Comparative Studies on The Transfer of Chemical Vapor Deposition Grown Graphene Using Either Electrochemical Delamination or Chemical Etching Method

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Abstract. In this research, the electrochemical delamination (ECD) and chemical metal etching (CME) techniques were performed to transfer the chemical vapor deposition (CVD) grown graphene onto glass and SiO2 substrates. Principally, graphene was grown on a copper substrate by chemical vapor deposition (CVD) under specified conditions. Atomic force microscopy (AFM), Raman spectroscopy and X-ray Diffraction (XRD) were employed to investigate the morphological aspects and qualities of transferred graphene samples, while the UV-VIS spectroscopy was also applied to compare their transparencies. The Raman spectra analyses result revealed that Raman-bands positions of the transferred graphene could be shifted by the using various transfer methods or substrate. However, the thickness and the visible light transparencies of the transferred graphene samples were almost similar. The graphene sample transferred via ECD has portrayed lowest D to G-bands ratio (ID/IG) which indicates better graphene.

1. Introduction
The Chemical vapor deposition (CVD) is the most common method used for growing graphene. The method excels other methods due to large production quantities and high graphene quality. In addition, the CVD method can use various carbon precursors and metallic substrates [1]. Usually, the CVD grown graphene is deposited on metallic substrates such as copper and nickel. The fact that graphene is exploited in various applications, it must be transferred onto various substrates such as polymers [2], oxides [3], metallic [4] and others substrates [5]. Typically, transferring graphene onto the SiO2/Si wafer was widely common. This substrate is optimally suitable to study the graphene characters. However, transferring monolayered graphene of an atom thickness without protection layer is almost an impossible task. To overcome this obstacle, a spin coating of a polymeric layer such as PMMA is required. The PMMA layer onto the graphene/substrate eases graphene holding and ensure its protection [6]. Some techniques used for graphene include thermal release tape (TRT), free-floating and Bubble transfer [7]. Though, the efficient technique to transfer graphene without altering its properties is challenging. In CME transferring processes the common chemical metallic etchants solutions like iron (III) chloride (FeCl3), iron (III) nitrate (Fe(NO3)3) and ammonium persulfate (APS) are used to etch the metallic substrates. During the process, the chemicals induced metallic contaminations into graphene film [8]. However, graphene transfer by the ECD technique occurs when an electrical field is applied to graphene/substrate (cathode) and another metallic electrode (anode) in an electrolyte solution. It leads
to the formation of the hydrogen bubbles between the graphene and the metallic substrate; this caused the detachment of PMMA/graphene film. It was reported that the ECD has fewer residues compared to CME. However, the PMMA residues involve defects which degrades graphene optical and electrical properties [9]. In this research, ECD (bubble transfer) and CME (free floating) techniques were used to transfer the deposited graphene/copper onto glass and SiO2/Si substrates. The qualities, defects intensities, and transparencies of transferred graphene samples were compared.

2. Materials and Methods

2.1 Atmospheric Pressure Chemical Vapor Deposition (APCVD) grown graphene:
Copper foil (Cu, thickness: 25 μm, purity: 99.9%, supplied by STREM) was used as a catalytic substrate to deposit graphene. The furnace temperature was ramped up to 1050°C. Cu foils loaded into the cold zone of furnace quartz tube. After that, the copper foils were purged under nitrogen (3000 sccm) for 5 min. Subsequently, the copper foils were annealed at 1050°C under the flowing gas mixture (H2:N2, 200:1000 sccm) for 10 min. The samples were subjected to a second purging process using nitrogen (1000 sccm) for 5 min. The graphene was synthesized by APCVD method where the methanol (purity: 99.8%) was used as a liquid precursor of carbon atoms. Thus, hydrogen (30 sccm) has flowed through a gas bubbler containing methanol. The N2 flow rate has remained the same (1000 sccm) during both growth and cooling process. The graphene growth time was 30 min. The samples were allowed to cool down under N2 environment to room temperature.

