IEC TS 62607-6-12

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TECHNICAL SPECIFICATION

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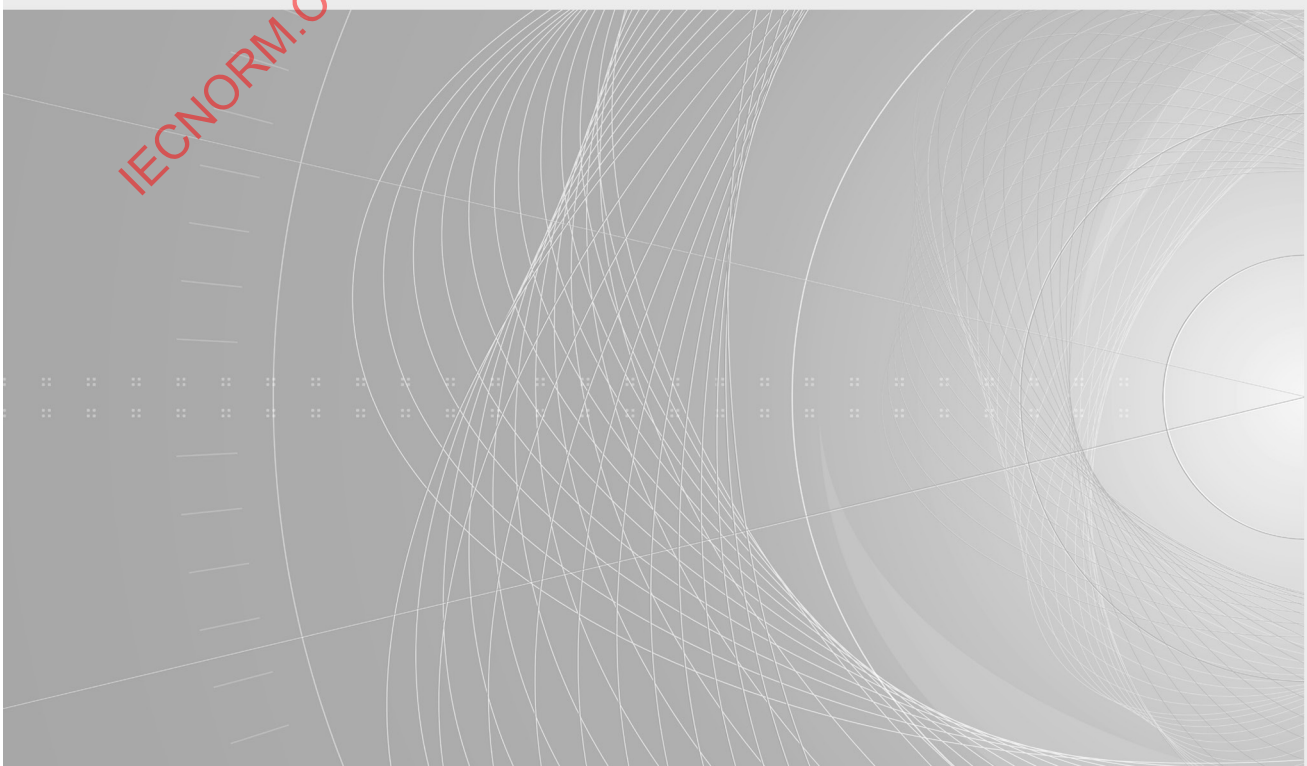
Nanomanufacturing – Key Control Characteristics – Part 6-12: Graphene – Number of layers: Raman spectroscopy, optical reflection



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Nanomanufacturing – Key Control Characteristics – Part 6-12: Graphene – Number of layers: Raman spectroscopy, optical reflection

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-12: Graphene – Number of layers: Raman spectroscopy, optical reflection

FOREWORD

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The text of this Technical Specification is based on the following documents:

Draft	Report on voting
113/701/DTS	113/726/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 www.iec.ch/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- withdrawn,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
- amended.

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INTRODUCTION

Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, has a high potential for future nanotechnology applications due to the excellent conductivity, transparency and flexibility of the material. Many physical properties of graphene and few-layer graphene depend on the number of layers. For example, monolayer and some few-layer graphene admit a linear dispersion relation of electronic bands and consequently show specific quantum hall effect and conductivity. Optical transparency and chemical activity are also related to the number of layers and their stacking angles.

Raman spectroscopy is a simple, fast and well-understood technique and has been proposed as a key experimental technique to evaluate the number of layers. The interpretation of Raman measurements however depends on many parameters such as laser wavelength, stacking angles, doping, strain, heating from laser, focus, graphene quality or defect density, residues and substrate. Raman spectroscopy can then not be used alone to determine the number of layers. In this document for the number of layers (N), we combine Raman spectroscopy with optical contrast on high quality graphene deposited on glass substrate and on SiO_2-on-silicon substrate. The present procedure is restricted to $N \leq 5$.

The analysis of the Raman spectra concentrates on two of the most dominating Raman peaks for graphene: the D-peak (around 1 340 cm^{-1}) and the G-peak (1 580 cm^{-1}). High quality graphene samples are characterized by a very low intensity of the D-peak. The number of layers is determined by the measurement of the integrated intensity of the G-peak of the graphene samples normalized to the integrated intensity of HOPG sample. The optical contrast of graphene is measured relative to the bare substrate.

In the literature, mainly three criteria have been proposed to determine N.

1) 2D-peak based criteria: the dependencies of the full width at half maximum of the 2D-peak (Γ_{2D}) and the ratio between 2D- and G-peaks integrated intensities (A_{2D}/A_G) as a function of N have been commonly used in the literature as metrics to distinguish monolayer graphene (1LG) and few-layer graphene (FLG): 1LG has been proposed to have the lowest Γ_{2D} and highest A_{2D}/A_G as compared to multilayer graphene (MLG). A systematic investigation evidences different and even opposite behaviours of these features with N [1][1]. It has been analysed as the consequences of different stacking order between consecutive graphene layers. In agreement with published reports on twisted bilayer graphene (2LG), higher values of the A_{2D}/A_G ratio and narrower 2D-peak widths than those measured on 1LG can be measured on twisted FLG. In terms of control characteristics, these results confirm that neither A_{2D}/A_G nor Γ_{2D} are valid criteria to identify 1LG or to count the number of layers in FLG. The sensitivity of these quantities to doping or strain also impacts their reliability. As a consequence, criteria based on the 2D-peak have been ruled out.

