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TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics –
Part 6-2: Graphene – Number of layers: atomic force microscopy, optical transmission, Raman spectroscopy

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IEC Secretariat
3, rue de Varembé
CH-1211 Geneva 20
Switzerland

Tel.: +41 22 919 02 11
info@iec.ch
www.iec.ch

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Part 6-2: Graphene – Number of layers: atomic force microscopy, optical transmission, Raman spectroscopy

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Draft	Report on voting
113/676/DTS	113/727/RVDTS

Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this Technical Specification is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at http://www.iec.ch/standardsdev/publications.

A list of all parts in the IEC TS 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
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INTRODUCTION

Graphene has attracted significant interest as a next-generation electronic material due to its good conductivity and mobility. It has been regarded as more advantageous than carbon nanotube (CNT) because of its isotropic and homogeneous electronic properties. For these reasons and many more, a Nobel prize in physics was awarded to A. Geim and C. Novoselov in 2010 for their efforts in discovering graphene when they isolated a single layer of graphene using clear adhesive tape.

Graphene has been widely studied by researchers from academic institutions, research institutes, and industries due to its unique and interesting properties such as conductivity [1][1], mechanical strength and flexibility [2], which are better than other metals or semiconductors. These properties are influenced by the number of layers of graphene and disappear as the number of layers increases. Graphene also shows an unusual reduction in optical transparency even considering a single atomic layer [3]. Therefore, graphene applications need to investigate the precise number of layers of graphene.

Many companies are now providing graphene samples to industries and research communities. These are prepared (or manufactured) by various methods such as CVD or mechanical exfoliation. Defining and evaluating the number of layers of this fabricated graphene is critical both from research and industrial points of view. Unfortunately, there are no commonly accepted standards for this purpose, hindering the reliable production and expansion of graphene applications.

The number of layers of graphene is usually observed by atomic force microscopy (AFM), light transmittance, Raman spectroscopy, transmission electron microscopy (TEM), and ellipsometry. Every analytical method has its own limitations in terms of precisely measuring the number of graphene layers and can also cause ambiguity for providing reliable information. For these reasons, developing an easy, fast, and reliable method for counting the number of graphene layers is needed.

This document describes a combined method to evaluate accurate number of layers of graphene, which includes measurement method.

Description of combined method and case studies illustrating the application of the standard are provided in Annex A and Annex B, respectively.

[1] Numbers in square brackets refer to the Bibliography.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-2: Graphene – Number of layers: atomic force microscopy, optical transmission, Raman spectroscopy

1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the key control characteristic

– number of layers

for graphene flakes by a combination of

– atomic force microscopy,
– optical transmission, and
– Raman spectroscopy

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- IEC Electropedia: available at https://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

3.1 General terms

3.1.1
graphene
single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure

Note 1 to entry: It is an important building block of many carbon nano-objects.

Note 2 to entry: As graphene is a single layer, it is also sometimes called monolayer graphene or single-layer graphene and abbreviated as 1LG to distinguish it from bilayer graphene (2LG) and few-layer graphene (FLG).

Note 3 to entry: Graphene has edges and can have defects and grain boundaries where the bonding is disrupted.

[SOURCE: ISO/TS 80004-13:2017 [4], 3.1.2.1]

3.1.2
graphene oxide
GO
chemically modified graphene prepared by oxidation and exfoliation of graphite, causing extensive oxidative modification of the basal plane

Note 1 to entry: Graphene oxide is a single-layer material with a high oxygen content, typically characterized by C/O atomic ratios of approximately 2,0 depending on the method of synthesis.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.13]

3.1.3
reduced graphene oxide
rGO
reduced oxygen content form of graphene oxide

Note 1 to entry: This can be produced by chemical, thermal, microwave, photo-chemical, photo-thermal or microbial/bacterial methods or by exfoliating reduced graphite oxide.

Note 2 to entry: If graphene oxide was fully reduced then graphene would be the product. However, in practice some oxygen containing functional groups will remain and not all sp^3 bonds will return back to sp^2 configuration. Different reducing agents will lead to different carbon to oxygen ratios and different chemical compositions in reduced graphene oxide.

Note 3 to entry: It can take the form of several morphological variations such as platelets and worm-like structures.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.14]

3.1.4
bilayer graphene
2LG
two-dimensional material consisting of two well-defined stacked graphene layers

Note 1 to entry: If the stacking registry is known it can be specified separately, for example as “Bernal stacked bilayer graphene”.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.6]

3.1.5
few-layer graphene
FLG
two-dimensional material consisting of three to ten well-defined stacked graphene layers

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.10]

3.1.6
graphite
allotropic form of the element carbon, consisting of graphene layers stacked parallel to each other in a three-dimensional, crystalline, long-range order

Note 1 to entry: Adapted from the definition in the IUPAC Compendium of Chemical Terminology.

Note 2 to entry: There are two allotropic forms with different stacking arrangements: hexagonal and rhombohedral.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.2]

3.1.7
highly oriented pyrolytic graphite
HOPG
highly pure and ordered form of synthetic graphite

Note 1 to entry: Material often used as reference material for calibration of measurement equipment.

