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Raman Spectroscopy-Based Studying the Physical Differences of Graphene Layers Prepared by Direct Exfoliation

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This study explores the physical characteristics of graphene layers through the application of Raman spectroscopy and atomic force microscopy. Graphene samples are meticulously prepared by exfoliating natural graphite onto 300-nm SiO₂/Si wafers. The analysis conducted at the Wolfson Nanomaterials and Devices Laboratory at Plymouth University in the UK focuses on examining the positions and intensities of the *G* and 2*D* bands in Raman spectroscopy, as well as scrutinizing atomic force microscope images. The investigation is aimed to assess various physical parameters, including the number of layers, quality, purity, domain size, and full width at half maximum (*FHWM*) of each graphene sample, providing valuable insights into their structural properties. This study suggests that the graphene layers on a SiO₂/Si substrate prepared by direct exfoliating are suited for mechanical and electronic applications.

Досліджено фізичні характеристики графенових шарів за допомогою спектроскопії Раманового розсіяння й атомно-силової мікроскопії. Графенові зразки було ретельно підготовлено шляхом відлущування природнього графіту на пластини SiO₂/Si у 300 нм. Аналізу, проведену у Вольфсоновій лабораторії наноматеріалів і пристроїв Плімутського університету у Великій Британії, було зосереджено на вивченні положення й інтенсивності *G*- й 2*D*-смуг у спектроскопії комбінаційного розсіяння, а також на ретельному вивченні зображень атомно-силової мікроскопії. Дослідження мало на меті оцінити різні фізичні параметри, в тому числі кількість шарів, якість, чистоту, розмір домени та повну ширину на половині максимуму (*FHWM*) кожного графенового зразка, що надає цінну інформацію про їхні структурні властивості. Це дослідження свідчать про те, що графенові шари на підкладинці SiO₂/Si, виготовлені прямим відлущуванням, підходять для механічних і електронних застосувань.

Key words: graphene, graphite, Raman spectroscopy, exfoliation.

Ключові слова: графен, графіт, Раманова спектроскопія, відшарування.

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1. INTRODUCTION

Graphene, a two-dimensional manifestation of graphite, was first isolated by Novoselov *et al.* at Manchester University [1]. This remarkable material is a single-atom-thick sheet of carbon, crystallized in a honeycomb structure monolayer. Widely recognized as the foundational building block for all sp^2 graphitic materials, it encompasses (0D) fullerenes, (1D) carbon nanotubes, and contributes to the composition of (3D) graphite [2]. These materials have unique electrical, mechanical, and thermal properties that make them promising for a wide range of applications. Due to these properties, graphene is a unique material that has exceptional attributes, which make it a versatile material for various applications. It has thermal conductivity reaching 5000 W/(m·K), which is ten times higher than copper, and surpasses carbon nanotubes (CNTs) and diamond, setting a new standard. Graphene's charge carrier mobility is 200.000 cm²/(V·S), which indicates minimal scattering or resistance when electrons traverse it. Additionally, graphene has a remarkable specific surface area of 2630 m²/g and outstanding mechanical properties, boasting an elastic modulus of 1 TPa and ultimate tensile strength of 130 GPa, making it the strongest material known to date. These features make graphene a promising candidate for advanced applications in nanoelectronics, heat dissipation, sensors, field emission, and transparent conductors. Notably, a single graphene layer achieves 97.7% transparency to incident light and absorbs only 2.3%, making it almost entirely transparent [6, 7].

Graphite is composed of multiple layers of graphene that are linked by two distinct types of bonds. The first bond is a weak Van der Waals attraction between the layers, which is approximately 0.34 nm long. This weak bond allows the layers to be easily separated. The second bond is a covalent bond between the carbon-carbon atoms within each layer, spanning a distance of 0.14 nm. Extensive theoretical and experimental studies have shown that the properties of graphene are largely determined by its geometric structures, as illustrated in Fig. 1.

