Assessing by Raman spectroscopy the quality of CVD graphene transferred on oxidized silicon and quartz substrates

Florin COMANESCU, Anca ISTRATE, and Munizer PURICA

Abstract. We present the results of a study regarding CVD graphene transfer from copper foil to other substrates - oxidized silicon and quartz by means of electrochemical delamination. Transfer results were examined by means of Raman spectroscopy using a laser at 633 nm and confocal optical microscopy to identify graphene in good optical contrast conditions. Characteristic Raman bands of graphene - D, G and 2D are certifying if a transfer process has been performed successfully. The quality of the transferred graphene are evidenced by the modifications in the main graphene Raman bands D, G, 2D from which quality (I_{2D}/I_{G}) and defect (I_{D}/I_{G}) ratio’s were extracted. We are also highlighting critical steps in the transfer process. The final step of Polymethyl methacrylate (PMMA) removal is the most critical one due to the partially folding of graphene. After transfer defects are induced in graphene which is confirmed by the increase of the ratio of the intensity of the D band to the G (I_{D}/I_{G}).

Key-words: Raman spectroscopy, CVD graphene, graphene transfer by electrochemical delamination, transferred graphene quality.

1. Introduction

Monolayer graphene consisting of a 2D hexagonal lattice of sp2-bonded carbon atoms has received a great attention for many applications due to its outstanding electrical, thermal, mechanical and optical properties, [1–4]. Current research and development of graphene and graphene based next generation electronic and optoelectronic devices is driven due to its high electrical conductivity at room temperature (electron mobility 200 000 cm²V⁻¹s⁻¹), quantum hall effect, high optical transmittance (~ 97 %), excellent thermal conductivity (3000 – 5000 Wm⁻¹K⁻¹)
and to advancement of its synthesis and transfer technologies on the target substrate, [5–7]. Applications of electronic and optoelectronic devices include: field-effect transistors, transparent display and touch screen, solar cells, various type of sensors, [8–11].

In two previous papers, the following graphene based electronic devices were reported: a Schottky diode on graphene monolayer having asymmetric metal contacts for use in millimeter waves applications, [12], and a study regarding fabrication and characterization of graphene-silicon heterojunctions by varying junction area obtained, [13]. To obtain these electronic devices it is essential to synthesize graphene having corresponding electronic properties which is a challenge both in the synthesis and the transfer method on the target substrate as well as in the techniques for the identification, characterization and processing of graphene. In order to properly exploit graphene properties it is necessary to assess the quality of the transferred graphene.

Synthesis of mono-layer graphene by chemical vapor deposition (CVD) is one of the most widely used deposition method. It is well known for exploit CVD grown graphene, it is crucial to transfer it from the catalyst metal to a desired substrate. Consequently the most used technological possibility for graphene processing in order to be integrated in micro / nano-electronic devices consists in two steps: the first step is CVD growth of graphene on a transition metal substrate (copper and nickel are the most suitable for graphene deposition due to their catalytic properties); the second step is the transfer of graphene to the target substrate. The most commonly used method is by wet transfer where the metal substrate is etched away with a metal etchant (i.e. FeCl3, CuCl2, etc.), then the graphene is fishing onto a target substrate, [14–15]. A polymeric support layer polymethylmethacrylate (i.e. PMMA) is typically spin-coated onto graphene before wet transfer to structurally protect it through the process and then removed after the transfer [16]. The presence of intercalated material is of particular concern whenever wet transfers are involved, as either water or other solvents may remain trapped between graphene and the target substrate, [17]. The main drawback of this method is the potential for contamination during the transfer process with residual Fe ions on transferred graphene, this is undesired because it degrades its mechanical and electronic properties. For example, the Fe ions are known to unintentionally dope the transferred graphene and decrease charge carrier mobility. More recently, the so-called "bubbling" transfer technique has been proposed, whereby the graphene is detached from the growth substrate via electrochemical delamination without the need to etch the metal [18]. This method is more controllable than chemical etching process is non-destructive, low-cost and copper catalyst can be reused. An appropriate graphene quality on dielectric substrates can be obtained by Electrochemical Delamination. This transfer process depends on the successful solution of defects, such as cracks and wrinkles that degrade the graphene quality.