3.1.8
two-dimensional material
2D material
material, consisting of one or several layers with the atoms in each layer strongly bonded to neighbouring atoms in the same layer, which has one dimension, its thickness, in the nanoscale or smaller, and the other two dimensions generally at larger scales

Note 1 to entry: The number of layers when a two-dimensional material becomes a bulk material varies depending on both the material being measured and its properties. In the case of graphene layers, it is a two-dimensional material up to ten layers thick for electrical measurements, beyond which the electrical properties of the material are not distinct from those for the bulk (also known as graphite).

Note 2 to entry: Interlayer bonding is distinct from and weaker than intralayer bonding.

Note 3 to entry: Each layer may contain more than one element.

[SOURCE: ISO/TS 80004-13:2017, 3.1.1.1]

3.1.9
chemical vapour deposition
CVD
deposition of a solid material onto a substrate by chemical reaction of a gaseous precursor or mixture of precursors, commonly initiated by heat

[SOURCE: ISO/TS 80004-8:2020 [5], 8.2.4]

3.2 Terms related to measurements

3.2.1
atomic force microscopy
AFM
method for imaging surfaces by mechanically scanning their surface contours, in which the deflection of a sharp tip sensing the surface forces, mounted on a compliant cantilever, is monitored

Note 1 to entry: AFM can provide a quantitative height image of both insulating and conducting surfaces.

Note 2 to entry: Some AFM instruments move the sample in the x-, y- and z-directions while keeping the tip position constant, and others move the tip while keeping the sample position constant.

Note 3 to entry: AFM can be conducted in a vacuum, a liquid, a controlled atmosphere or air. Atomic resolution may be attainable with suitable samples, with sharp tips, and by using an appropriate imaging mode.

Note 4 to entry: Many types of force can be measured, such as the normal forces or the lateral, friction or shear force. When the latter is measured, the technique is referred to as lateral, frictional or shear force microscopy. This generic term encompasses all of these types of force microscopy.

Note 5 to entry: AFMs can be used to measure surface normal forces at individual points in the pixel array used for imaging.

[SOURCE: ISO 18115-2:2021 [6], 3.1.2, modified – Note 6 to entry has been deleted.]

3.2.2
offset height
difference between the height of monolayer graphene on the substrate using AFM and the actual height of monolayer graphene

Note 1 to entry: The offset height can be affected by the type of substrate, AFM mode, and environment.

Note 2 to entry: Large thickness variation of monolayer graphene (0,4 nm to 1,7 nm) due to the offset height has been reported [7].

3.2.3
Raman spectroscopy
spectroscopy in which the radiation emitted from a sample illuminated with monochromatic radiation is characterized by an energy loss or gain arising from rotational, vibrational, or phonon excitations

[SOURCE: ISO/TS 80004-13:2017, 3.3.1.6]

3.2.4
G-peak
Raman peak related to the in-plane motion of the carbon atoms located near 1 580 cm^{-1} originating from scattering at the centre of the Brillouin zone

Note 1 to entry: The G-peak can be observed in graphite materials including pristine graphene and does not need lattice defects to occur.

3.2.5
D-peak
defect activated Raman peak related to lattice breathing modes in six-carbon rings away from the centre of the Brillouin zone

Note 1 to entry: The D-peak is located at approximately 1 350 cm^{-1} depending on the wavelength of the excitation laser. The dispersion with wavelength is ~50 cm^{-1}/nm.

Note 2 to entry: The D-peak is most intense at defective graphene lattices and disappears for perfect monolayer crystals. It is often called the disorder (defect) band.

3.2.6
2D-peak
second-order Raman peak related to a two-phonon process located at approximately twice the frequency of the D-peak

Note 1 to entry: As well as the D-peak, the 2D-peak is also dispersive with wavelength. The position of the 2D-peak changes strongly with laser energy.

Note 2 to entry: The 2D-peak is always present in the Raman spectrum of graphene and does not need defects to be activated.

3.2.7
Raman shift
wavenumber shift that has units of inverse length caused by Raman scattering effect, as this value is directly related to energy

Note 1 to entry: The Raman shift indicates the vibration frequency of a molecule.

3.2.8
Raman intensity
intensity where the Raman scattered light from the sample enters the detector and is perceived

Note 1 to entry: Raman intensity is directly proportional to the fourth power of the excitation frequency. So, the choice of the incident laser beam plays an essential role in the resulting intensities of the observed Raman signals.

Note 2 to entry: The measurements of the Raman intensities are used to determine quantitatively the amount, distribution and degree of crystallization of different phases in a material.

3.2.9
full width at half maximum
FWHM
range of a variable over which a given characteristic is greater than 50 % of its maximum value

Note 1 to entry: FWHM can be applied to characteristics such as radiation patterns, spectral linewidths, etc. and the variable can be wavelength, spatial or angular properties, etc., as appropriate.

