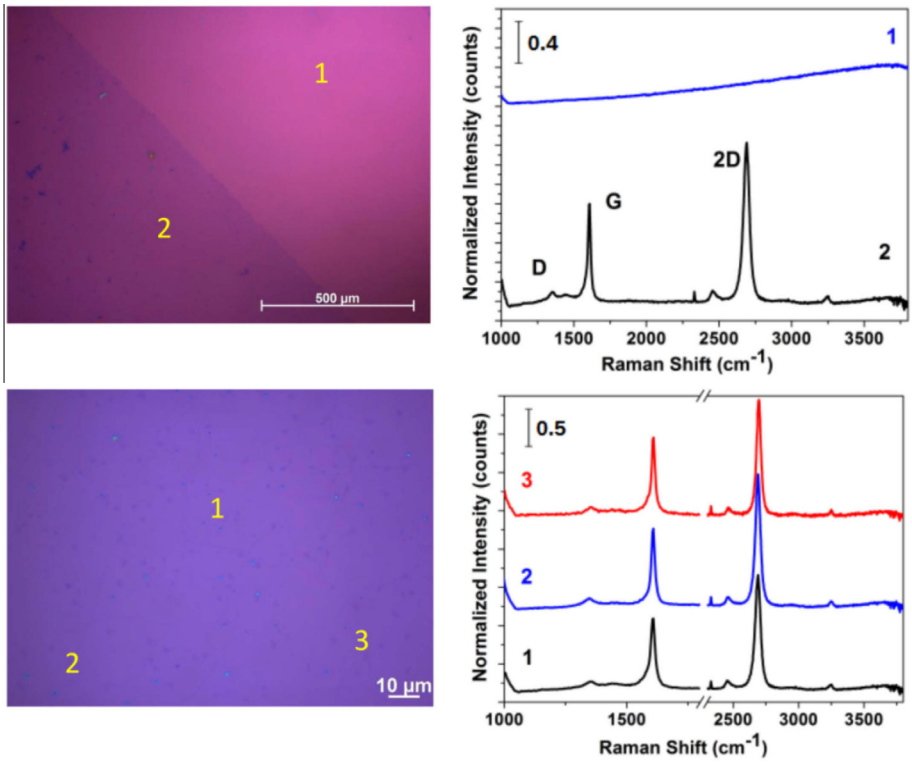

Fig. 2 – Raman and optical microcopy performed on different points of graphene monolayer and on bare SiO_2/Si. (A color version of this figure can be viewed online.)