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

2) G-peak area based criterion: A more robust parameter to count the number of graphene layers is the G-peak area or integrated intensity (A_G). Since it relies on Raman intensity measurement, it is important to define a reference for intensity normalization. HOPG has been chosen as a reference since it is a well-defined, easy to purchase material. A_G has the advantage to enable to distinguish between 1LG and FLG in all cases, if the signal-to-noise ratio is high enough. However, regarding the number of layers counting, two limitations related to the relative orientation and stacking of the graphene layers exist: First, an intensity enhancement can occur due to changes in the joint density of states, for given relative orientations of the layers [2]. Second, a significant G-peak intensity decrease (down to 70 % of the one of equivalent Bernal stacked structures) can occur for some relative orientations [3], [4], [5]. As an example, for 2LG and a laser wavelength of 532 nm, the optical resonance increases A_G for twist angles in the range 10° to 16° and A_G is found lower than in Bernal 2LG for twist angles in the range 16° to 23°. These two limitations circumvent the use of A_G alone as metrics for counting the number of layers.

3) Optical contrast based criterion: The optical contrast in the visible, defined as the ratio between the laser signal reflected by the sample and the laser signal reflected by the bare substrate minus one, has also been proposed as a tool for counting graphene layers. Indeed, the optical properties of MLG are, in most of the cases, directly related to the number of layers. However, the optical contrast is also changing near optical resonances. In this case, this criterion also leads to a wrong determination of the number of layers.

In summary, the last two methods enable to distinguish between graphene and multilayer graphene. However, neither method on its own nor the combination of the two enable a determination of the number of layers in all possible cases (especially regarding all possible stacking angles). But the comparison of the values deduced by each method allows to discriminate if the determined number of layers is correct and can be specified or not. For $N >> 5$, the variation of the measured parameters with N becomes too small as compared to the possible deviations from the reference values (obtained on Bernal stacked layers). An upper limit of five layers has been fixed for this document to avoid such problems.

Moreover, both A_G and optical contrast are strongly dependent on the nature of the substrate and on the laser wavelength used. Therefore, it is important that each substrate is specifically studied and a large set of experimental data is a prerequisite to validate theoretical predictions.

In conclusion, a standard method is proposed for the specification of the number of layers based on the combination of Raman spectroscopy (normalized G-peak area) and optical reflection (optical contrast) [3]. Both methods enable the user to distinguish unambiguously between single-layer graphene and multilayer graphene. However, neither method on its own nor the combination of the two enable a determination of the number of layers for all possible stacking orientations. But importantly, since the two methods always significantly disagree when they fail, the comparison of the values deduced by each method allows to discriminate if the determined number of layers is correct and can be specified or not.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-12: Graphene – Number of layers: Raman spectroscopy, optical reflection

1 Scope

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

– number of layers

for films consisting of graphene by

– Raman spectroscopy and
– optical reflection.

Criteria for the determination of the number of layers are the G-peak integrated intensity and the optical contrast. Both methods enable to distinguish between graphene and multilayer graphene. However, neither method on its own nor the combination of the two enable a determination of the number of layers in all possible cases (especially regarding all possible stacking angles). But the comparison of the values deduced by each method allows to discriminate whether the determined number of layers is correct and can be specified or not.

– The method is applicable to exfoliated graphene and graphene grown on or transferred to a substrate with a small defect density, low surface contamination (e.g. transfer residue) and number of layers up to 5.
– The method is suitable for the following substrates:
  a) glass (soda lime glass or similar with a refractive index between 1,45 and 1,55 at 532 nm);
  b) oxidized silicon (SiO_2 on silicon, with a SiO_2 thickness of 90 nm ± 5 nm).

  NOTE 90 nm and 300 nm are the most used SiO_2 thicknesses for graphene substrates. Due to the current state of the art, the method can securely be used for 90 nm ± 5 nm thick SiO_2 layers and a laser wavelength of 532 nm, but cannot be fulfilled for 300 nm ± 15 nm SiO_2 layers even by changing the laser wavelength. It is possible that future editions of IEC TS 62607-6-12 will include thick layers and other substrates also.
– The spatial resolution is in the order of 1 µm given by the spot size of the exciting laser.

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 terminological databases for use in standardization at the following addresses:

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

3.1 General terms

3.1.1
key control characteristic
KCC
key performance indicator
material property or intermediate product characteristic which can affect safety or compliance with regulations, fit, function, performance, quality, reliability or subsequent processing of the final product

Note 1 to entry: The measurement of a key control characteristic is described in a standardized measurement procedure with known accuracy and precision.

Note 2 to entry: It is possible to define more than one measurement method for a key control characteristic if the correlation of the results is well-defined and known.

Note 3 to entry: In ISO TC 16949 the term “special characteristic” is used for a KCC. The term key control characteristic is preferred since it signals directly the relevance of the parameter for the quality of the final product.

[SOURCE: IEC TS 62565-1, 3.1]

3.2 Graphene related terms

3.2.1
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 [1], 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.

Note 4 to entry: This includes bilayer graphene, trilayer graphene and few-layer graphene.

[SOURCE: ISO/TS 80004-3:2016, 3.1.1]

3.2.2
graphene
graphene layer
single-layer graphene
monolayer 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, 3.1.2.1]

3.2.3
graphene-based material
GBM
graphene material
grouping of carbon-based 2D materials that include one or more of graphene, bilayer graphene, few-layer graphene, graphene nanoplate and functionalized variations thereof as well as graphene oxide and reduced graphene oxide

Note 1 to entry: "Graphene material" is a short name for graphene-based material.