3.2.10
optical transmittance
ratio of the radiant flux transmitted through and emerging from a body to the total flux incident on it

Note 1 to entry: The transmittance (T) for two-dimensional Dirac fermions like graphene is given by $T = (1 + 0{,}5\pi\alpha)^{-2}$ where α is the fine structure constant, $\alpha = 1/137$. Accordingly, the T of monolayer graphene is about 2,3 %.

3.2.11
optical contrast
CTRS
spectra difference between substrate and graphene sheet

Note 1 to entry: Optical contrast is given by CTRS = $(R_0(\lambda) - R(\lambda))/R_0(\lambda)$, where $R_0(\lambda)$ is the reflection spectrum from the substrate and $R(\lambda)$ is the reflection spectrum from graphene sheet.

4 Method for preparation of graphene flake sample

4.1 Micromechanical cleavage

The concept of this method is the cleavage of graphene layers from the bulk HOPG surface. The exfoliation mechanics of this method are that clear adhesive tape is applied to top of the HOPG surface and thus exerts a normal force. If this exfoliation process repeats numerous times, the graphitic layer becomes thinner and thinner and finally it can be expected there will be monolayer graphene.

4.2 Sonication

Sonication-assisted liquid-phase exfoliation of graphite is considered one of the methods for large-scale production of graphene. Due to the sonication-induced cavitation, however, the graphene prepared by this method has many more defects than that prepared by other methods.

4.3 Ball milling

Ball milling is a method to laterally exfoliate graphite into graphene flakes by generating shear force. There are two ways to induce exfoliation and fragmentation effects in most ball milling devices. The most important thing is shear force, which is thought to be an excellent mechanical route for exfoliation. This method is very desirable to obtain large graphene flakes. The second is a collision or vertical impact applied by the ball in a rolling motion. This method can break large pieces into smaller pieces and sometimes even destroy crystal structures in an amorphous or non-equilibrium state. Therefore, in order to obtain high-quality, large-sized graphene, the secondary effect shall be minimized.

4.4 Fluid dynamics

Graphene flakes can move with the liquid and be exfoliated repeatedly with this method. The feature of fluid dynamics is intrinsically different from that of sonication and ball milling, making it a potentially efficient technique for the scalable production of graphene.

5 Measurement of the number of graphene layers using combined method

5.1 Basic concept of combined method

There are a number of methods which are used to define the number of graphene layers (3.2.1, 3.2.3, and 3.2.11). These methods are beneficial in certain aspects. However, none of them by a single method alone gives a precise measurement of the number of layers or is applicable in industry. Nonetheless, there is a way to define the number of graphene layers with a certain level of accuracy by combining AFM, light reflectance, and Raman scattering. By simultaneously measuring the topography, reflectance, and Raman scattering, the method can achieve a complementary determination of the precise number of layers.

5.2 General protocol

5.2.1 Sample preparation

In order to measure the AFM, reflectance, and Raman scattering, the sample should be prepared on a transparent substrate and can be prepared by mechanical exfoliation. The highly oriented pyrolytic graphite (HOPG) is mechanically exfoliated on a glass (e.g. soda lime glass with refractive index of about 1,5) or a quartz glass (e.g. fused quartz with refractive index of about 1,4) substrate by using a double-sided adhesive tape. The substrate should be thinner than 0,21 mm because the objective lens for a high resolution has a numerical aperture of 0,9 and the working distance of lens is 0,21 mm.

5.2.2 AFM calibration

In order to obtain a precise height of graphene flake, AFM calibration is needed by using a standard sample such as a grating with a known height.

5.2.3 Raman calibration

In order to obtain a precise value of Raman peak, Raman calibration should be conducted by using a SiO_2/Si substrate, which shows Raman peak value of 520 cm^{-1}. Raman calibration should be performed whenever changing the gratings in the spectrometer.

5.2.4 Optical reflectance calibration

The linearity of the photomultiplier tube (PMT) detector should be checked. When the voltage applied to the PMT is linearly increased, the voltage value that the detector represents by accepting the photons should increase linearly. The background voltage value depending on the kinds of substrates should be checked. The background value can be checked on the substrate region without a sample.

5.3 Measurement procedure

A configuration of system of the combined method to precisely measure the number of graphene layers is shown in Figure 1. AFM probe and laser beam should be perfectly coordinated with each other. The probe is placed within the laser spot with nanometre precision.

As the AFM probe scans a sample surface to obtain a topography, reflected laser light and Raman scattered light enter the photomultiplier tube (PMT) and charge-coupled device (CCD) detectors, respectively, to obtain a reflectance and Raman mapping image simultaneously (See details in Annex A and Annex B.

