Towards new IEC standards for the electrical characterization of graphene

26th IMEKO TC4 International Symposium
24rd International Workshop on ADC and DAC Modelling and Testing
IMEKO TC-4 2023
Pordenone, Italy / September 20-21, 2023

Towards new IEC standards for the electrical characterization of graphene

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Abstract – **New IEC technical specifications, for the standardized assessment of the sheet resistance R_S of monolayer graphene, recently published in June 2023 are here presented. These new standards of the series IEC TS 62607-6-xx describe protocols for the application of the contact methods i) in-line four point probe and ii) van der Pauw. The general IEC context of the main development steps for standards and and example of the scientific experiments used as input for the standard development are also presented.**

I. INTRODUCTION

Once graphene was unambiguously isolated in laboratory in 2004 [1], immediately academic research focused on its basic properties and industry begun to develop and place on the market several types of graphene and related products. The field progressed on even more encouraging results since the first evidence on academic journals of large-scale graphene synthesis [2] by chemical vapour deposition (CVD) in 2009. Still today, graphene used in academic research is hardly comparable to the raw materials offered by the industrial providers. Even within the same laboratory or industrial firm, repeatability and definition of materials' representative parameters (key control characteristics) is an issue that still holds. In fact, many available synthesis processes – such as mechanical exfoliation, chemical vapour deposition and reduction of graphene oxide dispersion, yield "graphene" with very different properties: graphene synthesized in labs rather than the one produced in industry has flakes of different size, possibly containing several types of defects and chemical contamination; research on scalable graphene is indeed facing a reproducibility gap [3].

For a successful uptake of products involving graphene and related materials, the availability of international standards is essential to define the key material properties and the appropriate measurement protocols. Within this framework, at the International Electrotechnical Commission, the Technical Committee 113 "Nanotechnology for electrotechnical products and systems" (IEC/TC 113) added the standardization of graphene and related materials into its work programme as early as 2012. The task was allocated to the Working Group 8 "Graphene related materials/Carbon nanotube materials". Currently, 36 graphene standards either published or under development within the IEC/TC 113. This TC established a liaison with the GRACE [1] research consortium [4], and since 2017 several standards about the electrical characterisation of graphene were initiated within this interaction, see the BOX 1 below.

> **BOX 1 - Standards Titles**
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> **IEC TS 62607-6-10:2020** Nanomanufacturing - Key control characteristics - Part 6-10: Graphene - sheet resistance: Terahertz time-domain spectroscopy.
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> **IEC TS 62607-6-7:2023** Nanomanufacturing - Key control characteristics - Part 6-7: Graphene - Sheet resistance: van der Pauw method.
>
> **IEC TS 62607-6-8:2023** Nanomanufacturing - Key control characteristics - Part 6-8: Graphene - Sheet resistance: in-line four-point probe.
>
> **IEC TS 62607-6-25** Nanomanufacturing - Key control characteristics - Part 6-25: Two-dimensional materials - Variation of doping concentration: Kelvin Probe Force Microscopy.

IEC TS 62607-6-10:2020 has been already published in 2020 [5], IEC TS 62607-6-7 and IEC TS 62607-6-8 have been published in June 2023 [6, 7], while IEC TS 62607-6-25 is scheduled for 2024 [8]. The technical input for the establishment of the new work item proposals that are now the presented draft/published technical specifications, emerged in good part from the interaction between the

[1]EMPIR 16NRM01 GRACE "Developing electrical characterisation methods for future graphene electronics". EMPIR is the European Metrology Programme for Innovation and Research, funded by EURAMET, the European Association of National Metrology Institutes.

GRACE research consortium an IEC/TC 113. Concerning the scientific and experimental work that backed the standards development, it is worth mentioning that the liaison between IEC/TC 113 and GRACE consortium did not restrict the publication of scientific results. In fact, within the GRACE project time span, two good practice guides [9, 10] and several papers about characterisation of graphene (e.g. [11, 12]) were published as open source documents by the GRACE consortium.

In the following and at the conference, the new standards IEC TS 62607-6-7:2023 (in-line four point probe method) [6] and IEC TS 62607-6-8:2023 (van der Pauw method) [7] will be presented and their technical background discussed.

