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Raman spectroscopy of gallium ion irradiated graphene

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A B S T R A C T

The successful integration of graphene in future technologies, such as filtration and nanoelectronics, depends on the ability to introduce controlled nanostructured defects in graphene. In this work, Raman spectroscopy is used to investigate the induction of disorder in graphene via gallium ion beam bombardment. Two configurations of CVD-grown graphene samples are used: (i) graphene supported on a Si/SiO_2 substrate, and (ii) graphene suspended on porous TEM grids. It is observed that the supported graphene experiences more damage in response to lower beam doses than suspended graphene. This phenomenon is attributed to the behaviour of the energetic ions impinging the sample. In suspended graphene, the ions pass through the graphene membrane once and disperse to the atmosphere, while in supported graphene, the ions embed themselves in the substrate causing swelling and backscattering events, hence increasing the induced disorder. In supported graphene, the ratio between the Gaussian D and G peaks attributed to amorphous carbon, and the Lorentzian D and G peaks attributed to graphene, (I_{DG}/I_{DL}) and (I_{GG}/I_{GL}), are suggested to be used to quantify the degree of amorphization. The results are relevant to the development of nanostructured graphene-based filtration or desalination membranes, as well as for graphene-based nanoelectronics.

1. Introduction

Understanding the nature of defects in graphene is key to the effective integration of graphene in several dedicated applications. Focused electron and ion beams have been used to introduce point defects, nanopores, or nanopatterned graphene structures. These nanostructures are in turn of great interest for use in next-generation desalination membranes whereby the nanoporous graphene can act as a filtration membrane [1,2], and nanoelectronics which often require graphene to be nanopatterned in specific geometries [2]. In the quest to realise these applications, significant work has been done to develop and establish an effective technique for graphene characterization. To this end, Raman spectroscopy has been successfully used to positively identify graphene [1] and determine the number of carbon atom layers in it [1,3,4]. Furthermore, Raman spectroscopy can be used to study the extent and type of defects present in graphene [3,5–7]. While the effect of different energetic particle beam parameters on supported graphene has been studied by Raman spectroscopy [2,5,8–12], the effects of such energetic particle bombardment on suspended graphene, i.e. unsupported graphene in the form of membranes, is less so investigated [7,13,14]. Furthermore, the immediate area surrounding the location directly irradiated by the beam may also be of significant interest due to the resulting damage profile [10].

In this work, the effects of gallium ion bombardment on both supported and suspended graphene is investigated. CVD-grown graphene supported on a Si/SiO_2 substrate is patterned with a focused gallium ion beam, while the surrounding area and the concomitant damage profile are characterized by Raman spectroscopy. The Raman spectra taken at various distances from the directly irradiated area are used to indicate the extent of damage imparted on graphene. In the second part of this study, freely suspended CVD-grown graphene membranes are also exposed to gallium ion treatments at different ion beam parameters, with Raman spectroscopy used to characterize the extent of damage imparted on the suspended graphene.

2. Experimental study

2.1. Supported graphene

Single layer graphene (nominal thickness and grain size 0.345 nm and 1 mm, respectively [15]) grown via chemical vapour deposition (CVD) and transferred on to SiO_2 substrate (Graphene on SiO_2, supplied by Nano Carbon Sp. z o.o.) was patterned by a focused gallium ion beam at an accelerating voltage of 5 kV and ion beam current of 47 pA, using a FEI Nova600 Dual Beam. Five different beam doses, ranging from 1.8×10^{-13} up to 1×10^{-10} C/μm^2 (equivalent to 1.12×10^6 to 6.24×10^8 Ga^+/μm^2) as listed in Table 1, were used to pattern different areas in the graphene sample.

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Table 1
Focused gallium ion beam treatments on supported graphene and suspended graphene.

Sample	Energy (kV)	Current (pA)	Incidence angle (°)	Dose (C/μm^2)		Fluence (Ga$^+$/μm^2)
Supported graphene	5.0	47	90	1.80×10^{-13}	(T0.18)	1.12×10^{6}
				5.00×10^{-13}	(T0.5)	3.12×10^{6}
				1.00×10^{-12}	(T1)	6.24×10^{6}
				5.00×10^{-11}	(T50)	3.12×10^{8}
				1.00×10^{-10}	(T100)	6.24×10^{8}
Suspended graphene	5.0	1.6	90	5.28×10^{-7}		3.30×10^{12}
				5.28×10^{-5}		3.30×10^{14}
				2.11×10^{-4}		1.32×10^{15}
				4.86×10^{-4}		3.03×10^{15}
				5.28×10^{-3}		3.30×10^{16}
				1.22×10^{-2}		7.62×10^{16}
	30.0	1.5	90	3.27×10^{-7}		2.04×10^{12}
				3.27×10^{-3}		2.04×10^{16}
				1.31×10^{-2}		8.18×10^{16}
	30.0	1.5	28	3.27×10^{-3}		2.04×10^{16}
			53			
			68			
			83			

2.2. Suspended graphene

CVD-grown monolayer graphene membranes (nominal thickness and grain size 0.345 nm and 10 μm, respectively [16]) suspended over Quantifoil TEM mesh grids with 2 μm diameter holes (Suspended Monolayer Graphene on TEM grids - Quantifoil R2/4, supplied by Agar Scientific Ltd., UK) were subjected to focused gallium ion beam bombardment using the same FEI Nova600 Dual Beam. The conditions of the ion beam for each treatment are listed in Table 1. To achieve different treatment doses, the pitch of the ion beam raster was changed. A total of four TEM grids were available, only three of which being exposed to the gallium ion treatment.