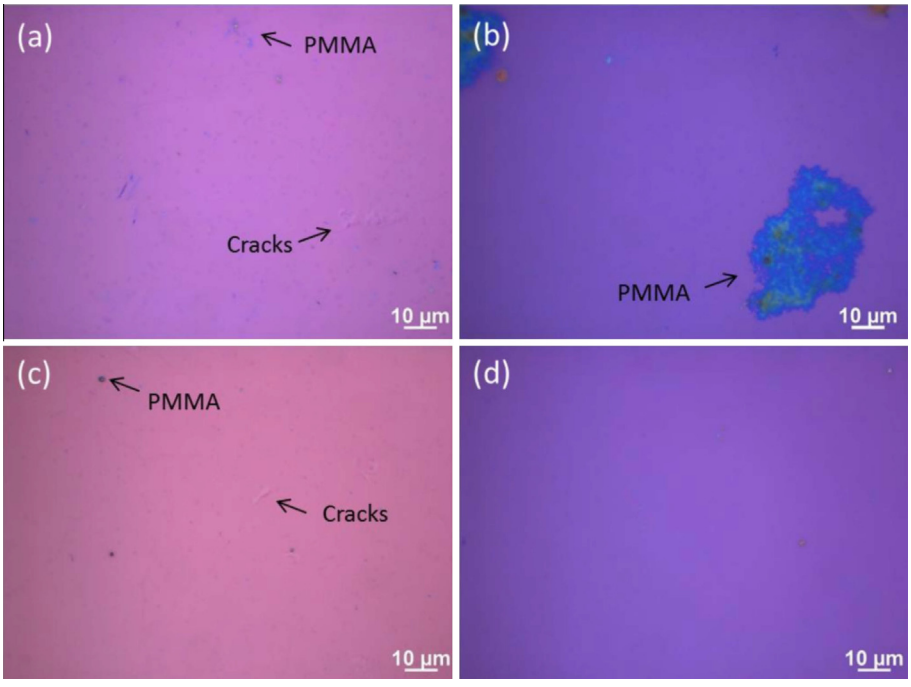

Fig. 3 – Optical microscopy images of (a) PMMA etched by immersion in acetone during 20 min (arrows highlight presence of PMMA residues and cracks) (b) PMMA etched by immersion in acetone during 2 h (arrow highlight presence of PMMA) (c) PMMA etched by immersion in acetone during 20 min followed by annealing (arrows highlight presence of cracks, PMMA and copper residues) (d) double layer PMMA etched by immersion in acetone during 20 min followed by annealing. (A color version of this figure can be viewed online.)

a result, the graphene film is more mechanically relaxed and consequently makes a better contact with the substrate. Thus, during etching the tensions between PMMA/graphene are lower which results in a less defective graphene layer [12].

However, further investigation allowed us to report that PMMA concentration has a determinant role on this matter. Indeed a double PMMA layer increases graphene quality, producing a film with fewer impurities and with higher continuity, although this behavior can only be observed when the second PMMA layer is diluted enough, since increasing PMMA concentration influenced negatively the graphene quality.

AFM and Optical microscopy results, Fig. 4, evidenced that using two layers of PMMA with correct dilution enhanced the quality and decreased the presence of cracks and impurities of the transferred graphene compared with transfer using either one or two layers of PMMA with higher concentrations. The use of PMMA as supportive layer in graphene transfer is already well known [14]. The first layer of PMMA need to be thick enough to prevent the damage of the graphene layer, but also should avoid as much as possible the formation of residues on the graphene surface. We chose to use an additional dilution of 50% in anisole as first layer, which resulted in a 4.5% PMMA layer due to optimized conditions investigated by previous experiments in our laboratory.

Raman spectroscopy is a non-destructive technique that allows quick and precise investigation of structural features and quality of graphene. Raman spectra of samples treated by different PMMA removal techniques are depicted in Fig. 5. The G band observed at 1595 cm^{-1} for samples treated

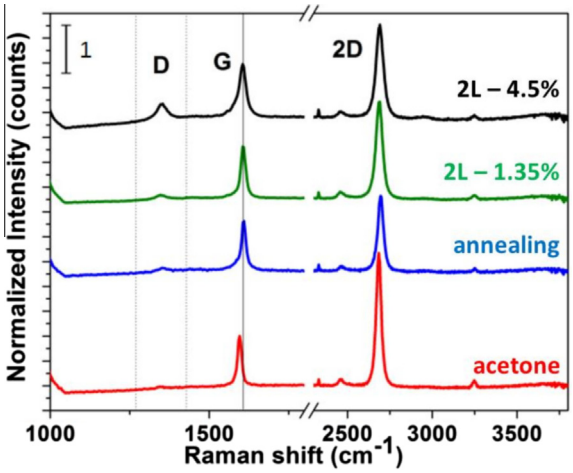

Fig. 5 – Raman spectra of graphene films obtained by using different PMMA etching techniques. (A color version of this figure can be viewed online.)

by acetone immersion is blue shifted to 1604–1606 cm^{-1} after annealing, along with a decrease in the relative intensity of the 2D-peak (also called G′ band). This behavior is consistent with hole doping, usually observed for samples annealed at high temperatures [19,20]. As reported in the literature, hole doping in graphene is caused by many factors. Former works indicate that hole doping occurs due to increased charge transfer between graphene and SiO_2 substrates and/or