3.2.4
bilayer graphene
2LG
two-dimensional material, either as free-standing films, on a substrate or flakes 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 80004-13:2016, 3.2.6]

3.2.5
trilayer graphene
3LG
two-dimensional material, either as free-standing films, bonded to a substrate or flakes consisting of three well-defined stacked graphene layers

Note 1 to entry: If the stacking registry is known it can be specified separately, for example, as "twisted trilayer graphene".

[SOURCE: ISO/TS 80004-3:2016, 3.2.9]

3.2.6
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]

3.2.7
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 primary allotropic forms with different stacking arrangements: hexagonal and rhombohedral.

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

3.2.8
highly oriented pyrolytic graphite
HOPG
highly pure and ordered form of synthetic graphite

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

3.2.9
Bernal stacking
AB stacking
stacking of 2D material layers on top of another in such a way that the neighbouring layers only have half of their atoms positioned equivalently in the out of plane direction with every third layer located in the same position in the out of plane axis

Note 1 to entry: The second layer is horizontally displaced with respect to the first layer by half the lattice constant.

[SOURCE: ISO/TS 80004-13:2017, 3.4.1.10]

3.2.10
rhombohedral stacking
ABC stacking
stacking of 2D material layers consisting of three repeating layers where the second layer is displaced in plane with respect to the first layer by half a lattice constant, and the third layer is horizontally displaced in the same direction, thus every fourth layer is located in the same position in the vertical axis

Note 1 to entry: The three layer system may repeat. The layers are stacked on top of one another in the vertical axis in such a way that the neighbouring layers only have half of their atoms positioned equivalently.

[SOURCE: ISO/TS 80004-13:2017, 3.4.1.11]

3.2.11
turbostratic stacking
stacking of layers of 2D materials that cannot be described as Bernal or rhombohedral stacking, instead having a relative stacking angle between the layers and which does not allow to develop atomic plane families other than that parallel to the basal plane, because the stacked layers exhibit a relative and random rotational angle or commensurate rotation between the layers

Note 1 to entry: Correspondingly, the only diffraction peaks with three Miller indices seen in XRD patterns are 001 peaks (002, 004, etc.), the others are 2-indices only (typically 10 and 11).

[SOURCE: ISO/TS 80004-13:2017, 3.4.1.13]

3.2.12
stacking angle
angle measured in the horizontal plane between the orientations of two layers of 2D material that are stacked vertically on top of one another

[SOURCE: ISO/TS 80004-13:2017, 3.4.1.12]

3.2.13
defect
local deviation from regularity in the crystal lattice of a 2D material

[SOURCE: ISO/TS 80004-13:2017, 3.4.1.1]

3.3 Key control characteristics measured in accordance with this document

3.3.1
number of layers
N
number of graphene layers stacking on top of one another

Note 1 to entry: As a reasonable estimation for the thickness of the graphene layer, the “number of layers” can be multiplied by 0,355 nm.

Note 2 to entry: The measurement of the number of layers and the estimation of the film thickness is hampered due to potential variations of the stacking angle between the layers.

3.4 Terms related to the measurement method described in this document

3.4.1
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.

3.4.2
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 between 1 270 cm^{-1} and 1 450 cm^{-1} depending on the wavelength of the excitation laser. The dispersion with wavelength is around 50 cm^{-1}/eV.

Note 2 to entry: The D-peak is most intense at defective graphene lattices and disappears for perfect monolayer crystals.

3.4.3
D-peak integrated intensity
A_D
integral over the intensity of the D-peak in the range between 1 250 cm^{-1} and 1 400 cm^{-1} using on a Lorentzian fit function

Note 1 to entry: Only the data with a coefficient of determination (R^2) greater than 0,99 are considered.

3.4.4
doping
addition of a quantity of different material to the host material with a view to modifying properties

[SOURCE: ISO/TS 80004-13:2017, 3.4.2.3]

3.4.5
G-peak
Raman peak related to 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 pristine graphene and does not need lattice defects to occur.

3.4.6
G-peak integrated intensity
A_G
integral over the intensity of the G-peak in the range between 1 400 cm^{-1} and 1 700 cm^{-1} using one or two Lorentzian fit functions

Note 1 to entry: Only the data with a coefficient of determination (R^2) greater than 0,99 are considered. In some cases, a sum of two Lorentzian functions can be necessary to reach such values (the G-peak integrated intensity being then the sum of the integrals of the two Lorentzians). The integrated intensity of the G-peak, A_G, in counts per second per watt is the Lorentzian integrated intensity normalized versus the laser power and acquisition time of the spectrum.

3.4.7
optical contrast
C
ratio between the laser signal reflected by the sample and the laser signal reflected by the bare substrate minus 1

Note 1 to entry: $C = \frac{R}{R_0} - 1$, where C is the optical contrast, R is the laser signal reflected by the sample and R_0 is the laser signal reflected by the bare substrate.

3.4.8
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]

3.4.9
surface contamination
material, generally unwanted, on the sample surface which either is not characteristic of that sample and any process investigated or has arisen from exposure of the sample to particular environments other than those relevant for the original surface or the process to be studied

Note 1 to entry: Common surface contaminants are hydrocarbons and water. Local reactions with these and the environment can lead to a wide range of oxidation and other products.

[SOURCE: ISO 18115-1:2013, 4.459]

3.4.10
transfer residue
surface contamination that is left after the transfer of a 2D material from one substrate to another

Note 1 to entry: An example is the unwanted surface contamination that is left due to sacrificial polymer used to transfer graphene grown by CVD on a metal catalyst to a different substrate.

[SOURCE: ISO/TS 80004-13:2017, 3.4.22]

4 General

4.1 Measurement principle

The measurement method described in this document takes advantage of the change of Raman spectra and optical reflection of graphene with increasing numbers of layers. Nevertheless, the relation between measurements and the number of layers is not simple and straightforward as there are multiple ways for the stacking arrangement of the layers and interaction with the substrate can lead to misinterpretation of the results. Fortunately, this problem can be solved by a simultaneous measurement of optical reflection and Raman spectroscopy under the assumption that the number of layers is not larger than five. To perform the simultaneous measurement with a regular Raman spectrometer, the only required modification in the Raman setup is to implement a way to measure the reflected light of the excitation laser.