In our previous studies we also compared graphene transfer by drop-casting and lamination from copper substrate to polymer substrate (PVA or PVA/PEN). Due to PVA characteristics: non-toxicity, solubility in water, good biocompatibility the targeted applications are in the developments of fibrous constructs for tissue engineering or controlled drug delivery, [19].

Another study was aimed at determining optimal conditions for graphene processing using electron beam lithography either direct / or through a PMMA mask by taking into account electron beam parameters (acceleration voltage and exposure dose), [20].

Raman spectroscopy is considered one of the nondestructive and powerful techniques which have been successfully applied to investigation and characterization of carbon based nanomaterials such as graphene, graphene oxide, carbon nanodots and nanotubes and to study other two-dimensional materials beyond graphene. In graphene, the Stokes phonon energy shift by He-Ne laser (λ= 633 nm) interaction creates two main peaks in Raman spectrum: G (∼1580 cm−1),
in-plane vibration mode and 2D (\(\sim 2700 \text{ cm}^{-1}\)), a second-order overtone of a different in-plane vibration [21–22]. Raman spectroscopy is also one of the best tools to assess the quality and the degree of structural properties modification of graphene in various technological processes such as synthesis followed by graphene transfer on different substrates.

In this work we present the results of micro-Raman studies of graphene grown by CVD on copper foil surface and then transferred on SiO2/Si and quartz substrates by means of electrochemical delamination. Raman spectra were collected at room temperature by using LabRAM HR 800 system and the main Raman bands characteristics and their intensities ratio highlighted the quality of transferred graphene sheets.

2. Experimental details

Samples of graphene layer grown by CVD on polycrystalline copper foil from Graphene Supermarket were used for graphene transfer by means of electrochemical delamination.

The graphene sheets on copper were transferred on two types of substrates - SiO2/Si and quartz by electrochemical delamination method using a home-made system described in previous paper, [12]. A brief description of the transfer process contains the following steps:

- 300 nm PMMA film is deposited on graphene/Cu by spinning,
- annealing at 150°C for 2 minutes backed,
- taking the PMMA/graphene/Cu stack and inserting as the cathode in the electrochemical cell (graphite | 0.05 mM K2S2O8 | GR/Cu),
- an electrical potential of 40 V was applied to the cell until the entire film of PMMA/graphene was delaminated and floating on the surface of the electrolyte solution,
- collecting the PMMA /graphene from the electrolyte solution and placing it on the target substrates,
- removal of PMMA in acetone.

Each of these steps is characterized using Raman spectroscopy in order to determine the critical step in the process of transferring the CVD graphene on the target substrate. Raman investigation has been performed by using LabRam HR800 Raman spectrometer with confocal optical microscope in backscattering configuration using He-Ne laser (633 nm), a grating of 1800 gr/mm and a 100x objective having 0.9 numerical aperture.

3. Raman Spectroscopy: characterization and imaging of transferred graphene quality on SiO2/Si and quartz substrates

Graphene having unit cell from two carbon atoms sp² bonded, there are six phonon branches - three optical phonons (O) and three acoustic (A). For two optical phonon and two acoustic phonons, the atomic vibrations are in-plane (i) and for one optical and acoustic branch the vibrations are out-of-plane (o), perpendicular to the graphene plane. Depending if the vibrations are parallel or perpendicular to the wave-propagation direction (specified by wave k vector), phonon
modes are known as longitudinal (L) or transverse (T). LO and LA modes are always in-plane along with i-TO and i-TA and for main Raman bands in graphene are responsible LO and i-TO modes.