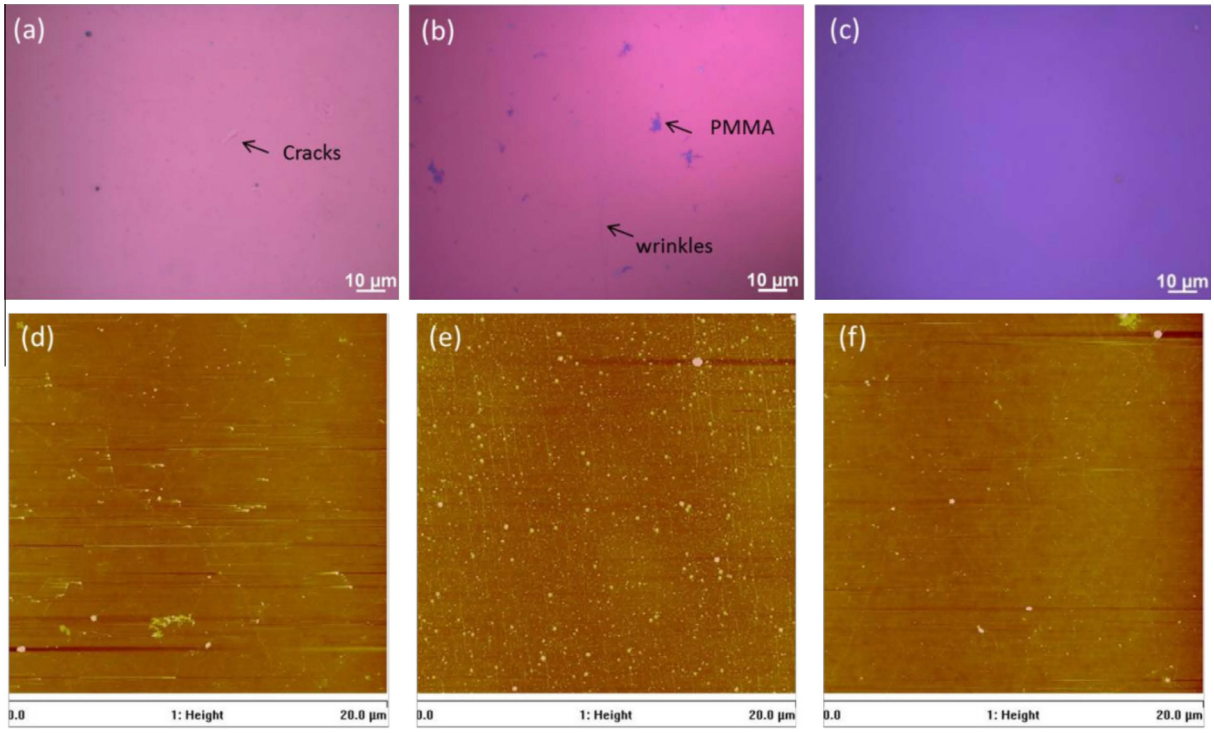

Fig. 4 – Optical microscopy (upper panels) and AFM (lower panels) images of graphene films obtained after deposition of (a and d) one PMMA layer 4.5% (arrow indicate presence of cracks), (b and e) two layers of PMMA both with 4.5% (arrows indicate presence of PMMA residues and wrinkles) and (c and f) two layers of PMMA (the first one with 4.5% and the second one with 1.35%). (A color version of this figure can be viewed online.)

Table 1 – Positions and FWHM of G and 2D bands obtained through line shape analysis of Raman spectra showed in Fig. 5.

Samples	G (cm^{-1})	FWHM (G)	2D (cm^{-1})	FWHM (2D)
Acetone	1595	14	2684	30
Annealing	1606	25	2695	33
2L-4.5%	1604	26	2690	44
2L-1.35%	1606	17	2686	39

adsorption of H_2O and O_2 molecules on graphene induced by high temperature annealing [19,21,22].

Adding a second PMMA layer did not result in G mode shift, although the so-called disorder-induced Raman mode (D band) at 1350 cm^{-1} (laser excitation at 2.41 eV) has been found to be more pronounced when using two layers of PMMA 4.5%, thus suggesting that PMMA residues contributed with the rising of D band intensity. 2D Raman modes centered at 2684–2695 cm^{-1} in all samples were fitted using single Lorentzian curve with FWHM ranging between 30 and 44 cm^{-1}. This was found to be distinct from bilayer graphene that presents broader bands with four fitting components [23,24]. Table 1 summarizes position and FWHM of G and 2D bands from Raman spectra presented in Fig. 5.

In intrinsic graphene, based on theoretical calculations, the mobility can reach 200,000 cm^2/Vs at room temperature (for carrier density of 10^{12} cm^{-2}), which yields sheet resistance of 30 Ohms [25]. However, these estimated values assumed that graphene is flat, single crystalline and measurements made in vacuum in which only electron–phonon scattering contributes to the electrical resistance. In practice, it is observed other sources of carriers scattering such as wrinkles, domain boundaries, substrate interactions and charged impurities which make it difficult to achieve that ideally high mobility, especially for graphene grown by CVD [25].