II. GRAPHENE KEY CONTROL CHARACTERISTICS

A key control characteristic (KCC) is a property of a material or an intermediate product that can affect the safety or the compliance with regulations, performance, quality, reliability or subsequent processing of the final product. Graphene related KCC include mechanical (elastic modulus), electrical (carrier density, carrier mobility, sheet resistance), chemical (metallic impurity content) and biological (skin sensitisation) ones. KCC may or may not already have been assigned a corresponding standard for their measurement. Some basic KCC are considered mandatory by IEC for all types of graphene and related material. For example, the indication of the availability of the safety documentation (MSDS data) or the manufacturing method. On the other hand, different forms of graphene may require different subsets of KCC to be defined. In the case of chemically exfoliated graphene oxide dispersion, the KCC Carbon-Oxygen ratio (C/O) is considered relevant (it shall be characterised following the standard IEC TS 62607-06-21:2022 [13] wherever needed). The same does not hold for chemical vapour deposited monolayer graphene, for which the KCC sheet resistance (R_S) is relevant instead; CVD graphene shall be characterised following available standards of the series IEC 62607-06-xx , e.g. IEC TS 62607-06-23 (Hall bar method) or the recently published IEC TS 62607-06-8 (van der Pauw method).

III. IEC STANDARDS DEVELOPMENT PROCESS

The development of the standards IEC TS 62607-6-7 and IEC TS 62607-6-8 followed the IEC workflow (see Sec. 2.1.3.1. in [14]). The main development stages are summarized in Fig. 1, the document types abbreviations are reported in the BOX 2. The process starts at the *preliminary* stage, with a standardisation topic of potential interest presented by either a TC member or an invited external expert. The topic eventually becomes a Preliminary Work Item (PWI) and is discussed at TC level within the *proposal* stage. If approved, the PWI becomes a New Work Item Proposal (PNW) which is then assigned a project leader (usually the author of the proposal itself); a project team (PT) is also formed on the basis of voluntary participation of other TC members. The PT works on a first working draft (WD) of the technical specification. When the WD prepared at PT level is considered mature enough, the technical discussion proceeds, at TC level, during the *committee stage* by iterative editing of the committee draft (CD) versions of the standard. During the technical discussion, the PT meet periodically, resolving the TC comments to the CD, eventually adding experimental and theoretical elements to bolster the document; the *committee* stage may take several iterations before the document is considered ready for the *approval* stage, where Draft Technical Specification (DTS) is considered in terms of technical contents (a DTS may also be returned to the CD stage for solving technical flaws). Once the technical discussion is concluded, two cases may occur. For Technical Specifications (lower level of consensus required) the DTS is approved for *publication* (APUB); at a higher level of consensus (required for International Standards) the DTS is approved as Committee Draft for Vote (CDV) and later, if the vote is positive, as Final Draft International Standard (FDIS) which enters the *publication* stage. Editorial and copyright revision is made on APUB documents, prior the publication as IEC documents. Each IEC standard is assigned a stability date, within which the document can be confirmed, revised, or withdrawn.

BOX 2 - Abbreviations

TS Technical Specification;

IS International Standard;

PWI Preliminary Work Item;

PNW New Work Item Proposal.;

WD Working Draft;

CD Committee Draft;

DTS Draft Technical Specification (TS);

CDV Committee Draft for Vote (IS);

FDIS Final Draft International Standard (IS);

APUB Approved For Publication;

IEC Published standard;

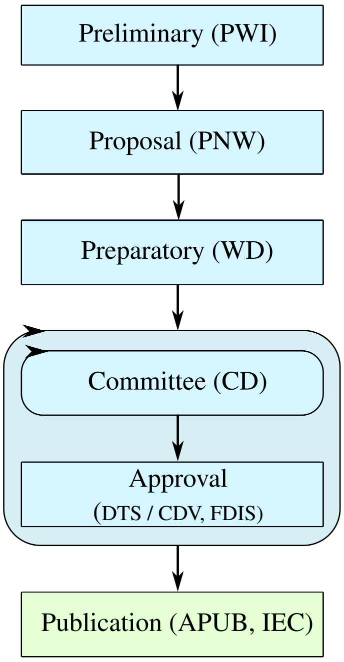

Fig. 1. Stages for the development of IEC standards. Abbreviations are defined in BOX 2. The circulating arrows enclosing "Committee" and "Approval" represent stages where iterative discussion and revision typically occur.