The analysis of the Raman spectra concentrates on the G-peak (1 580 cm^{-1}) for graphene. The method is limited to high quality graphene. In the content of this document, “high quality” is related to a low intensity of the D-peak, $[A_D/A_G] < 0{,}1$ measured with an excitation wavelength of 532 nm, corresponding to a defect density below 10^{11} per cm^2, low enough to prevent the Raman and optical reflection measurements to be affected by defects. The quantity that should be extracted is the G-peak integrated intensity of the sample normalized to a HOPG reference sample. Typical Raman spectra for graphite (HOPG), high quality graphene and defective graphene are shown in Figure 1.

Analysis of the optical contrast is performed from reflectance measurements on both the bare substrate and the substrate with the graphene sample.

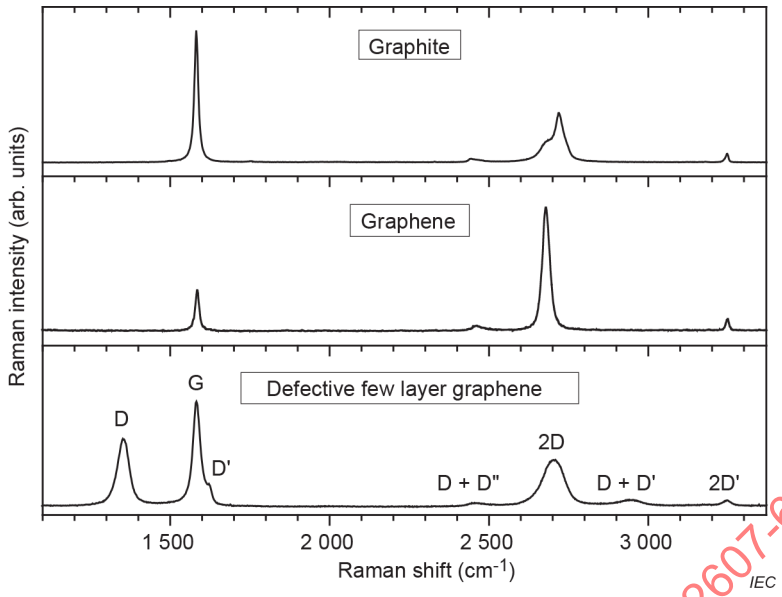


Figure 1 – Raman spectra of HOPG (top), pristine graphene (middle) and defective few-layer graphene (bottom)

The main peaks are labelled.

4.2 Sample preparation method

The sample should be measured as it is delivered by the supplier. No special sample preparation is required. Any treatment of the sample can change the structural quality and morphology.

It should be ensured that the Raman peaks of graphene and few-layer graphene, the D-peak (around 1 340 cm^{-1}) and the G-peak (around 1 580 cm^{-1}) are not masked by Raman modes originating from the substrate material. The exact same bare substrate shall be used as a reflectance reference.

As an initial test, the sample shall fulfil the quality requirement in terms of defects: $[A_D/A_G] < 0,1$. Otherwise, this document is not applicable.

4.3 Measurement environment

The measurements shall be performed at room temperature.

4.4 Description of test equipment

The tests are performed by using a Raman set-up consisting of an optical microscope, laser light source, Raman filters and a spectrometer. The setup is optimized to measure the low level of Raman scattered light from a well stabilized laser; in other words, with a long-term power stability better than 2 %. Due to the low level of Raman scattered light, the system shall be able to accumulate individual Raman spectra with a high measurement rate to achieve results with a high signal-to-noise ratio in a reasonable time (few seconds). The sample shall be mounted on a high precision translation stage allowing Raman mappings of the sample to be performed with an XY-spatial resolution below 1 µm.

The laser wavelength is 532 nm.

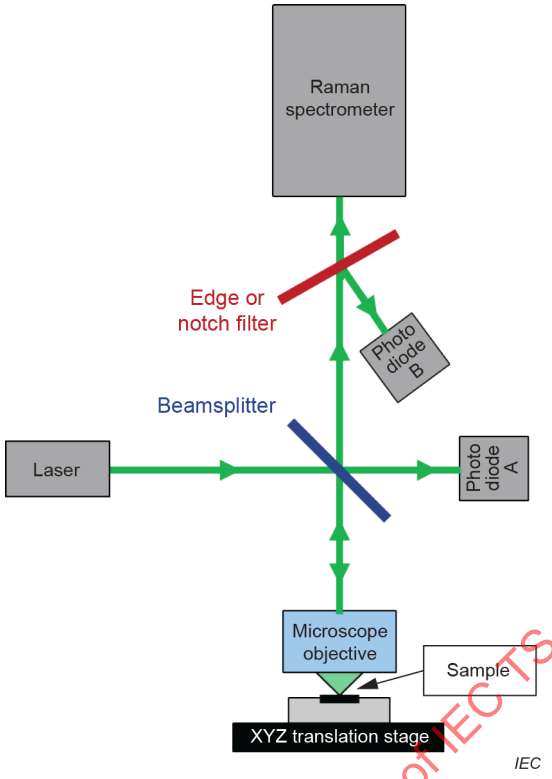
Additional equipment is also needed to measure the laser light power reflected from the samples (Photodiode B in Figure 2). It can be a commercial photodiode power sensor or merely a photodiode from which the photocurrent at zero bias is measured. With such devices, the

reflected laser light power shall be measured on the same locations on the graphene samples as the Raman spectra since the measured quantities (integrated intensity of the G-peak and optical contrast) shall be compared. The reflected laser light power can be measured before or after the acquisition of each Raman spectrum by intercepting the reflected laser beam with photodiode while keeping the laser at the same location on the sample. It is however preferable to perform both measurements simultaneously. This can be achieved either by measuring the power of the laser beam reflected from the Raman (edge or notch) filter or by using a beam-sampler to pick-up a small amount (typically 10 %) of the signal reflected from the sample and direct it to the photodiode sensor. It should be ensured that at least a few percent of the light reflected from the sample is impinging on the photodiode. The optical power range, sensitivity and resolution of the photodiode should be chosen accordingly. For graphene on glass or on 90 nm SiO_2-on-silicon substrates and within the experimental configuration specified here, the optical power range received by the photodiode varies typically from 100 nW to 1 mW and the resolution needed is around 1 nW.