Here we observed that hole mobility values varied according to PMMA etching method. Samples treated by acetone immersion, which were found to be less doped, presented hole mobility around 1500 cm^2/Vs while annealed samples showed values around 1200 cm^2/Vs. Hole mobility for samples in which the second PMMA layer was used with 1.35% was found around 1180 cm^2/Vs while the worst mobility was found using the second layer of PMMA with 4.5% around 780 cm^2/Vs.

Sheet resistance was measured using Van der Pauw's method and the distribution of sheet resistance values for samples obtained using different technique of PMMA etching (values acquired from at least 3 samples of each condition) are shown in Fig. 6. Samples treated by acetone immersion presented higher values of sheet resistance, around 650 ohm/square. Annealed samples showed decreased sheet resistance around 330 ohm/square, due to the hole doping process as already described (carrier concentration for annealed samples = 1.5×10^{13} cm^{-2}). Concerning the evaluation of the effect of PMMA concentration, sheet resistance results suggested that this factor strongly influenced the graphene electrical properties. Specifically, the results showed a significant difference between samples transferred

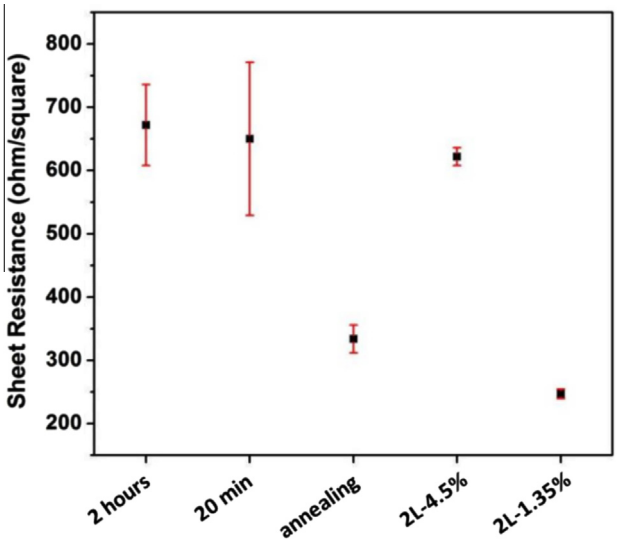

Fig. 6 – Sheet Resistance of graphene films transferred using different PMMA etching techniques. (A color version of this figure can be viewed online.)

using double PMMA layer technique but with different concentrations: 620 ohm/square for both PMMA layer with 4.5% against 247 ohm/square for samples transferred using the second PMMA layer with 1.35%. We suggest that depositing a second PMMA layer with higher concentration left residues on graphene surface which acted as carrier scattering center, which is in accordance to the observations from Raman, AFM and optical microscopy images. On the other hand, introducing a second PMMA coating from diluted solution, after the PMMA/graphene transfer to SiO_2/Si substrate, improved significantly graphene quality, thus producing a less cracked film, free from wrinkles and with less polymer impurities.

We also investigated the influence of both baking time and temperature of the PMMA layer after transfer of PMMA/graphene stack to SiO_2/Si. This is important since it has been observed that PMMA/graphene film should make total contact with the substrate, otherwise the unattached regions tend to break and form cracks that remain when the PMMA film is dissolved away [12].

Works in the literature report two kinds of gaps usually found between the PMMA/graphene stack and the target substrate [12,26]. The first type of gap appears due to the reconstruction of metal surface at high temperatures, resulting in a rough surface. During the growth step, graphene morphology follows the metal surface and later during transfer when copper is etched away, the PMMA/graphene stack mimics the metal surface morphology. Due to that, graphene does not lie flat on top of the target substrate leading to "small" gaps between the graphene and the target substrate surface. The second type of gap is resulted from trapped water between PMMA/graphene and the substrate. Once the water is released large gaps can arise causing large folds and/or wrinkles [12,26].