2. MECHANICAL EXFOLIATION OF GRAPHENE

Exfoliation of graphene refers to the process of separating individ-

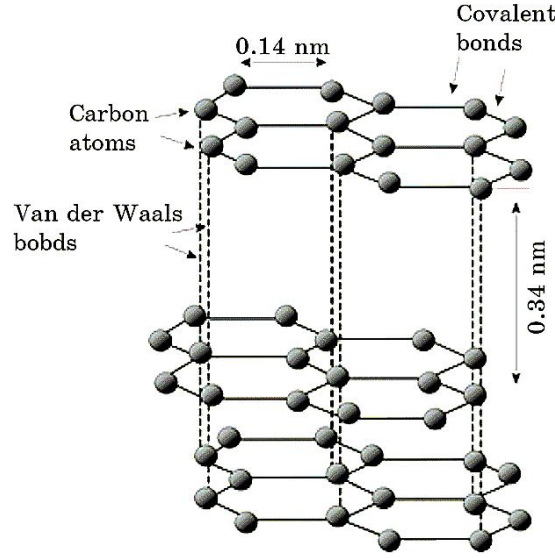


Fig. 1. The geometric structures for graphite [8].

ual layers of graphene from a bulk material. There are several methods for exfoliating graphene, including mechanical exfoliation, chemical exfoliation, and liquid-phase exfoliation [9]. To separate two layers of graphite, the Van der Waals attraction between them needs to be overcome. One way to achieve this is by applying normal force, demonstrated in micromechanical cleavage using Scotch tape. Graphite's inherent self-lubricating ability in the lateral direction can be exploited to apply lateral force and facilitate relative motion between the layers. The force generated through the exfoliation technique serves the dual purpose of fragmenting large graphite particles or graphene layers into smaller ones. This fragmentation effect has a two-fold strategy. On one hand, it can decrease the lateral size of graphene, which may not be desirable for achieving large-area graphene. On the other hand, it aids in exfoliation, as smaller graphite flakes are more easily exfoliated due to the reduced collective Van der Waals interaction force between layers in these smaller flakes.

The total energy (E_T) required to exfoliate graphite in a liquid environment is the sum of Van der Waals forces (E_{vwf}) and the change in surface energies (E_s), as expressed by the following equation [12]:

$$E_T = \Delta E + E_{vwf}, \quad (1)$$

$$E_T = E_{vwf} + E_g + E_s. \quad (2)$$

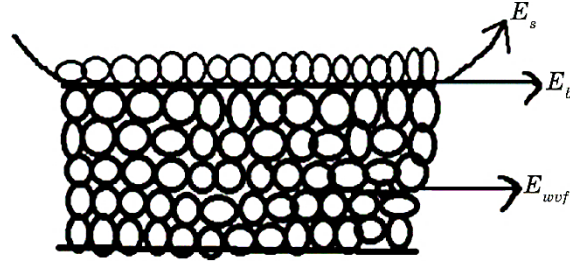


Fig. 2. Attractions in the layers of graphene [12].

In the context of exfoliation, the total energy required (E_T) encompasses the Van der Waals force between graphite layers (E_{vwf}), the changes in surface energies (E), and the surface energy associated with the mixing organic solvent (E_s). The exfoliation process involves overcoming these energies. Typically, graphene layers adhere to each other through a weak Van der Waals attraction, and this attraction is sufficiently robust to facilitate the exfoliation of a single graphene layer from the graphite.

3. RAMAN SPECTROSCOPY TECHNIQUE

There are several methods for discovering graphene layers in a material; one of these is Raman spectroscopy, which is a powerful tool for analysing the vibrational modes of graphene and can be used to determine the number of graphene layers present in a material. This technique is particularly useful for identifying the number of graphene layers samples and determining the size, shape of the graphene layers and their properties. Raman spectrum is a graph of the intensity of scattering of light from the sample as a function of the incident light frequency. The interpretation of Raman results for exfoliated graphene samples is less complicated than the other methods [13].

Two distinct spectral features characterize the Raman spectrum of graphene. The most prominent is the *G*-band, which corresponds to the in-plane vibration of the carbon atoms in the graphene lattice. It lies close to (1580 cm^{-1}). The *G*-band serves as the predominant mode in both graphene and graphite, symbolizing the planar arrangement of sp^2 -bonded carbon that defines graphene. Its utility in determining the thickness of graphene layers is notable. The second feature is the *D*-band ($\cong 2700\text{ cm}^{-1}$), which corresponds to the out-of-plane vibrations caused by defects, such as vacancies or edges of the graphene sheet. The *D*-band, also known as the disorder or defect band, is a subtle feature in graphite and a less noticeable

band in graphene. Its significance lies in its ability to indicate the presence of defects within a material. As per Ref. [14], the intensity of the D -band is directly proportional to the degree of defects present in the sample. In addition, there are two small peaks (G^* and G'). It is well known that the D band originates from disordered carbon atom symmetry. In well-ordered graphene and graphite, the D band is absent.