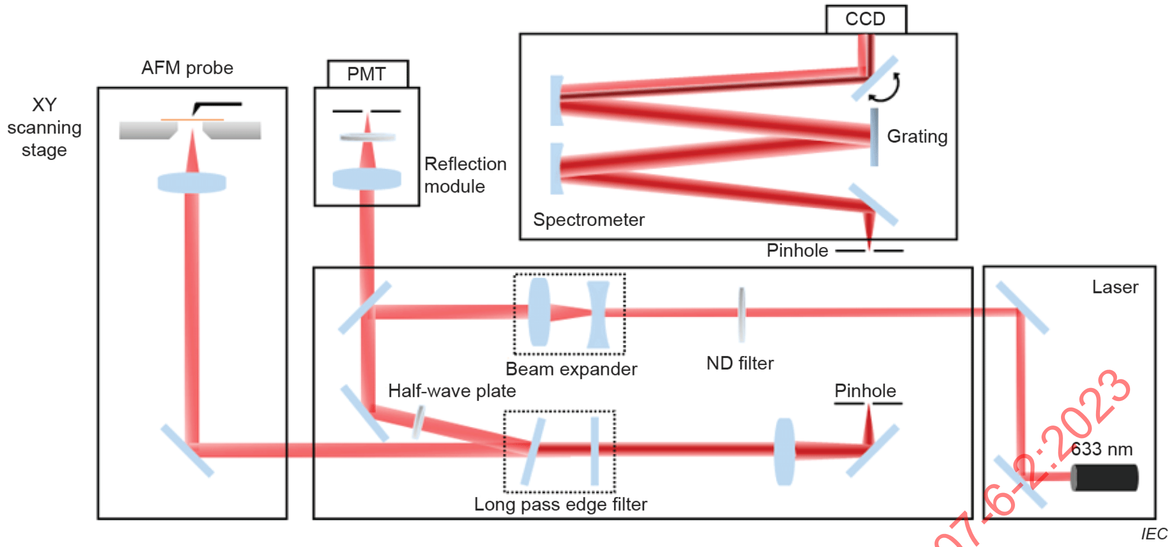


Figure 1 – Schematic of simultaneous measurement of AFM, Raman scattering, and light reflectance

6 Data analysis and interpretation of results

6.1 General protocol for data analysis

The data analysis should be performed in a particular sequence to accurately count the number of graphene layers through simultaneous measurement. First, the analysis of Raman scattering properties can be prioritized to determine whether the number of graphene layers consists of monolayer or bilayer. Second, the analysis of AFM topography can be conducted as a next step for Raman interpretation. Third, on the basis of the analysis for Raman and AFM measurements, reflectance analysis can be simply performed. According to the specific sequence, the data analysis for the simultaneous measurement results in an accurate number of graphene layers (See details in Annex C and Annex D).

6.2 Analysis of number of layers of graphene using Raman spectroscopy

Monolayer and bilayer graphene can be accurately distinguished by using Raman scattering properties when using the excitation laser in a wavelength of 633 nm. In the case of monolayer graphene, the 2D-peak show a single Lorentzian line shape and the 2D-peak value should be below 2 645 cm^{-1}. The value of the 2D/G ratio should be more than 1. In the case of bilayer graphene, the 2D-peak shows an overlapped Lorentzian curve which can be deconvoluted into four spectra and the 2D-peak value should be estimated to be about 2 650 cm^{-1}. The value of 2D/G ratio should be larger than 0,5 and smaller than 1. When these conditions are established, the number of graphene layers is determined as either monolayer or bilayer graphene.

6.3 Analysis of number of layers of graphene using AFM topography

The number of graphene layers can be counted by the AFM measurement. However, in this system, the offset height should be considered to accurately determine the number of layers. The monolayer graphene has a thickness of 0,335 nm and the few-layer graphene has a distance between the layers of 0,14 nm. According to these values, the thickness of the bilayer, trilayer, four-layer, five-layer, six-layer, seven-layer, eight-layer, and nine-layer graphene is 0,81 nm, 1,285 nm, 1,76 nm, 2,235 nm, 2,71 nm, 3,185 nm, 3,66 nm, and 4,135 nm with the layer distance of 0,14 nm, respectively. Therefore, considering the offset height, the number of graphene layers can be precisely distinguished.

6.4 Analysis of number of layers of graphene using reflectance (Rayleigh scattering)

The transmittance of graphene reduces by about 2,3 % per each layer in the air. According to the rate of decrease of transmittance, the reflectance of graphene also grows by about 4,6 % per each layer. Furthermore, the refractive index and reflectance of the bare substrates should be considered with the values of magnification and numerical aperture (NA) for objective lens. The differential value of the reflectance increases linearly as the number of layers increases.

7 Report

The report includes the following:

– sample preparation;
– measurement procedure;
– Raman intensity (I_{2D}) and full width at half maximum ($FWHM_{2D}$) of 2D-peak, Raman intensity (I_G) of G-peak, and Raman peak intensity ratio (I_{2D}/I_G);
– optical contrast (CTRS) between graphene flake and substrate;
– thickness (t) of graphene flake.

Annex A
(informative)

Summary of three simultaneous measurements and their analysis

A.1 Flowchart for determining the number of layers of graphene

See Figure A.1.