The laser power impinging on the sample should be checked (Photodiode A in Figure 2) to be stable during the measurements or, better, it should be measured during each measurement.

A state-of-the-art scanning Raman spectroscopy tool with a minimal XY scan range of 10 µm × 10 µm is required. XY scan steps of 1 µm will be typically used for the Raman mapping. A laser with around or lower than 1 mW power on the sample and a wavelength of 532 nm is used for excitation. With a good combination of laser beam diameter and divergence, microscope objective and confocal hole dimension, the spatial resolution on sample can achieve 400 nm to 500 nm (close to a diffraction limited system). Here, a confocal system is not required but can be used, the microscope objective should be a 100× with a numerical aperture of 0,85 to 0,95.

For signal detection a spectrometer with a charge-coupled device (CCD) array detector and a suitable grating should be used to ensure best instrumental parameters compromise for graphene application: sufficient spectral resolution and full fingerprint spectral range on the detector without moving the grating. A typical Raman setup is illustrated in Figure 2.



Photodiode A measures the laser power.

Photodiode B measures the power of the laser beam reflected from the Raman (edge or notch) filter.

Figure 2 – Schematic illustration of the Raman and reflectance setup used for the described graphene classification

4.5 Calibration standards

4.5.1 Raman reference sample

The reference sample is HOPG grade ZYA or single crystal graphite. The Raman spectrum is plotted as the Raman intensity as a function of the Raman shift (cm^{-1}). The Raman spectrum should show no observable D-peak. The laser power should be recorded during the measurement and used for intensity normalization. The extracted quantity is the G-peak integrated intensity normalized versus laser power and effective acquisition time. The Raman spectrum of the reference should be acquired in the same experimental configuration and conditions as the one used for the test sample (laser wavelength, optimized focus conditions, microscope objective, and spectrometer and detector configurations (grating, spectral range, slits, gain)).

4.5.2 Reflection reference sample

As reference for the R_0 measurement, a bare and clean substrate should be used which is the same as the one supporting the graphene to be characterized. Alternatively, a bare and clean region of the substrate supporting the graphene materials to be characterized can be used. R_0 is the laser signal reflected by the bare substrate normalized versus laser power. R_0 should be measured in the same experimental configuration and conditions as those used for the test sample (laser wavelength, optimized focus conditions, microscope objective, and photodiodes configurations).

5 Measurement procedure

5.1 Calibration of test equipment

5.1.1 Raman spectrometer

Calibration shall be performed according to manufacturer's requirements. In particular, the nonlinearity of the signal as a function of the acquisition time should be lower than 1 %.

5.1.2 Optical reflection setup

The zero and the linearity of the photodiodes or detectors used to measure the laser power and the power of the reflected laser beam should be checked. The nonlinearity should be lower than 1 %.

5.2 Description of the measurement procedure

The laser wavelength used is 532 nm, the microscope objective is a plan achromat for the visible range with a numerical aperture of 0,9. First, the Raman (HOPG) and reflection (bare substrate) reference samples should be measured. Then, spatially resolved Raman and reflectance maps are recorded simultaneously in optimized focus conditions on the test sample. The sample should be mounted on a movable table with a precision of at least 500 nm to record spatially resolved, two-dimensional maps of Raman spectra and reflectance.

On each sampling point, given by the sample-specific sampling plan (see below), an area of 10 µm × 10 µm is scanned at optimized focus conditions. Within each scan area 100 Raman spectra and reflectance values (10 × 10) are recorded. The spectral range should be chosen such that the relevant Raman peaks (D-peak (1 340 cm^{-1}), G-peak (1 580 cm^{-1})) are covered. It is recommended to use a setup where all Raman peaks can be measured in a single spectrum to reduce measurement time. The laser power should not exceed 1 mW on the sample during the measurement to avoid excessive laser induced heating. The laser power should be recorded during the measurements and used for intensity normalization on each point. The spectra are plotted as the Raman intensity as a function of the Raman shift (cm^{-1}). The Raman intensity is normalized with the incident laser power and expressed in counts per second per watt.

5.3 Sampling plan

Two fundamentally different kinds of sampling plan can be used the measure the number of layers: Mapping and point measurements.

a) Mapping shall be used if it is assumed that the graphene layer is spatially inhomogeneous and the method shall be used to generate a spatially resolved image of the distribution of the number of layers over the sample. For the mapping technique, the distance between measurement points and the number of measurements per point shall be specified.

b) Point measurements shall be used if the graphene layer is homogeneous over the specified area on a substrate. In this case, the point sampling plan shall be used. The number of points measured shall be selected according to the technical maturity of the fabrication process. Mature processes are characterized by a reasonable reproducibility of the layer distribution over the specified area of the sample. Therefore, selecting a plan with multiple measurement points at different spatial positions on the sample can be used to control systematic changes over the specified area. See Annex B for point sampling plans.

5.4 Measurement accuracy

The integration time for each individual spectrum should be adjusted to exceed a signal-to-noise ratio of 50 for the G-peak. The signal-to-noise ratio is defined as the difference between the peak signal and the DC component of the background signal divided by the root mean square value of the noise on the background signal.

The relative fluctuations of reflectance measured on the bare substrate should be lower than 1 % root mean square.

6 Data analysis and interpretation of results

6.1 Analysis of the Raman spectra

It is recommended that a reference spectrum of the bare substrate is taken and subtracted from every measured spectrum. Care should be taken to correctly subtract the baseline. While scanning the graphene sample and recording a full Raman spectrum for each spot, the acquired data is further processed by standard peak fitting techniques.

