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TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 6-21: Graphene-based material – Elemental composition, C/O ratio: X-ray photoelectron spectroscopy

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IEC TS 62607-6-21 has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems. It is a Technical Specification.

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

Draft	Report on voting
113/607/DTS	113/630/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/standardsdev/publications.

A list of all parts of 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- withdrawn,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 has unique electrical, thermal and mechanical properties and has wide potential industrial application, especially in the electronics industry: batteries, integrated circuits, high-frequency electronics, displays, etc. [1], [2], [3], [4], [5][1]. The content of main elements, especially oxygen element and the ratio of carbon to oxygen are the significant parameters influencing the electronic and thermal application performance of graphene materials [3]. The main elements in graphene materials include carbon (C), oxygen (O), nitrogen (N), sulfur (S), chloride (Cl), and silicon (Si). The C/O ratio is a key parameter to identify the type of graphene or graphene-oxide (GO), and reflects directly the degree of reduction and product quality of reduced graphene oxide (rGO). Because of multiple different production processes and manufacturers for graphene powder, the main elemental composition and C/O ratio are also different. For the development of industrial application, a standard measurement method with reliability, accuracy and reproducibility needs to be established. The X-ray photoelectron spectroscopy (XPS) technique can measure multiple elements simultaneously and obtain accurately the relative abundance of each element in a test sample [6], [7].

The purpose of this document is to provide an optimized preparation, measurement and analysis procedure for graphene powder, to enable accurate and quantitative determination of the C, O, N, S, Cl, Si elements and C/O ratio using the XPS technique.

This document has been developed based on study in VAMAS Technical Working Area 41 (TWA 41).

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

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-21: Graphene-based material – Elemental composition, C/O ratio: X-ray photoelectron spectroscopy

1 Scope

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

– elemental composition, and
– C/O ratio

for powders of graphene-based materials by

– X-ray photoelectron spectroscopy (XPS).

The elemental composition (species and relative abundance) is derived by the elemental binding energy and integral peak area at corresponding portion of XPS spectrum.

– The elemental composition refers to main elements in graphene powders, typically including carbon (C), oxygen (O), nitrogen (N), sulfur (S) , chloride (Cl) and silicon (Si).
– This document is applicable to graphene powders consisting of graphene, bilayer graphene (2LG), trilayer graphene (3LG), few-layer graphene (FLG), graphene nanoplate (GNP), reduced graphene oxide (rGO), graphene oxide (GO), and functionalized graphene powders.
– Typical application areas are the microelectronics and thermal management industries, e.g. batteries, integrated circuits, high-frequency electronics. This document can be used by manufacturers in research and development and by downstream users for product selection.

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
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 [8], 3.1.2.1]

3.1.2
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.

3.1.3
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 [8], 3.1.2.6]

3.1.4
trilayer graphene
3LG
two-dimensional material 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 80004-13:2017 [8], 3.1.2.9]

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 [8], 3.1.2.10]

3.1.6
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 [8], 3.1.2.13]

3.1.7
reduced graphene oxide
rGO
reduced oxygen content form of graphene oxide

Note 1 to entry: rGO can be produced by chemical, thermal, microwave, photo-chemical, photo-thermal, microbial or 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 [8], 3.1.2.14]

3.1.8
graphene nanoplate
graphene nanoplatelet
GNP
nanoplate consisting of graphene layers

Note 1 to entry: GNPs typically have thickness of between 1 nm to 3 nm and lateral dimensions ranging from approximately 100 nm to 100 µm.

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.11]

3.1.9
X-ray photoelectron spectroscopy
XPS
method in which an electron spectrometer is used to measure the energy distribution of photoelectrons and Auger electrons emitted from a surface irradiated by X-ray photons

Note 1 to entry: X-ray sources in common use are unmonochromated Al Kα and Mg Kα X-rays at 1 486,6 eV and 1 253,6 eV, respectively. Modern instruments also use monochromated Al Kα X-rays. Some instruments make use of various X-ray sources with other anodes or of synchrotron radiation.