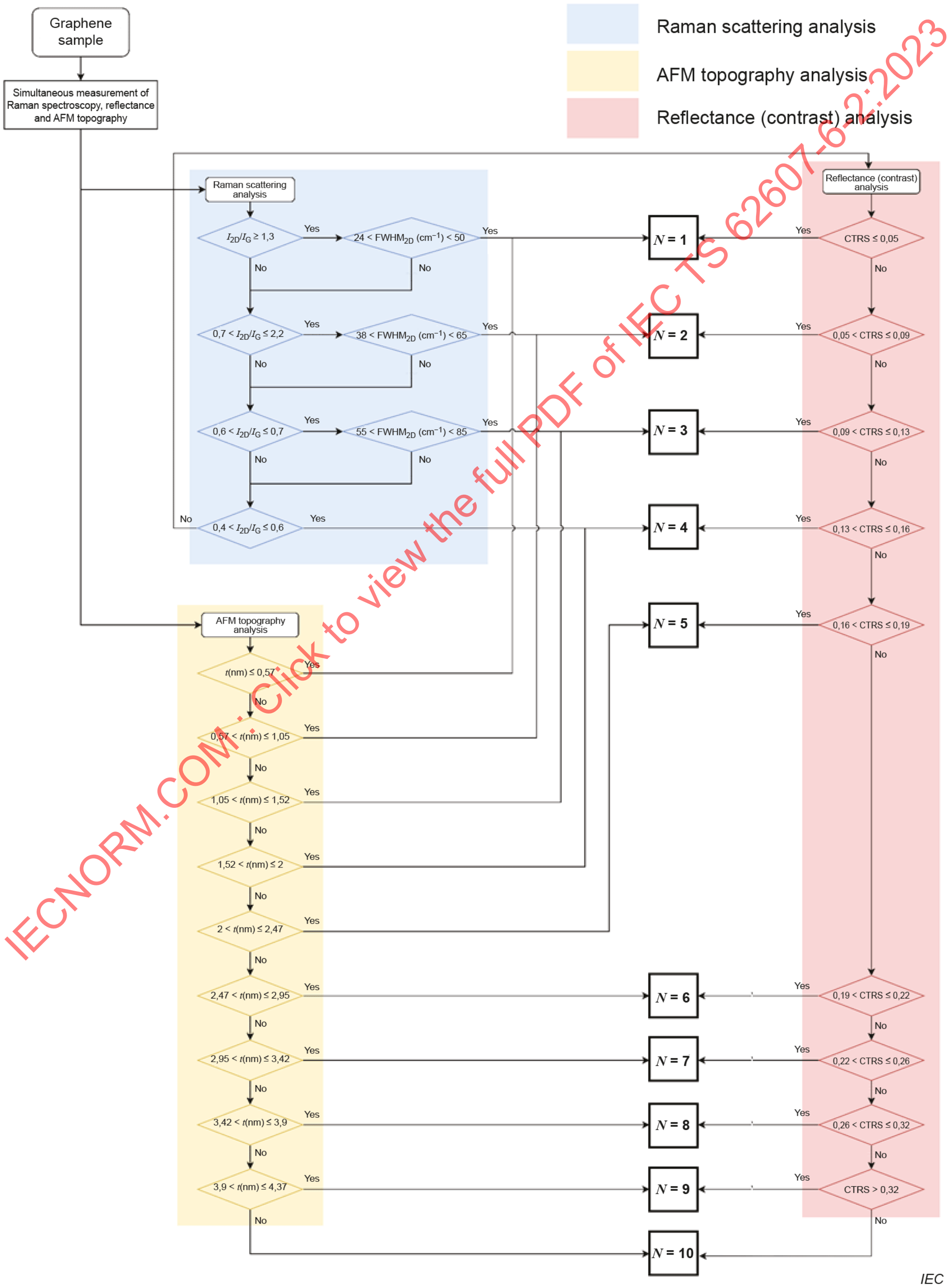


Figure A.1 – Flowchart for determining the number of layers of graphene

A.2 Summary table of analysis process

According to each analysis method, the distinguished number of graphene layers and their corresponding parameters are shown in Table A.1.