The $2D$ -band in graphene spectra is sometimes called the G' -band, but it is more commonly referred to as the $2D$ band. Unlike the D -band, the $2D$ -band is the second order and consistently appears as a robust feature in graphene, even in the absence of the D -band. This indicates that the $2D$ band is independent of defects. The $2D$ -band is crucial in determining the thickness of graphene layers, as highlighted in [15]. The position and shape of the $2D$ band offer a straightforward means of determining the number of graphene layers. For example, a shift of the $2D$ band peak position to higher values indicates an increase in the number of graphene layers, that means there are more layers of graphene [16].

In this work, the variations in graphene layers were studied using Raman spectroscopy (RS) and atomic force microscope (AFM). Four graphene samples were prepared by exfoliation of the graphite on the wafer of 300-nm SiO_2/Si . The positions and the intensities of G -band, $2D$ -band and ($G/2D$) ratio of (RS) and (AFM) images were checked to estimate the different layers, quality, purity, domain size, Grüneisen parameters, and $FHWM$ of the graphene sample. The experiments and preparations were conducted in Wolfson Nanomaterials and Devices Laboratory–Plymouth University (UK).

4. EXPERIMENT AND MATERIALS

The basic mechanical way to separate the layers from the bulk graphite surface is called exfoliation. To obtain one, two or a few layers of graphene on the silicon wafer by exfoliation method: scotch tape is pressed onto a surface of the bulk graphite and then pulled off very carefully; after numerous repetitions, the graphite layer becomes thinner after each pull until there is just a single layer of graphene left (Fig. 4); four samples of graphene by exfoliating graphite flakes, and were lied on 300 nm SiO_2/Si substrates (L_1 , L_2 , L_3 , and L_4).

The number of graphene layers was identified approximately with an optical microscope. Although the graphene layers could be estimated, the number of graphene layers through the colour and the contrast is caused by the interference between the graphene and the SiO_2 layers [18]. Then the number of graphene layers was exactly

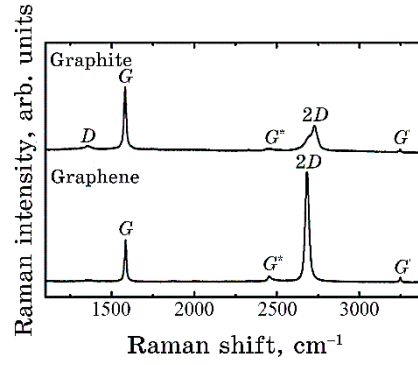


Fig. 3. Raman spectrum of graphene [17].

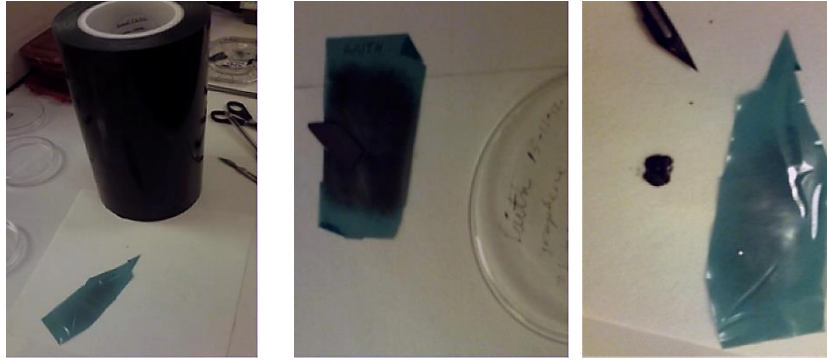


Fig. 4. The scotch-tape-based exfoliation.

identified using an AFM, and the Raman spectrum of the graphene samples was obtained with a micro-Raman spectroscopy system ($\lambda = 532 \text{ nm}$, $E = 2.33 \text{ eV}$).