The integrated intensity ratio as obtained from the single Lorentzian fits of the Raman D- and G-peaks A_D/A_G can be used to classify the defect density because intensity of the D-peak is related to deviations from high quality graphene. The intensity ratio shall be reported in the test report. As the method described in this document focuses on nearly defect-free graphene, the D-peak is possibly not visible in most cases. This shall be noted in the test report.

As a next step, for each measurement point, the extracted Raman integrated intensity of the G-peak, A_G is normalized versus the one of the reference Raman sample (HOPG) in order to obtain A_G^{Norm}.

$$A_G^{Norm} = \frac{A_G}{A_G^{HOPG}}$$

To be compared, the integrated intensities (A_G and A_G^{HOPG}) should be normalized as a function of the laser power and the acquisition time.

N_G, the number of layers estimated using A_G^{Norm}, is obtained by the following expression with a 100× objective with numerical aperture of 0,9.

– On soda lime glass with a refractive index of 1,52 at 532 nm:

$$N_G = 7{,}16 \times A_G^{Norm} + 3{,}36 \times (A_G^{Norm})^2$$

– On other glasses with a refractive index (n) between 1,45 and 1,55 at 532 nm:

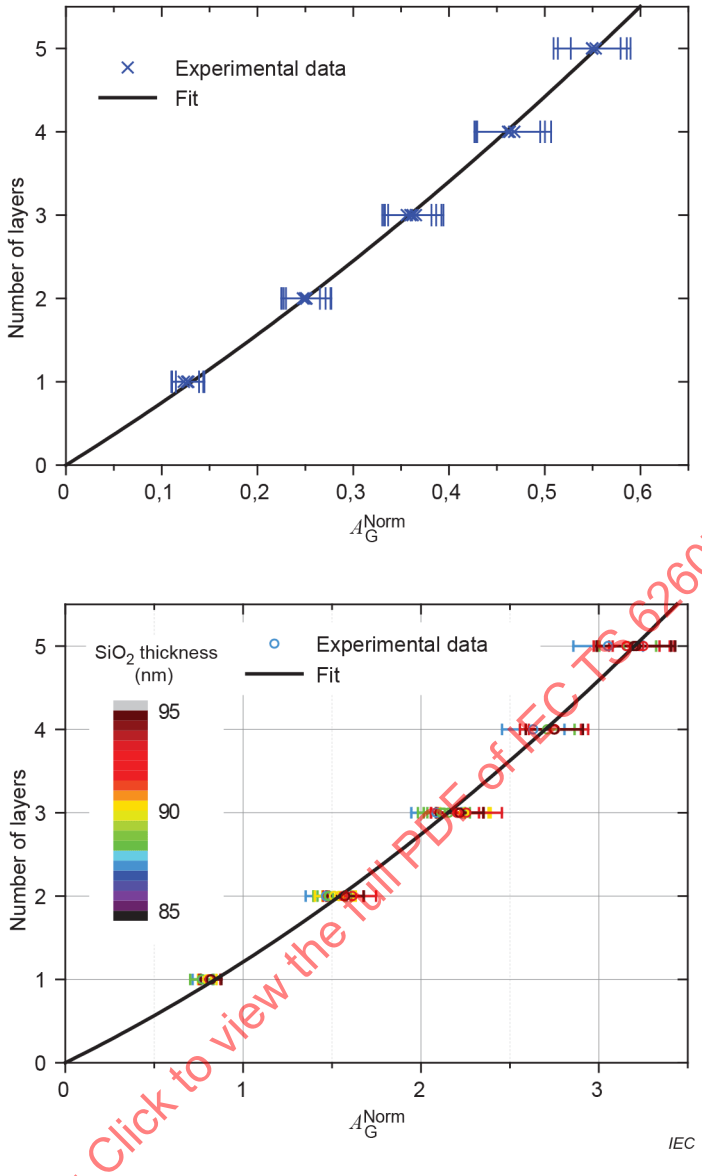
A correction factor $\alpha(A_G)$ should be applied to the measured values:

$$A_{G,\,corr}^{Norm} = \propto (A_G) \times A_{G,\,meas}^{Norm}$$

and $A_{G,\,corr}^{Norm}$ should be used instead of A_G^{Norm} in the previous expression to obtain N_G.

– On 90 nm ± 5 nm SiO_2 on Si: $N_G = 1{,}05 \times A_G^{Norm} + 0{,}16 \times \left(A_G^{Norm}\right)^2$

Figure 3 displays the associated curves together with experimental data points. Note here that non-integer values of N_G can be obtained (see section 6.3).



NOTE Open circles are experimental data (colour coded with the SiO_2 thickness of the sample as displayed on the graph) and the solid black line is a polynomial fit with the above expression (R^2 = 0,999 8 (top) and 0,999 (bottom)).

Figure 3 – Number of layers as a function of G-peak integrated intensity on glass (top) and on 90 nm ± 5 nm SiO_2 on Si (bottom)

6.2 Analysis of the reflectance measurement

For each measurement point, the optical contrast is obtained from the measured sample reflectance R and the bare substrate reflectance R_0 and with a 100x objective with numerical aperture of 0.9. To be compared, R and R_0 should be normalized as a function of the laser power.

N_C, the number of layers estimated using C, is obtained with the following equation.