Table A.1 – Summary table of analysis process

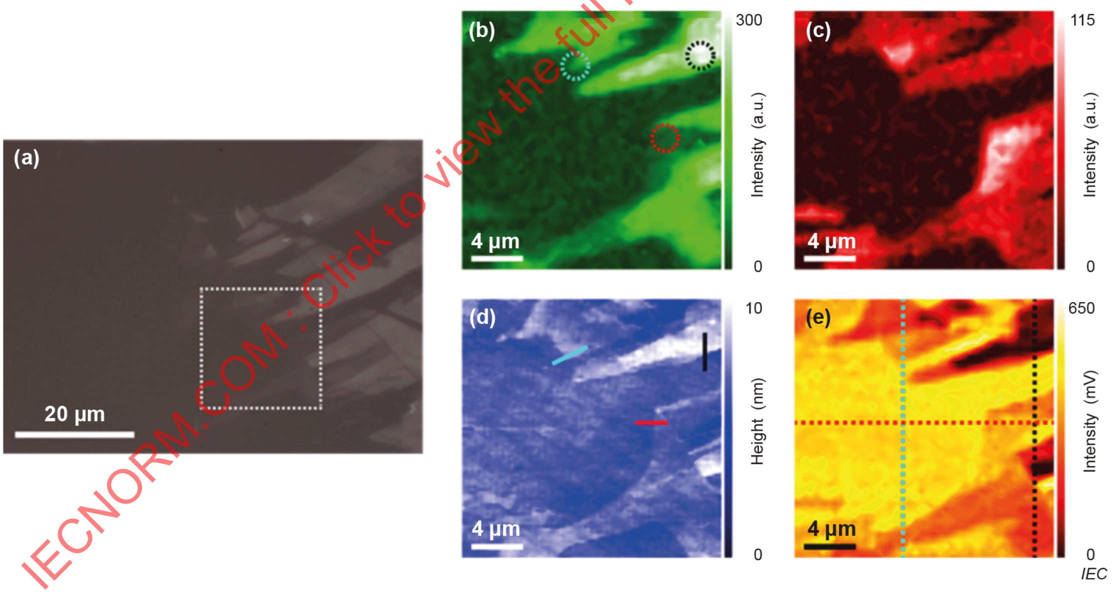
	Raman spectroscopy [8]	Reflectance (optical contrast)	AFM topography
Range of distinguishable number of layers	1 to 4	< ~20	> 1
Criterion	I_{2D}/I_G	Contrast	Thickness (nm)
Number of layers (N)	**Corresponding values**		
1	$1,3 \leq I_{2D}/I_G$	CTRS ≤ 0,05	$0 < t \leq 0,57$
2	$0,7 < I_{2D}/I_G \leq 2,2$	0,05 < CTRS ≤ 0,09	$0,57 < t \leq 1,05$
3	$0,6 < I_{2D}/I_G \leq 0,7$	0,09 < CTRS ≤ 0,13	$1,05 < t \leq 1,52$
4	$0,4 < I_{2D}/I_G \leq 0,6$	0,13 < CTRS ≤ 0,16	$1,52 < t \leq 2,00$
5		0,16 < CTRS ≤ 0,19	$2,00 < t \leq 2,47$
6		0,19 < CTRS ≤ 0,22	$2,47 < t \leq 2,95$
7		0,22 < CTRS ≤ 0,26	$2,95 < t \leq 3,42$
8		0,26 < CTRS ≤ 0,32	$3,42 < t \leq 3,90$
9		CTRS > 0,32	$3,90 < t \leq 4,37$
10			$4,37 < t \leq 4,61$

Annex B
(informative)

Interpretation of the simultaneous measurement for Raman scattering, AFM, and reflectance – case studies

The simultaneous measurement using AFM, reflectance, and Raman scattering has been performed to count the graphene layers. As shown in Figure B.1(a), an optical microscope image shows multilayer graphene which was prepared on a transparent quartz substrate with a thickness of 200 nm by using mechanical exfoliation.

The number of graphene layers can be approximately distinguished by Raman scattering measurements using an excitation laser with a wavelength of 633 nm in Figure B.1(b) and (c). The thin graphene layers show the weak G-peak intensity and the strong 2D-peak intensity, whereas the thick layers present the strong G-peak intensity and the weak 2D-peak intensity. The monolayer and bilayer graphene can be determined by using the ratio of G- and 2D-peaks and the 2D-peak position. Although the Raman measurement can discern the difference of monolayer and bilayer graphene, the few-layer graphene of more than three layers can be hardly distinguished due to the similar Raman properties. In order to determine the number of graphene layers accurately, the measurements of AFM and reflectance images were also conducted simultaneously with the Raman scattering, as shown in Figure B.1(d) and (e). The AFM image displays the distinct height differences of the graphene flakes. However, despite the flat surface of the substrate, the height differential of the substrate appears in the region where there are no samples. Furthermore, the reflectance image shows well the thickness differences of graphene.



Key

(a) optical microscope image of mechanically exfoliated graphene on a transparent quartz substrate (the white dotted square indicates the measured area)

(b) confocal Raman scattering image of G-peak area intensity

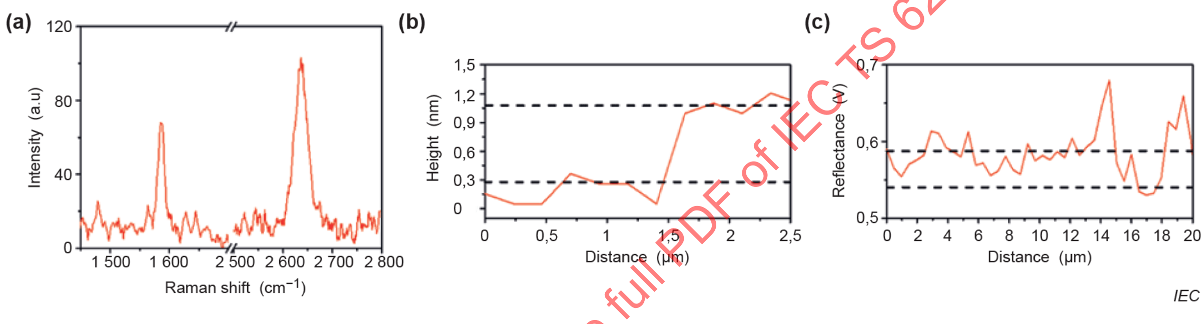
(c) confocal Raman scattering image of 2D-peak area intensity