2.2 Transferring of Graphene Films onto Desired Substrates:
The deposited graphene on copper was transferred onto glass to measure the visible light transparency while the SiO2/Si substrates (commercial wafer of 300nm oxide thickness on P-type Si (111)) were used for better characterizations. Initially, a layer of polymethyl methacrylate PMMA was spin-coated on graphene/copper foil (2000 rpm for 10 sec). Then, the PMMA coated sample was dried in ambient for 2 min at 175°C. The previous process is essential to hold and protect the graphene sample. Secondly, the PMMA/graphene layer was released from Cu substrate by using three chemical etching solutions, that were ferric chloride (FeCl3), ferric nitride (Fe(NO3)3, 2M) and ammonium persulfate (APS,0.6M). The suspended PMMA/graphene film is transferred to DI water to eliminate the copper residues. The sample is transferred onto insulating substrates such as glass or SiO2/Si. The samples were dried at 150°C for 15 min to achieve more adhesion on the new substrate. Then, the acetone is used to dissolve the PMMA. Subsequently, the graphene/glass is dried for 5 min at 70°C. Finally, an additional annealing ambient at 400°C for 20min is required to eradicade the PMMA residues. In ECD, the Power supply of (3-4V) has been applied to the graphene/substrate (cathode) and Pt electrode (anode) inside (NaCl0.5M) electrolyte solution. Then the sample rinses with distilled water and ethanol much time until release from the substrate. After that, the sample has been scooped by the desired substrate.

2.3 Graphene Characterization
Atomic force microscopy (AFM) was used to scan the morphological aspects of the transferred graphene samples on SiO2/Si and glass substrates. Raman spectroscopy (JOBIN-YVON HR 800) measurements were conducted on the graphene/Si-SiO2 and graphene/glass. The wavelength of incident LAZER was 514.45 nm operated at 20 mW. Furthermore, the XRD (PAnalytical X’ Pert PRO MRD-PW3040) measurements were carried out to identify the graphene growth for the samples on SiO2/Si substrates. In addition, UV-Vis spectroscopy (Agilent-Cary 5000) was utilized to study the transparencies of graphene/glass samples.

The positions of Raman bands depend on the lattice vibrational frequency (ν). The vibrational frequency (ν) depends on the bonds force constant (k) and the mass of atoms (m) in the vibrated lattice as shown in equation. 1. The bonds force constant (k) can be changed by the variations of carbon atoms positions and the atoms bonds length. Consequently, when these features alter under any effects, the frequency of Raman bands will be changed. These effects include stress or strain in the graphene sheets,
which causes changes in lattice spacing, resulting to a change in vibrational modes wavenumbers[10]. The graphene number of layers ($n$) which depending on its transparency (T%) can be calculated [11] using equation 2:

$$V = \left(\frac{1}{2\pi}\right)\sqrt{\frac{k}{m}}$$

$$n = \frac{100 - T\%}{2.3\%}$$

3. Results and Discussion

The samples were presented according to the chemical etching solutions that have been used in the transferring processes S-FeCl$_3$, S-Fe(NO$_3$)$_3$ and S-APS. The S-ECD is denoted for the sample which has been transferred by electrochemical delamination. Figure (1-a) shows a $(10\mu m \times 10\mu m)$ selected image of transferred graphene sample on SiO$_2$/Si substrate which scanned under (AFM). From the figure, the morphological layer can be observed which indicates the multi-layered graphene based on the root mean square (RMS) of surface roughness ($\sim$20 nm). Moreover, the coverage area of the transferred graphene showed similar colour in their appearance. Both the wrinkles and impurities were pointed out in the figure. Figure (1-b) presents the XRD spectra of transferred graphene on SiO$_2$/Si substrate. The spectrum revealed that the synthesis of multi-layered graphene film of carbon peak was obtained at 26.4 degree.