– On soda lime glass with a refractive index of 1,52 at 532 nm:

$$N_C = 10{,}6 \times C - 1{,}1 \times (C)^2$$

– On other glasses with a refractive index (n) between 1,45 and 1,55 at 532 nm:

A correction factor $Cf(C)$ should be applied to the measured values:

$$Cf(C) = 2{,}409n - 2{,}661$$

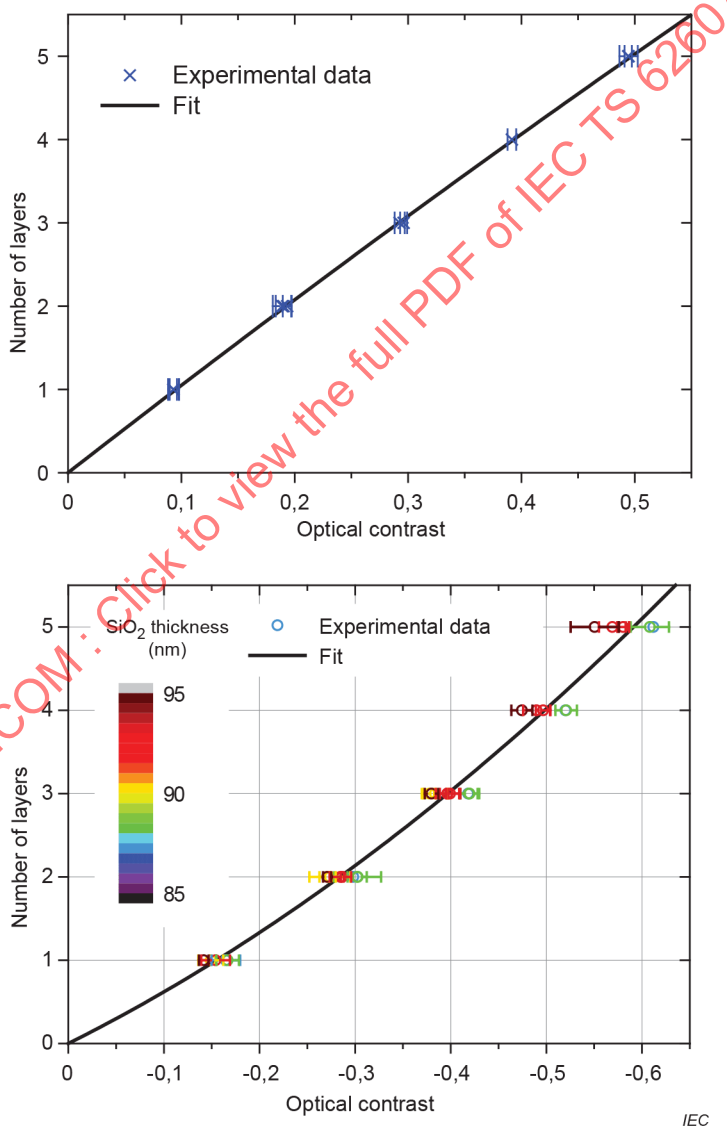
$$C_{\text{corr}} = Cf(C) \times C_{\text{meas}}$$

and C_{corr} should be used instead of C in the previous expression to obtain N_C.

– On 90 nm ± 5 nm SiO_2 on Si:

$$N_C = -5{,}74 \times C + 4{,}61 \times C^2$$

Figure 4 displays the associated curves together with experimental data points. Note here that non-integer values of N_C can be obtained (see section 6.3).



NOTE Open circles are experimental data (colour coded with the SiO_2 thickness of the sample as displayed on the graph) and the solid black line is a polynomial fit with the above equation (R^2 = 0,999 9 (top) and 0,997 (bottom)).

Figure 4 – Number of layers as a function of the optical contrast on glass (top) and on 90 nm ± 5 nm SiO_2 on Si (bottom)

6.3 Interpretation of the combined measurement

The obtained estimations of the number of layers from the Raman G-peak (N_G) and from the optical contrast (N_C) come with uncertainties related to the experimental errors and, more important, to the effect of stacking and optical resonance. The exact number of layers N can be obtained if N_G and N_C agree. Table 1 to Table 3 (decision tables A to C) specify the value of N according to the ranges of N_G and N_C. In Table 2, the two values of N means that the exact number of layers cannot be specified but a range of N. In Table 3, specific cases are reported where the values of N_G are found slightly lower than N_C but where N can still be specified. This situation is found for some specific relative orientations between the layers and has been clearly identified [3], [4], [5].

The measured data are classified and a number of layers, N, is specified according to the rules described in Table 1 to Table 3.

Table 1 – Number of layers decision table A, if the estimates of N_G and N_C agree

Result Raman measurement N_G		Result reflectance measurement N_C		Number of layers N
Lower limit	Upper limit	Lower limit	Upper limit	
	0,1		0,1	0
0,7	1,3	0,7	1,3	1
1,7	2,3	1,7	2,3	2
2,7	3,3	2,7	3,3	3
3,7	4,2	3,7	4,2	4
4,6	5,2	4,6	5,2	5

Table 2 – Number of layers decision table B, if the estimates are between numbers. Exact number of layers cannot be specified but a range of N

Result Raman measurement N_G		Result reflectance measurement N_C		Number of layers N
Lower limit	Upper limit	Lower limit	Upper limit	
0,1	0,7	0,1	0,7	0 to 1
1,3	1,7	1,3	1,7	1 to 2
2,3	2,7	2,3	2,7	2 to 3
3,3	3,7	3,3	3,7	3 to 4
4,2	4,6	4,2	4,6	4 to 5

Table 3 – Number of layers decision table C, if the values of N_G are slightly lower than N_C

Result Raman measurement N_G		Result reflectance measurement N_C		Number of layers N
Lower limit	Upper limit	Lower limit	Upper limit	
1,25	1,7	1,7	2,3	2
1,9	2,7	2,7	3,3	3

2,6	3,7	3,7	4,2	4
3,4	4,6	4,6	5,2	5

Figure 5 is the graphical representation of the Table 1 to Table 3. If the combined measurement results do not conform to a combination of N_G and N_C in any of Table 1 to Table 3 and are both larger than 1,3, the number of layers is larger than one but cannot be determined more accurately and should be specified as "> 1 but exact N unknown". In any other case, the number of layers should be reported as "undetermined".

Table 1 to Table 3 are only valid if the number of layers is homogeneous under the laser spot.