(d) AFM topography image of the sample area

(e) reflection image of the sample area

Figure B.1 – Simultaneous measurement of Raman scattering, AFM, and reflectance images to determine the number of graphene layers

In order to accurately count the number of graphene layers, the Raman spectra, the line profiles of AFM image, and the reflectance were investigated concurrently. First, the Raman spectrum was extracted from the region where the weakest G-peak intensity and the strongest 2D-peak intensity with a single Lorentzian curve appear, as shown in Figure B.2(a). The values of G- and 2D-peaks are estimated to be about 1 585 cm^{-1} and 2 636 cm^{-1}, respectively. The value of the 2D/G ratio is about 1,52. The values of peak position and ratio indicate that the number of graphene layers is monolayer. Although the Raman peaks show the exact features of monolayer graphene, the height from the AFM profile indicates the bilayer graphene. This phenomenon can be attributed to the offset height of the AFM measurement. Therefore, the offset height can be estimated to be about 0,465 nm because the Raman scattering properties indicate the precise monolayer graphene of which the height value is estimated to be about 0,335 nm. Moreover, the reflectance difference between the regions without the sample and with the monolayer graphene shows about 8 %. It is well known that the transmittance of graphene reduces by an average 2,3 % per each layer. According to the rate of decrease of transmittance, the reflectance of graphene also grows by about 4,6 % per each layer. In this measurement, considering the fused quartz substrate with the refractive index of about 1,4 and the thickness of 200 nm, the value of reflectance difference can be estimated to be about 8 % per each layer.



Key

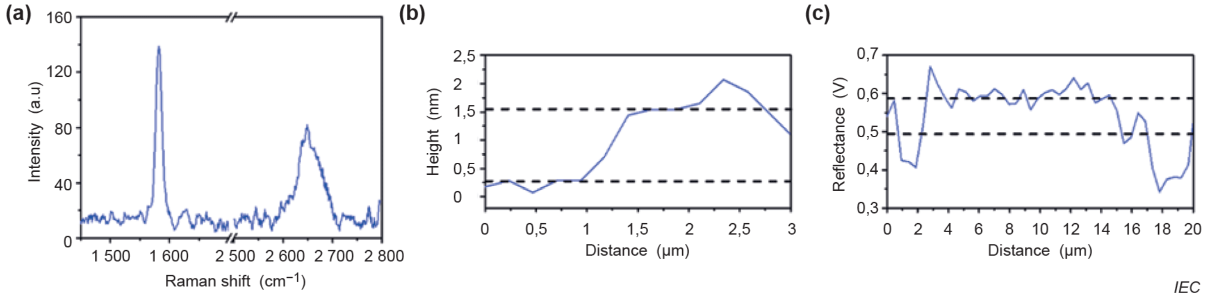
(a) confocal Raman spectrum of monolayer graphene measured at the red dashed circle in Figure B.1(b)

(b) AFM line profile of monolayer graphene along the red solid line in Figure B.1(d)

(c) Reflectance intensity profile of monolayer graphene along the red dashed line in Figure B.1(e)

Figure B.2 – Confocal Raman spectrum, AFM line profile and reflectance intensity profile of graphene flake extracted along red line in Figure B.1

Second, the Raman spectrum was extracted from the region where the second strongest signals of 2D-peak appear as shown in Figure B.3(a). The values of G- and 2D-peaks are about 1 582 cm^{-1} and 2 649 cm^{-1}, respectively. The G- and 2D-peaks are red- and blue-shifted, respectively, in comparison with those of monolayer graphene. The value of the 2D/G ratio is estimated to be about 0,59. These values indicate the bilayer graphene. The height from the AFM line profile in Figure B.3(b) is about 1,28 nm. As considering the offset height, the height of sample can be estimated to be 0,82 nm. The bilayer graphene has the thickness of 0,81 nm because the thickness of monolayer graphene is 0,335 nm and the distance between graphene layers is 0,14 nm. Therefore, the AFM result as well as the Raman features indicate the bilayer graphene. Furthermore, in Figure B.3(c), the value of reflectance difference is about 16 % which means the bilayer graphene because the value of reflectance difference is about 8 % per each layer in this measurement.



