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TECHNICAL SPECIFICATION

colour inside

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

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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- withdrawn,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]