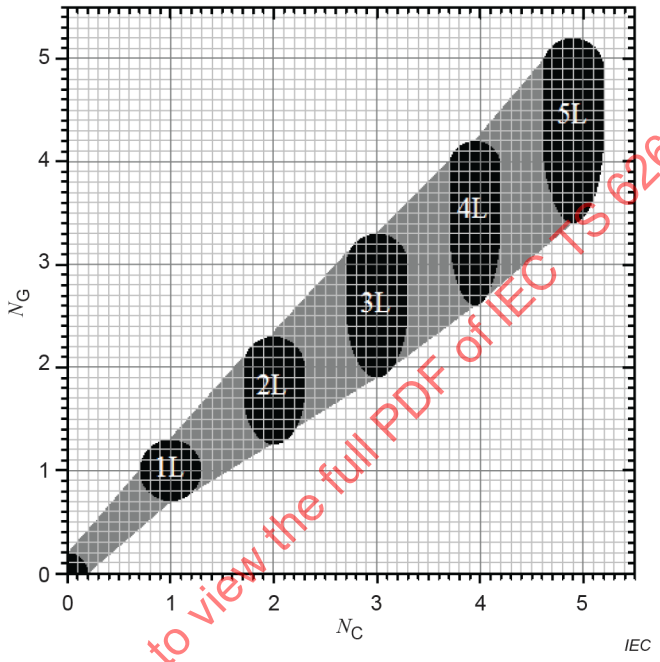


Figure 5 – Decision criteria regarding the number of layers

The exact number of layers N can be obtained if the estimates from the Raman measurement (N_G) and the optical contrast (N_C) agree.

7 Test report

7.1 General

The results of the measurement shall be documented in a measurement report, including the date and time of the measurement as well as the name and signature of the person responsible for the accuracy of the report. Guidelines are given in Annex A (Format of the test report) and Annex B (Sampling plan).

7.2 Sample identification

The report shall contain all information to identify the test sample and trace back the history of the sample:

1) General procurement information, in accordance with the relevant blank detail specification.
2) General material description in accordance with the relevant blank detail specification, including a technical drawing:
   – top view, indicating the inspected area and location of the measurement positions;

– cross section, showing the layer structure.

7.3 Test conditions

The laboratory ambient conditions during the test:

1) Atmosphere air.
2) Temperature range: 18 °C < T < 25 °C.
3) Range of relative humidity: 40 % < RH < 60 %.

7.4 Measurement specific information

– Calibration status of equipment.
– Spectral resolution of the spectrometer.
– Wavelength, spot size and power of the laser used for Raman spectroscopy and reflection (if not the same).
– Signal-to-noise ratio for the Raman spectra based on the G-peak.
– Signal-to-noise ratio for the reflection measurement.
– Typical measured Raman spectrum.
– Typical reflection signal.
– Ratio of D-peak and G-peak integrated intensity, A_D/A_G. If the D-peak is not visible this shall be noted and the maximum value of the ratio shall be estimated based on the signal-to-noise ratio of the spectra.

7.5 Test results

– Coordinate system used in the measurement setup in absolute positions with a definition of the origin so that the measurement locations can be related to the technical drawing of the sample.
– Table of mean values and standard deviation of the KCC number of layers at the positions defined by the sampling plan.
– Colour maps for the number of layers. The colour map shall be scaled in absolute positions in respect of the origin of the coordinate system. The colour code should be calibrated in absolute values of the measured KCC.

Annex A
(informative)

Format of the test report

The form of the report is oriented on the relevant material specification, a related sectional blank detail specification or detail specification. Table A.1 to Table A.5 are guidelines to write the report and can be modified to fulfil the requirements of the involved parties.

Table A.1 – Product identification

Item No	Item		Information
1.1	Supplier		
1.2	Trade name		
1.3	ID number		
1.4	Typical batch quantity	Number of wafers	
1.5	Traceability requirements	☐ Batch number ☐ Serial number ☐ Others, specify	
		Manufacturing date	
1.6	Specification	Number	
		Revision level	
		Date of issue	
1.7	Material Safety Data Sheet (MSDS) available	☐ No	
		☐ Yes Reference	

Table A.2 – General material description

Item No	Item		Information
2.1	Material type		
2.2	Manufacturing method		
2.3	Substrate	Material	
		Technical drawing (top view)	
		Technical drawing (cross section)	
2.4	Shelf life		
2.5	Typical batch size		

Table A.3 – Measurement related information

Item No	Item	Information
3.1	Sampling plan	☐ Circular, specify C-.... ☐ Square, specify S-....
		☐ drawing attached

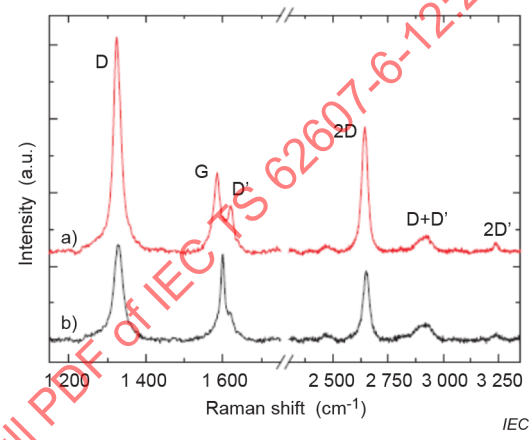
3.2	Number of spectra per location	☐ 3 ☐ others, specify	
3.3	Excitation wavelength	Raman	532 nm
		Reflection	532 nm
3.4	Laser power on sample	Raman	
		Reflection	
3.5	Laser spot size on sample	Raman	
		Reflection	
3.6	A_D/A_G	☐ not visible	
		A_D/A_G=	
3.7	Typical Raman spectrum		
3.8	Signal-to-noise ratio	Raman	
		Reflection	
3.9	Raman data	☐ attached ☐ available on request	
3.10	Environmental humidity (mean)		
3.11	Environmental temperature (mean)		

Table A.4 – Measurement results

Measurement point in accordance with sampling plan (Annex B)	Result Raman measurement N_G	Result reflectance measurement N_C	Decision	Uncertainty
1				
2				
3				
4				
5				
6				
7				
8				
9				

Table A.5 – Colour map of KCC

Item No	Location of the mapped area on the sample	Map of the number of layers
5.1		