Graphene has a unique Raman fingerprint evidenced by the following Raman bands, [21–22]:
- G band (localized at \( \sim 1580 \text{ cm}^{-1} \)) come from first-order Raman scattering process is a double-degenerate and corresponds to in-plane vibrations modes of sp\(^2\) carbon-carbon bond which belongs to \( E_{2g} \) symmetry according with group theory. This band is characteristic for all sp\(^2\) carbon system – carbon nanotubes, graphite and amorphous carbon. The G band originates from phonon at zone-center \( \Gamma \) point of Brillouin Zone-BZ) and involves phonon modes LO and i-TO,
- 2D band (also called G’ band) come from second-order double resonant process consisting in different in-plane vibration modes (breathing-like mode of carbon rings) and involves two phonon modes, \( A'_1 \) in the vicinity of the K point of BZ. Since the process involves electronic state near K point is known as intervalley scattering process. 2D Raman peak is located at \( \sim 2700 \text{ cm}^{-1} \) for \( E_{\text{laser}} = 2.414 \text{ eV} \) and at \( \sim 2650 \text{ cm}^{-1} \) for \( E_{\text{laser}} = 1.959 \text{ eV} \) and does not require a defect for its activation and its shape determines the number of layers,
- D band (located at \( \sim 1350 \text{ cm}^{-1} \) for \( E_{\text{laser}} = 2.414 \text{ eV} \) and at \( \sim 1326 \text{ cm}^{-1} \) for \( E_{\text{laser}} = 1.959 \text{ eV} \)) come also from an intervalley scattering process in the vicinity of the K point of BZ which involves an inelastically scattering by a i-TO phonon and the second elastic scattering by a defect or at boundary zone of graphene flakes. D peak is not visible in Raman spectra of defects free graphene. D and 2D modes have dispersive behavior in Raman spectra,
- D’ peak at \( \sim 1620 \text{ cm}^{-1} \) come from an intervalley scattering process and involves a near \( \Gamma \) point phonon (\( E_{2g} \) phonon) and an elastic scattering by defects or a high degree of crystalline disorder;
- 2D’ band (\( \sim 3240 \text{ cm}^{-1} \)) is a two phonons process and the second order overtone of D’. These bands are significantly weaker than the 2D and D band.

Structural properties and defects of graphene were extracted from graphene Raman band parameters as quality \( I_{2D}/I_G \) and defect \( I_D/I_G \) ratios. These indicators allow a quick estimation of graphene quality.

In figure 1 is presented a typical Raman spectrum acquired on CVD grown monolayer graphene on copper substrate where the characteristic Raman bands of graphene: G (\( \sim 1586.6 \text{ cm}^{-1} \)) and 2D (\( \sim 2642 \text{ cm}^{-1} \)) are evidenced.

![Fig. 1. Typical Raman spectrum acquired on graphene / copper sample and a picture of the area where the spectrum has been acquired.](image-url)
The shape of 2D band is Gaussian which confirms that the investigated graphene area is single layer. This Raman spectrum presents no defects which evidences the high quality of the investigated area of graphene. The picture presented in figure 1 corresponds to the area where the Raman spectrum was acquired. In the case of graphene on copper optical contrast cannot help identify areas with graphene.

The average and standard deviation corresponding to the parameters extracted from the Raman spectra acquired on graphene / copper samples are presented in table 1. The average value of the defect ratio $I_D/I_G$ is 0.22, slightly higher than the acceptable limit for CVD grown graphene which is 0.2. The corresponding standard deviation value is 0.33. The average value corresponding to the quality ratio is 2.33 which evidence a good quality of the investigated graphene. Corresponding standard deviation value is 0.8 which is a high variation of graphene quality on the surface.

Table 1. Average Raman bands parameters and standard deviation corresponding to graphene / Cu source for transfer

<table>
<thead>
<tr>
<th>Graphene on copper before transfer</th>
<th>Average values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band</td>
<td>Position (cm$^{-1}$)</td>
</tr>
<tr>
<td>D</td>
<td>1328.37</td>
</tr>
<tr>
<td>G</td>
<td>1584.02</td>
</tr>
<tr>
<td>2D</td>
<td>2659.54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band</td>
</tr>
<tr>
<td>Position (cm$^{-1}$)</td>
</tr>
<tr>
<td>FWHM (cm$^{-1}$)</td>
</tr>
<tr>
<td>$I_D/I_G$</td>
</tr>
</tbody>
</table>

In figure 2 is presented a Raman spectrum acquired on PMMA deposited on graphene / copper having an inside picture of sample surface. We find characteristic Raman bands of graphene: G (1589.2 cm$^{-1}$), 2D (2641.5 cm$^{-1}$) and the characteristic Raman bands of PMMA: 601.7, 813.8, 994, 1453.2, 1731.9, 2844.7, 2950.6, 3001.9 cm$^{-1}$, [23]. 2D band shape is Gaussian which confirms that the investigated area contains single layer graphene.

![Fig. 2. Raman spectrum acquired from PMMA / graphene / copper and corresponding image.](image)
High intensity corresponding to PMMA Raman bands is due to the SERS effect on graphene surface. The picture acquired on the sample shows small areas where the microscope can focus resulting that the sample already contains wrinkles.