![Figure 1. (a) AFM image of CVD grown graphene on SiO$_2$/Si substrate. (b) XRD-spectrum of graphene/SiO$_2$: the carbon peak appears at 2\theta = 26.4^\circ$.](image)

Raman analyses are an efficient tool for extracting the graphene thicknesses and qualities. Raman spectra of graphene showed the three notable bands which are considered as a fingerprint of the graphitic compounds, the D, G, and 2D-peaks were centered at 1350, 1580 and 2700 cm$^{-1}$ respectively [12]. The 2D- to G-peak intensities ratios ($I_{2D}/I_G$) and the full width of half Maximum FWHM of 2D-band were used to obtain the number of graphene layers, while the ($I_D/I_G$) ratio indicates to graphene quality and defects/lattice disorder. Figure (2-a,b) presents the Raman spectrum for the transferred graphene samples on SiO$_2$/Si and glass substrates. The Raman-bands (D, G, and 2D) have been shifted according to various graphene transfer techniques.
The Lorentzian curve fit was carried out to obtain the shift of D, G and 2D-bands positions concerning their ideal positions (1350, 1580 and 2700 cm\(^{-1}\)) respectively. From Figure. (3-a, b) it can be noted that SiO\(_2\) caused higher G and 2D-bands shifts than the glass substrates for all samples under study. In addition, the G-bands shifts of transferred graphene on glass substrates were very small. However, Figure. (1-f) Showed that the sample (S-ECD) has the highest 2D-bands upshift for different substrates, while the sample (S-Fe(NO\(_3\))\(_3\)) has the lowest 2D and G-bands shifts. From Figure. (3-c), it can be observed that the D-band shift occurred by changing either the graphene transfer method or the substrate type. The upshift of D-band for the studied samples was higher than other Raman-bands (2D and G). Briefly, Raman spectra analyses revealed that the Raman-bands of the transferred graphene could be shifted by using various transfer methods or different substrates. Furthermore, the unintentionally doping of graphene films are the potential reason for the 2D and G-bands shifts[13]. Whereby the D-bands shift attributed to various impurities types in various samples [14].

Figure. 2 : Raman spectra of transferred graphene samples using different transfer techniques. for (a) SiO\(_2\)/Si and (b) glass substrates.
Figure 4 displayed the primary features of the transferred graphene samples. It was observed that the transferred graphene samples on SiO2 and glass substrates showed multi-layered graphene according to I₂D/I_G ratios (∼0.5-0.6) as shown in Figure. (4-a). This range short indicates a similar number of layers which signifies that the graphene thickness was not affected by the changing of transfer methods. The transparencies values which appear in Figure. (4-b) has been employed to obtain the graphene number of layers. The visible light absorption of monolayered graphene is ∼ 2.3%. The transparencies values were ranging between 76% to 80% as shown in Figure. (4-b). The convergence of transparencies values was noticed to reflects the convergence in I₂D/I_G ratios which resulted in obtaining the same number of graphene layers, starting from 9 to 10 layers. The slight differences in transparencies measurements could be due to the existence of various defect levels. Furthermore, the increasing of attenuation coefficient (∝) caused by wrinkles could change the graphene transparency [15]. However, the quality of graphene and the defects levels in its structures can be verified based on the I₂D/I_G ratios. According to Figure. (4-c), it can be noted that the (S-ECD) graphene sample has the lowest I_D/I_G ratio leading to better graphene quality and lower defect level. Furthermore, the SiO2 substrates showed better graphene characters than glass. These results are consistent with other studies where the SiO2 substrate was described as the best choice for graphene characterizations [16]. The crystallite size (Lₐ) and the average distance between defects points (L_D) have been calculated based on Tuinstra-Koenig empirical relation [17]. From Figure (4-d, e) it can be noted that the Lₐ and L_D of graphene on silicon oxide substrates were more significant than its values on glass substrates. Moreover, the S-ECD sample has the highest Lₐ and L_D comparing with other samples. These results are expected because the Lₐ and L_D are inversely proportional to I₂D/I_G ratios.
4. Conclusion

The ECD and CME have been performed to transfer the CVD grown graphene deposited on copper substrates to either glass and SiO2 substrates. The transferred graphene samples were multi-layered (9-10 layer) according to Raman spectroscopy, XRD, AFM and UV-Vis spectroscopy. Raman spectra analyses revealed that the Raman-bands positions of the transferred graphene were shifted using various transfer methods or different substrates. The notable shifts in D-bands are attributed to various impurities types in the samples. The convergence of the transparencies values reflects the convergence in the I2D/IG ratios that gave almost the same graphene thickness for the samples. Comparatively, the SiO2 substrate is better than glass for graphene characterization. The graphene sample transferred via ECD has portrayed lowest D to G-bands ratio (I_D/I_G) which indicates better graphene quality.
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