Optical microscopy images show that a more continuous layer with fewer cracks is obtained when both time and temperature of baking PMMA/graphene stack are increased,

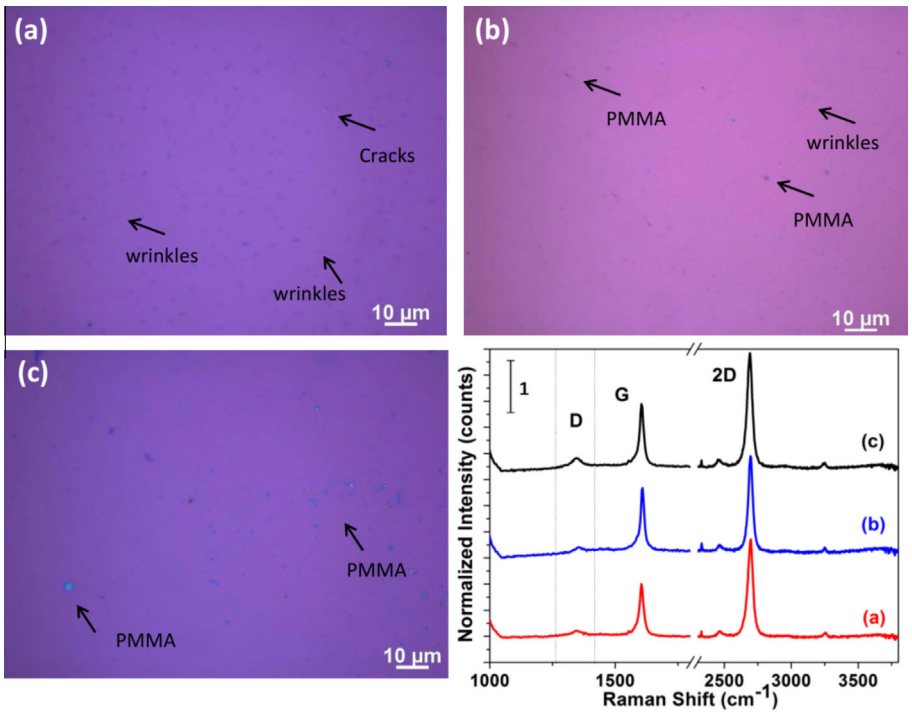

Fig. 7 – Optical microscopy and Raman spectra of samples baked during (a) 5 min at 80 °C, (b) 5 min at 80 °C + 20 min at 130 °C and (c) 5 min at 80 °C + 40 min at 130 °C – all samples in this section was transferred using single layer PMMA 4.5%. (A color version of this figure can be viewed online.)

when compared to PMMA/graphene stack baked in lower temperature, Fig. 7. Liang et al. reported similar results baking PMMA/graphene stack at 150 °C for 15 min and assigned this behavior to the improved contact between the stack and the SiO_2/Si substrate, which resulted in reduced surface roughness of PMMA/graphene stack [26]. Besides the morphological improvements observed here, it can be observed that upon increasing baking time and temperature, higher amounts of PMMA residues were found on graphene surface. We suggest that longer baking time lead to PMMA layer hardening, which make it more difficult to remove PMMA residues on top of graphene film.

Raman spectra showed graphene fingerprint with Raman modes centered at 1604 cm^{-1} and 2690 cm^{-1}. For all samples it is possible to observe a discrete D mode around 1350 cm^{-1}, thus suggesting the presence of defects on graphene structure. Disorder in a graphene monolayer can be quantified by analyzing the I_D/I_G intensity ratio between D and G bands [27]. Analyzing I_D/I_G ratio calculated as 0.17; 0.12; 0.39 for samples baked during 5 min at 80 °C, 5 min at 80 °C + 20 min at 130 °C and 5 min at 80 °C + 40 min at 130 °C, respectively, larger I_D/I_G ratio was found for the sample baked for longer times, revealing that even though longer baking period may provide better contact between graphene/substrate, the amount of PMMA left on graphene surface degrades graphene quality. The smallest I_D/I_G ratio was found by using a total baking time of 25 min.

AFM images of samples with PMMA layer baked in different conditions show the presence of wrinkles on those samples treated at lower temperatures and lower time (5 min). Increasing baking time, fewer wrinkles were found, but on the other hand we still can observe the presence of PMMA residues on graphene surface, Fig. 8, as already discussed on previous results. It is important to highlight that some of these wrinkles could be generated during the CVD growth. By baking for longer times we may be able to avoid additional wrinkles generated during transfer process.

Sheet resistance ranged from 330 to 360 ohm/square with values slightly higher for samples baked during longer time (45 min), Fig. 9, with hole mobility ranging between 1000 and 1200 cm^2/Vs. Compared with results discussed above we conclude that the introduction of a second diluted PMMA layer influenced the graphene electrical properties much more effectively, producing graphene films with lower density of defects and enhanced electrical properties.