In figure 3 are presented Raman spectra acquired from copper foils after separation by means of electrochemical delamination and a picture of the sample surface. In the inside picture we see a shrinkage of the area on which the confocal microscope is able to be focused. The copper foil may present more wrinkles in comparison to its state before introduction in the electrochemical cell. In the inset picture areas containing graphene cannot be distinguished. The Raman spectra are showing that after transfer there are areas without graphene and areas with graphene. The Raman spectra acquired in the areas with remnants of graphene are confirming large values of the full with half maximum (FWHM) for G and 2D bands. These values are roughly 25 cm$^{-1}$ for G and a range of 50–55 cm$^{-1}$ for 2D. Such values are much higher than the average values presented in table 1 for graphene on copper samples.

![Fig. 3. Raman spectra acquired from copper foils after graphene transfer process and a picture of the sample surface.](image)

Graphene / PMMA is extracted from the electrochemical delamination cell and placed on a glass substrate, Fig.4.

![Fig. 4. Typical Raman spectrum acquired from graphene / PMMA /sample extracted from the electrochemical delamination cell and placed on a glass substrate.](image)
In figure 4 is presented a typical Raman spectrum acquired from graphene / PMMA / glass sample and a picture of the sample surface. Although there is very poor optical contrast we can also determine areas containing graphene. We find the characteristic Raman bands of graphene D (1318 cm\(^{-1}\)), G (1582.2 cm\(^{-1}\)) and 2D (2638.8 cm\(^{-1}\)) and also the characteristic peaks of PMMA: 600.8, 810.9, 991.1, 1125.9, 1449.5, 1726, 2841.2, 2952.1, 3002 cm\(^{-1}\), [23]. 10 Raman spectra were acquired on the sample surface. From these only one did not present graphene characteristic Raman bands. As in the previous case the high intensity corresponding to PMMA characteristic Raman bands is due to the SERS effect caused by the plasmons in graphene.

In figure 5 is presented an optical image of the wrinkles that are forming on the surface of graphene / PMMA / glass placed in a wafer box. Here we can observe the wrinkles that were formed on the sample surface.

![Image](image.png)

**Fig. 5.** Optical image of the wrinkles on the surface of graphene / PMMA / glass placed in a wafer box.

These wrinkles are results of copolymer evaporation. By comparing images from figures 4 and 5 and taking into account the scale it results that after placing the sample in the electrochemical cell the graphene is transferred almost completely on the PMMA intermediary substrate.

In table 2 are presented average Raman bands parameters and standard deviation corresponding to graphene / PMMA / glass.

**Table 2.** Average Raman bands parameters and standard deviation corresponding to graphene / PMMA / glass

<table>
<thead>
<tr>
<th>Graphene / PMMA / glass</th>
<th>Average values</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band</td>
<td>Position (cm(^{-1}))</td>
<td>FWHM (cm(^{-1}))</td>
</tr>
<tr>
<td>D</td>
<td>1321.16</td>
<td>21.74</td>
</tr>
<tr>
<td>G</td>
<td>1581.38</td>
<td>14.57</td>
</tr>
<tr>
<td>2D</td>
<td>2637.2</td>
<td>38.06</td>
</tr>
</tbody>
</table>

\(I_D/I_G\): Intensity ratio of D band to G band
\(I_{2D}/I_G\): Intensity ratio of 2D band to G band
Average value of G band FWHM 14.57 cm$^{-1}$ is close to stress free value – 15 cm$^{-1}$.

After a short comparison with table 1 data results the following,
- Graphene Raman bands (D, G, 2D) are red shifting on PMMA,
- Quality ratio is improved (I$_{2D}$/I$_{G}$),
- Defect ratio is increased (I$_{D}$/I$_{G}$) although it has a smaller range,
- G band FWHM is smaller on oxidized silicon substrate.

In figure 6 is presented a typical Raman spectrum acquired from graphene transferred on oxidized silicon samples after PMMA removal and a surface image. In this spectrum we can identify D (1323.9 cm$^{-1}$), G (1589.8 cm$^{-1}$), and 2D (2646.8 cm$^{-1}$) characteristic Raman bands of graphene.

![Fig. 6. Typical Raman spectrum acquired from graphene / oxide / silicon samples and corresponding picture.](image)

The Gaussian shape of 2D peak confirms that in the investigated area we find single layer graphene. In the surface image due to optical contrast we can distinguish surface coverage with graphene. We see immediately that in the investigated area the coverage percentage is close to 90%.