5. RESULTS AND DISCUSSION

Figure 5, *a* (the Raman spectrum of graphene) shows that there are two prominent peaks *G* and *2D*. The *D* band is absent in the Raman spectrum of single-layer graphene. (*b*) An optical microscope image shows the variation of colour due to the thickness variation in a thin graphite flake. The purple area is the SiO_2 substrate, and the variation of the colour originates from the interference between the graphene and the SiO_2 layer. It is observed that the sample consists of monolayer graphene. The first-order *D* peak itself is not visible in pristine graphene because of crystal symmetries [19]. The second-order prominent peak, *2D*, is always allowed because the second

scattering (the $e-h$ process) is also an inelastic scattering from a second phonon, [20, 21].

In Figure 5, there is a small D -peak at the centre of the graphene layers, indicating minimal significant defects.

The G band is a defining spectral feature of graphene, which is found at approximately 1580 cm^{-1} . This characteristic is highly sen-

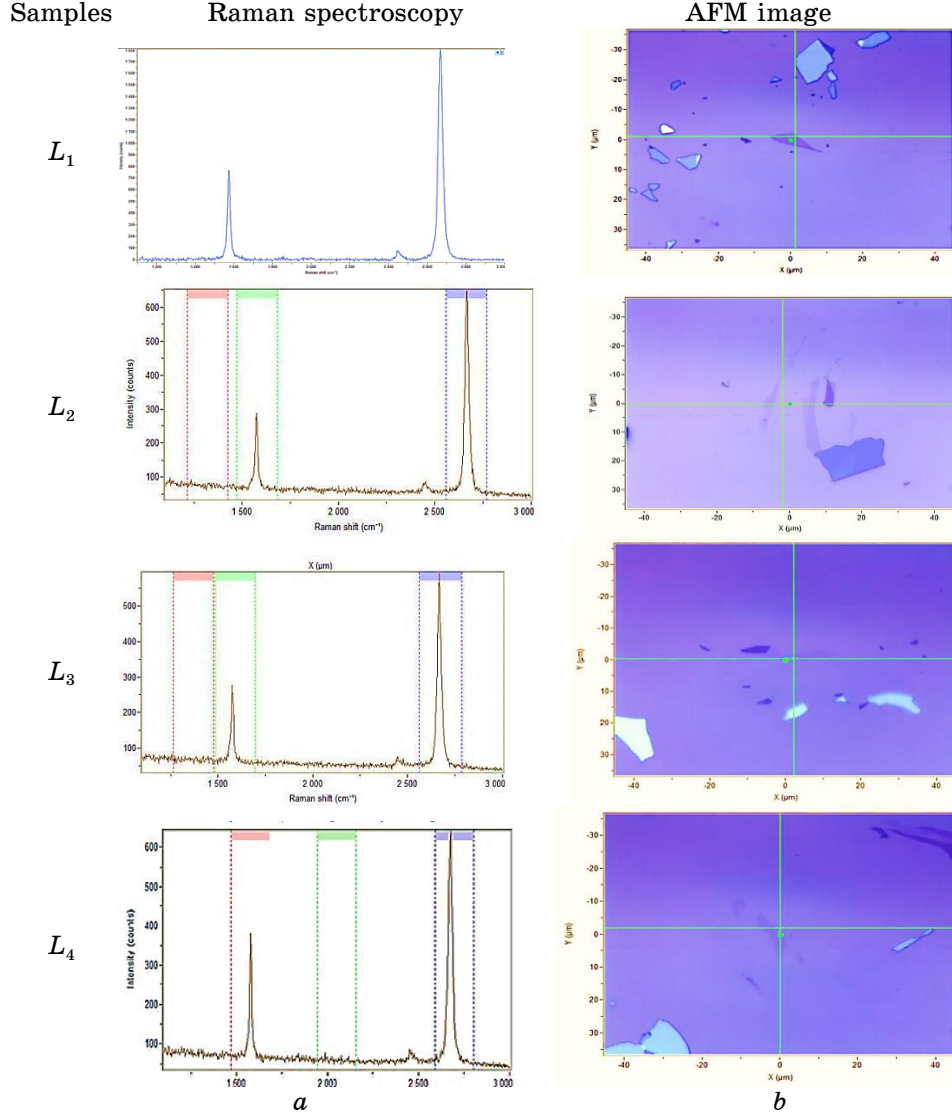


Fig. 5. (a) Raman spectroscopy and (b) optical microscope images for the graphene samples.

sitive to strain effects and provides an indication of the number of layers present in graphene. It is worth noting that the position of the G band shifts towards lower frequencies as the number of layers increases.