Key

(a) confocal Raman spectrum of bilayer graphene measured at the cyan dashed circle in Figure B.1(b)

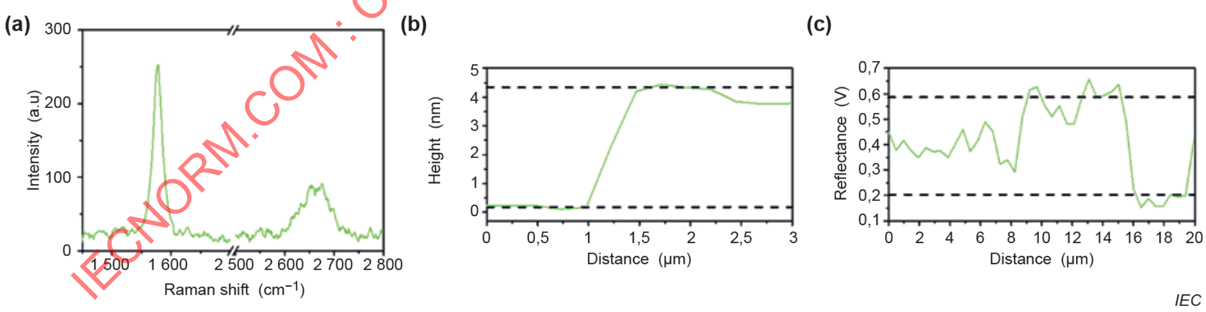
(b) AFM line profile of bilayer graphene along the cyan solid line in Figure B.1(d)

(c) Reflectance intensity profile of bilayer graphene along the cyan dashed line in Figure B.1(e)

Figure B.3 – Confocal Raman spectrum, AFM line profile and reflectance intensity profile of graphene flake extracted along cyan line in Figure B.1

Third, the Raman spectrum was extracted from the region where the strongest intensity of G-peak appears, as shown in Figure B.4(a). The values of G- and 2D-peaks are about 1 578 cm^{-1} and 2 675 cm^{-1}, respectively. The G- and 2D-peaks are quite red- and blue-shifted, respectively, in comparison with those of monolayer and bilayer graphene. The value of the 2D/G ratio is estimated to be about 0,36. These values indicate the few-layer graphene. The accurate number of graphene layers cannot be determined by using only Raman measurement. Thus, the AFM line profile and the reflectance data are required to count the number of layers. In Figure B.4(b), the thickness subtracting the offset value is estimated to be about 3,69 nm. According to the thickness of monolayer graphene and the layer distance, the thickness of eight-layer graphene is 3,66 nm. Therefore, the result of AFM data indicates the eight-layer graphene. In Figure B.4(c), the reflectance value is estimated to be about 65 %, which almost corresponds to the value for eight-layer graphene of 64 %. Thus, the number of graphene layers is eight.

Therefore, it is possible to precisely count the number of graphene layers through these combined measurement results, which indicate the Raman scattering, the AFM topography, and the reflectance images.



Key

(a) confocal Raman spectrum of eight-layer graphene measured at the black dashed circle in Figure B.1(b).

(b) AFM line profile of eight-layer graphene along the black solid line in Figure B.1(d).

(c) Reflectance intensity profile of eight-layer graphene along the black dashed line in Figure B.1(e).

Figure B.4 – Confocal Raman spectrum, AFM line profile and reflectance intensity profile of graphene flake extracted along black line in Figure B.1

Annex C
(informative)

Description of the measurement apparatus

C.1 General

The system of simultaneous measurement of AFM, Raman scattering, and reflectance consists of two components:

1) an AFM measurement unit;
2) a spectroscopy unit combined with Raman scattering and transmittance.

C.2 AFM system

The AFM system has an inverted microscope to measure the optical signals and AFM images simultaneously. The microscope includes an objective lens of 0.9 NA with 100× magnification (the lens specification requires NA < 1.0, magnification greater than 50× for measuring the graphene in the ambient condition) to focus an excitation laser on a sample and a CCD camera to observe the sample surface. In order to measure the three kinds of image, the microscope is equipped with a piezo stage operated by a piezoelectric actuator, which provides x-, y-, and z-directional motions with nanometre-scale precision. The piezo stage includes a feedback sensor driven by a controller, which provides a closed-loop operation. The thermal drift of the stage system is about 15 nm/min/°C for x- and y-axes for scanning and about 10 nm/min/°C for z-axis scanning.

C.3 Spectroscopy system

The spectroscopy system is composed of optical filters, spectrometer part, reflection module, and excitation laser. The optical filters include a neutral density (ND) filter, a collimator lens, a half-wave plate, and a long pass edge filter.

The ND filter controls the power of the excitation laser. The collimator expands a laser beam with the aligned parallel ray. The half-wave plate changes the polarization direction of the linearly polarized laser. The long pass edge filter is thin-film coating or an absorptive coloured glass filter that rejects shorter wavelengths than the excitation wavelength and transmits longer wavelengths (Raman signals) over the active range of the target spectrum.

The spectrometer part consists of diffraction gratings and a CCD detector. The spectrometer is a device for measuring optical signals like the wavelength of light over a range of the electromagnetic spectrum. In this simultaneous measurement system, the spectrometer is used to measure the Raman scattering signals from the graphene.

The reflection module includes a PMT detector to measure the reflectance by collecting the reflected laser light (Rayleigh scattering). The PMT converts the incident photons into electrical signals. In order to measure the Raman properties of graphene, the wavelength of the excitation laser can be the visible light range. Among the lasers in the visible region, the laser with a wavelength of 633 nm can generate the strongest Raman intensity from the graphene.