In figure 7 is presented a typical Raman spectrum acquired from graphene transferred on quartz samples after PMMA removal and a surface image. In this spectrum we can identify G (1585.7 cm$^{-1}$) and 2D (2640.5 cm$^{-1}$) characteristic Raman bands of graphene.

![Fig. 7. Typical Raman spectrum acquired from graphene / quartz samples.](image)
The Gaussian shape of 2D peak confirms that in the investigated area we find single layer graphene. In the surface image due to optical contrast we can distinguish surface coverage with graphene. We see immediately that in the investigated area the coverage percentage is smaller than for oxidized silicon.

In table 3 are presented average Raman band parameters extracted from Raman spectra acquired from graphene transferred on oxidized silicon and quartz substrates.

**Table 3.** Average Raman bands parameters and standard deviation corresponding to graphene transferred by electrochemical delamination on oxidized silicon and quartz substrates

<table>
<thead>
<tr>
<th></th>
<th>Average values</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (cm(^{-1}))</td>
<td>FWHM (cm(^{-1}))</td>
</tr>
<tr>
<td><strong>Graphene on quartz</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1326.27</td>
<td>13.05</td>
</tr>
<tr>
<td>G</td>
<td>1586.07</td>
<td>14.20</td>
</tr>
<tr>
<td>2D</td>
<td>2642.12</td>
<td>32.10</td>
</tr>
<tr>
<td><strong>Graphene on oxidized silicon</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1325.73</td>
<td>28.20</td>
</tr>
<tr>
<td>G</td>
<td>1587.42</td>
<td>17.11</td>
</tr>
<tr>
<td>2D</td>
<td>2647.28</td>
<td>35.08</td>
</tr>
</tbody>
</table>

The quality ratio presented in table 3 is roughly 2 for graphene / oxidized silicon samples and roughly 4 for graphene on quartz samples. This variation is due to substrate effect.

By comparing these results with the ones in table 1 results the following:

- Standard deviation for G and 2D bands is reduced,
- Defects are induced after transfer indicated by the increase of the defect ratio (I\(_D/I_G\)). Graphene transferred on quartz substrate has a more reduced standard deviation. One can conclude intuitively that this reduction is caused by the high degree of substrate crystallinity opposed to silicon oxide which is amorphous,
- G band position blue shifts after transfer,
- D and 2D band positions are red shifting as result of transfer,
- By comparing results presented in table 3 with the ones presented in table 2 results that D, G, 2D Raman bands are blue shifted after PMMA removal.
4. Conclusions

In this paper we used Raman spectroscopy and imaging with confocal optical microscopy to investigate and to determine the critical steps in graphene transfer from CVD graphene on copper foil to oxidized silicon and quartz substrates by electrochemical delamination. First step consist in PMMA deposition on graphene / copper substrate followed by annealing. Raman spectroscopy has confirmed the presence of PMMA and graphene characteristic bands. PMMA / Graphene / copper sample is placed in the electrochemical cell where PMMA / graphene is separated from the copper substrate. After each of these steps wrinkles are forming on copper foil and also on graphene / PMMA when placed in contact with the target substrate. Almost all the spectra acquired on graphene / PMMA / oxidized silicon and graphene / PMMA / quartz are confirming the presence of graphene. Graphene remnants on the copper substrate are having a high degree of crystalline disorder while also covering a much reduced area.

Flakes of graphene that remained on copper substrate are having a high degree of crystalline disorder while also covering a much reduced area and are not suitable in further processing. Optical microscopy and Raman spectroscopy are confirming a good coverage with graphene in the both cases of graphene / PMMA / target substrate which confirms that PMMA is a very good polymer carrier. The presence of wrinkles is also confirmed on the surface of graphene / PMMA / glass sample. During final step - PMMA removal in acetone parts of graphene are folding or rolling which evidences that this step is the critical one. After transfer process the increase of defect ratio ($I_D/I_G$) evidenced the defects induced in graphene in comparison with the starting samples. Substrate effect is evidenced by the value of the quality ratio of graphene on other substrates ($\sim 2$ for graphene / oxidized silicon and $\sim 4$ for graphene / quartz).

Acknowledgements. This work was supported by IMT Core Program, MICRO-NANO- SIS-PLUS.

References