2.3. Characterization

Scanning electron microscopy (SEM) (Zeiss Merlin Gemini, Germany) and atomic force microscopy (AFM) (UHV SPM700, RHK Inc., USA) were used to study the topography of the graphene. Electron dispersive spectroscopy (EDS) (Apollo X Ametek, USA) was also used to assess the elemental composition of the samples.

Raman spectroscopy (Witec Alpha300) with an excitation wavelength of 633 nm (1.9587 eV), a 60× objective, and a 600 g/mm grating was used to characterize the graphene. Raman spectra were recorded from the untreated and treated areas to compare the quality of graphene before and after ion beam bombardment. For the supported graphene, the damaged graphene surrounding the treated areas was also analysed, with the distance away from the edge of the 1×10^{-10} C/μm^2 treated area, *R*, ranging from 0 to 66 μm (denoted as $T100_0$ to $T100_{60}$, respectively), in steps of 6.6 μm.

Both single spectra and 2D spectral maps were gathered for each treated area. For the single spectra, an integration time of 10 s was used for a total of 10 accumulations. For the 2D spectral maps (a sample of which is included in the Supporting Information), an integration time of 5 s was used with an acquisition step size varying from 0.1 to 0.5 μm. For each map, sets of ten consecutive spectra obtained from circular areas of freely suspended graphene, and hence those featuring minimal substrate-generated background noise, were selected and averaged.

To eliminate background noise due to fluorescence, a 2nd order polynomial for supported graphene, or a 3rd order polynomial for suspended graphene, was fitted using the modified polyfit method outlined in [17] after manually removing sporadic spikes associated with cosmic rays from the raw spectra. An additional weighting function was added to the fitting procedure to improve the polynomial fit and better represent the less-active regions, namely $< 1000\,cm^{-1}$, between $1600\,cm^{-1}$ and $2500\,cm^{-1}$, and $> 2750\,cm^{-1}$. The above-outlined mathematical processing was performed using Matlab (The MathWorks Inc., MA). The program used is available in the Supporting Information.

The Peak Analyzer in OriginPro 9 software was used to fit the peaks in the Raman spectra. The majority of the fits have a χ^2 value smaller than 3×10^{-3} and an adjusted R^2 value larger than 0.9. For clarity, the peak position or frequency, intensity, full width at half maximum (FWHM), and integrated area will be denoted by *P*, *I*, *F*, and *A*, respectively, while subscripts indicate the peak i.e. *D*, *G* or *2D*.

3. Results

3.1. Untreated supported graphene

Several Raman measurements were taken at different areas of the untreated supported CVD graphene, with the spectra obtained mainly falling into two categories. Representative spectra of each category are shown in Fig. 1.

Both types of spectra have sharp Lorentzian profiles for the G and 2D peaks, the latter indicating the presence of single layer graphene. The G peak is found at around $1595\,cm^{-1}$, and has a FWHM of $\sim 14\,cm^{-1}$. The 2D peak is found at $\sim 2652\,cm^{-1}$ with a FWHM of

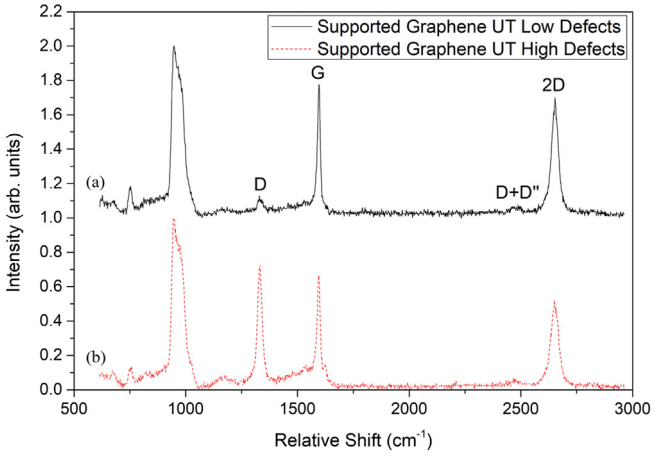

Fig. 1. Untreated (UT) supported graphene. (a) The top solid black line is representative of areas with a small D peak, while (b) the bottom dashed red line is representative of areas with a larger D peak. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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