Although the mobility is still lower than the highest value reported of CVD grown graphene [28], it is already higher than the devices fabricated via regular transfer method, which are concentrated around 200–800 cm^2/(Vs). This indicates that when the residual particles were removed, the local scattering of carriers was reduced and hence the mobility was improved [26].

Liang et al. [26] reported that baking PMMA/graphene after placing it on SiO_2/Si substrate is much more efficient for producing high quality graphene when compared to the introduction of double layer PMMA reported by Li et al. [12].

Summarizing our results, we can conclude that baking process is important to improve graphene/substrate contact, but the introduction of a second layer of PMMA with proper dilution (15% in anisole from PMMA A9, resulting in a PMMA layer of 1.35%) greatly increased graphene quality, with less density of defects, less PMMA residues on graphene surface

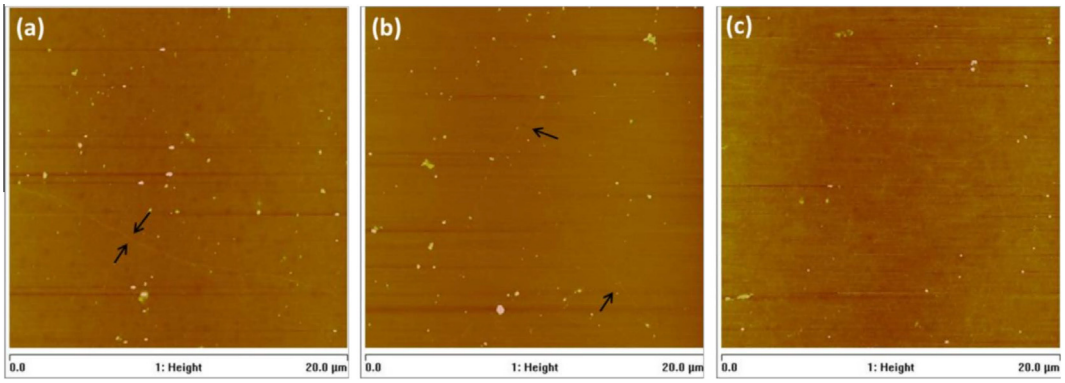

Fig. 8 – AFM images of graphene films baked during (a) 5 min at 80 °C, (b) 5 min at 80 °C + 20 min at 130 °C and (c) 5 min at 80 °C + 40 min at 130 °C. (A color version of this figure can be viewed online.)

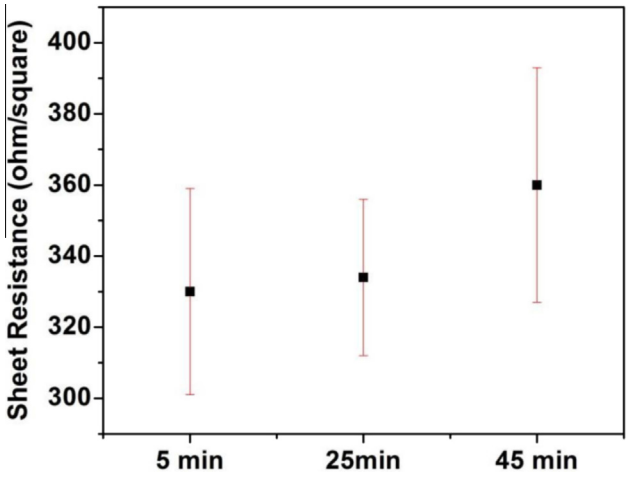

Fig. 9 – Sheet resistance of graphene films baked during (a) 5 min at 80 °C, (b) 5 min at 80 °C + 20 min at 130 °C and (c) 5 min at 80 °C + 40 min at 130 °C. (A color version of this figure can be viewed online.)

and lower sheet resistance. Using only one PMMA layer independently of baking time and temperature we observed graphene layers with lower quality than those obtained with double layer of PMMA. Shorter baking times (around 5 min) are insufficient to allow evaporation of remaining water between graphene/substrate, resulting in cracks and wrinkles during PMMA etching, while longer periods left higher amount of residues on graphene surface. Comparing samples baked under the same conditions but with different number of PMMA layers, we conclude that the concentration of the 2nd PMMA layer plays a determinant role, producing high quality graphene using the combination of 4.5%/1.35% and really low-quality graphene when higher concentrations are used (4.5%/4.5%).

Acknowledgments

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