The thickness of a graphene layer can be determined using the following equation: $C' = 0.0046 + 0.0925N - 0.00255N^2$, where N is the number of layers (< 10). These results can be applied directly to a 300-nm SiO_2 capping layer, which is also commonly used [22].

Below, Table summarized the physical properties of graphene samples (L_1 , L_2 , L_3 , and L_4) on SiO_2/Si . These parameters calculated from RS and AFM. Here, the strain ratios were taken from Ferrari 2008 for each sample.

TABLE. The physical properties of graphene samples calculated from RS and AFM. Under condition ($\lambda_{\text{Laser}} = 532 \text{ nm}$ and $E_{\text{Laser}} = 2.33 \text{ eV}$).

Samples' parameters	L_1	L_2	L_3	L_4
D -position	1350 cm^{-1}	1350 cm^{-1}	1350 cm^{-1}	1350 cm^{-1}
G -position	1565 cm^{-1}	1580 cm^{-1}	1580 cm^{-1}	1580 cm^{-1}
$2D$ -position	2670 cm^{-1}	2685 cm^{-1}	2700 cm^{-1}	2680 cm^{-1}
$I(D)$ intensity	70	70	70	70
$I(G)$ intensity	770	290	270	390
$I(2D)$ intensity	1800	650	600	650
$2D/G$ ratio	2.32	2.22	2.22	1.51
or $G/2D$ ratio	0.43	0.45	0.45	0.66
D/G ratio	0.1	0.24	0.26	0.18
Layer	mono	mono	mono	Bi-layer
C'	$\cong 0.1$	$\cong 0.095$	$\cong 0.095$	$\cong 0.184$
Quality	Hi	medium	medium	hi
Domain size	18.03 nm	6.88 nm	6.41nm	9.25 nm
C_{lamda}	16.61	16.61	16.61	16.61
$FHWM(G)$	16 cm^{-1}	$\cong 21.3 \text{ cm}^{-1}$	26 cm^{-1}	$\cong 32.8 \text{ cm}^{-1}$
Strain, % (from [23–25])	(G): -0.60% $\Delta\omega = -17.0 \text{ cm}^{-1}$ Grüneisen $\Gamma = 1.8$ $-0.30\%(2D)$: $\Delta\omega = -22.0 \text{ cm}^{-1}$ Grüneisen $\Gamma = 2.7$	(G): -0.07% $\Delta\omega = -2.0 \text{ cm}^{-1}$ Grüneisen $\Gamma = 1.8$ $-0.1\%(2D)$: $\Delta\omega = -7.0 \text{ cm}^{-1}$ Grüneisen $\Gamma = 2.7$	(G): -0.07% $\Delta\omega = -2.0 \text{ cm}^{-1}$ Grüneisen $\Gamma = 1.8$ $0.11\%(2D)$: $\Delta\omega = 8.0 \text{ cm}^{-1}$ Grüneisen $\Gamma = 2.7$	(G): -0.11% $\Delta\omega = -3.0 \text{ cm}^{-1}$ Grüneisen $\Gamma = 1.8$ $-17\%(2D)$: $\Delta\omega = -12 \text{ cm}^{-1}$ Grüneisen $\Gamma = 2.7$

Table shows that there are three monolayers and one bilayer out of four samples prepared on SiO₂/Si. The domain size and quality of these samples have high quality and are good for electronic applications. Note that the *FWHM* for the peaks were broadened due to disorder.

6. CONCLUSION

The combination of Raman spectroscopy and atomic force microscopy (AFM) has demonstrated its efficacy as a valuable tool in graphene research for assessing its physical properties. The analysis of the positions, widths, and intensities of the *D*, *G*, and *2D* peaks allows for exploring various attributes such as strain, quality, impurity, thickness, and disorder within the Raman spectrum of graphene, provided optimal conditions are maintained. This tandem approach of Raman spectroscopy and AFM imaging proves instrumental in examining diverse facets of graphene structure and quality, providing an efficient means to ascertain the number of graphene layers. Furthermore, our study suggests that the graphene layers on a SiO₂/Si substrate are well suited for mechanical and electronic applications.

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