[SOURCE: ISO/TS 80004-6:2021 [9], 5.19]

3.1.10
relative elemental sensitivity factor
coefficient proportional to the absolute elemental sensitivity factor, where the constant of proportionality is chosen such that the value for a selected element and transition is unity

Note 1 to entry: Elements and transitions commonly used are C 1s or F 1s for XPS and Ag $M_{4,5}VV$ for Auger electron spectroscopy.

Note 2 to entry: The type of sensitivity factor used should be appropriate for the analysis, for example, of homogeneous samples or segregated layers.

Note 3 to entry: The source of the sensitivity factors should be given in order that the correct matrix factors or other parameters have been used.

Note 4 to entry: Sensitivity factors depend on parameters of the excitation source, the spectrometer, and the orientation of the sample to these parts of the instrument. Sensitivity factors also depend on the matrix being analysed and in secondary-ion mass spectrometry, this has a dominating influence.

[SOURCE: ISO 18118:2015 [10], 3.2]

3.2 Key control characteristics measured in accordance with this document

3.2.1
elemental composition
species and relative abundance of main elements in the test sample of graphene powder

3.2.2
C/O ratio
carbon to oxygen ratio
ratio of relative abundance (atomic fraction) of carbon element to oxygen element in the test sample of graphene powder

4 General

4.1 Measurement instrument

A modern XPS instrument equipped with monochromated X-rays is required, in order to measure the relative abundance of each element detected on the surface of a solid test sample. The sampling depth, D_s (normal to the surface of the test sample, $D_s = 3\lambda$), is decided by inelastic mean free path, IMFP(λ). The actual values for the IMFP of electrons in matter are a function of the energy of the electrons and nature of the sample through which they travel [11]. For organics and polymers, IMFP of C 1s is about 4 nm to 10 nm. Annex B provides a detailed discussion.

4.2 Calibration of measurement instrument

The XPS instrument should be calibrated prior to measurement. For the calibration of X-ray photoelectron spectrometers with monochromated Al X-ray sources, use reference materials (RMs) of Cu, of Au and of Ag. The RMs shall be polycrystalline and of at least 99,8 % purity metals which, for convenience, are usually in the form of foils typically of an area 10 mm by 10 mm, and 0,1 mm to 0,2 mm thick. The test samples of RMs for instrumental calibration shall be clean.

The energy resolution of the system should be specified by use of the full width at half maximum (FWHM) of the silver Ag $3d_{5/2}$ peak, and the accuracy of the binding energy scale calibration as a function of time should also be specified at the energy for the Cu 2p 3/2 or Au 4f 7/2 peaks from RMs [12], shown in Table 1.

Table 1 – Reference values for the peak positions on the binding-energy scale, $E_{\mathrm{ref}\ n}$

Peak number, n	Assignment	$E_{\mathrm{ref}\ n}$ (eV)		
		Al Kα	Mg Kα	Monochromatic Al Kα
1	Au $4f_{7/2}$	83,95	83,95	83,96
2	Ag $3d_{5/2}$	(368,22)	(368,22)	368,21
3	Cu L_3VV	567,93	334,90	/
4	Cu $2p_{3/2}$	932,63	932,62	932,63
NOTE The Ag data included in parentheses are not normally used for calibrations.				

4.3 Charge control

In some cases, charge control (the effort to control the buildup of charge at a surface or to minimize its effect) is needed [13]. The amount and distribution of surface and near-surface charge for a specific experimental system are determined by many factors, including specimen composition, homogeneity, magnitude of bulk and surface conductivities, photo-ionization cross-section, surface topography, spatial distribution of the exciting X-rays, and availability of neutralizing electrons. Charge buildup occurs along the specimen surface and into the material. The presence of particles on or different phases in the specimen surface can result in an uneven distribution of charge across the surface, a phenomenon known as differential charging. Charge buildup can also occur at phase boundaries of interface regions within the specimen that is