IV. NEW IEC STANDARDS FOR GRAPHENE SHEET RESISTANCE

CVD graphene is of particular interest for the development of new graphene based electronics, electrotechnical products, integration in established fabrication processes and sensors. Concerning this type of graphene, the new standards IEC TS 62607-6-7 [6] and IEC TS 62607-6-8 [7], describe standardized measurement protocols for the assessment of graphene's KCC sheet resistance R_S by means of contact methods, respectively the four in-line probe (4PP, [15]) and the van der Pauw methods (vdP, [16]) and represent complementary standards to others of the same series describing non-contact methods (e.g. [5]). The sheet resistance, R_S, is a quantity which can be used as global measure of the local conductivity of a sample with finite geometrical dimensions. In order to check the repeatability of the electrical properties of graphene, R_S is considered a KCC for monolayer CVD graphene. IEC standards TS 62607-6-7 and TS 62607-6-8 explain how to apply standardized methods on large area (mm^2 to cm^2) CVD graphene on rigid insulating support and how to perform a reliable estimation of the sample R_S and the measurement uncertainty, also considering the non-ideal nature of large-area commercial graphene. These two standards give instructions about i) how to prepare and store samples, ii) the required instrumentation specifications, iii) the ambient conditions within which the measurements shall be performed, iv) the standardized procedure to follow to perform the measurements, and v) the interpretation and reporting of the results.

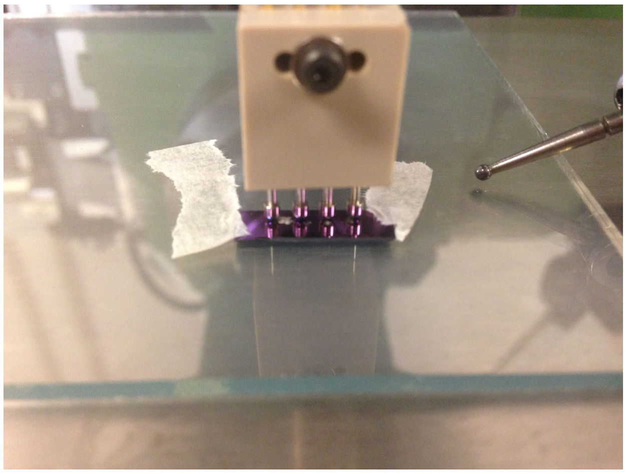

Fig. 2. A graphene sample is standing on an insulating glass slab placed on the balance plate. The test probe is in contact on the sample, while the lever indicator is placed in contact with the glass slab to measure the balance plate vertical displacement.

V. EXAMPLE OF SCIENTIFIC BACKGROUND PROVIDED TO THE PRESENTED STANDARDS

An example of scientific evidence provided IEC/TC 113 for the IEC TS here considered is given in the following. Here is briefly described one of a series of experiments performed during the TS development process, aimed to check the quality and the effect of purely mechanical electrical contacts on CVD graphene to perform multi-terminal electrical measurements. The use of this type of contacts was desirable to avoid any additional fabrication process that would certainly alter the pristine material conditions. To this aim, a custom probe provided of four equally spaced spring-loaded tips with round head profile was used to perform four terminal resistance measurements. The setup also included a digital balance (Sartorius LP8200S) a lever indicator (Mitutoyo 513-404), a 3-axis moving tool and position indicator (Anilam SENC 125 linear transducers, Anilam Wizzard 411 visualizer). An HP 34401 was used in 4-wire (4W) configuration to perform resistance measurements R_{4W} (from which R_S can be calculated). 4W resistance is measured by applying current through the outermost tips of the test probe and measuring the voltage drop between the two innermost tips. The probe standing on the graphene sample, the lever indicator and the balance plate are shown in Fig. 2. The sample was cut from a 4 inches wafer of commercial CVD graphene on Silicon (Pi-Kem Ltd., UK). The wafer was Boron-doped Silicon with thermal oxide coating, with graphene placed on the polished side of the wafer. The tests were performed to

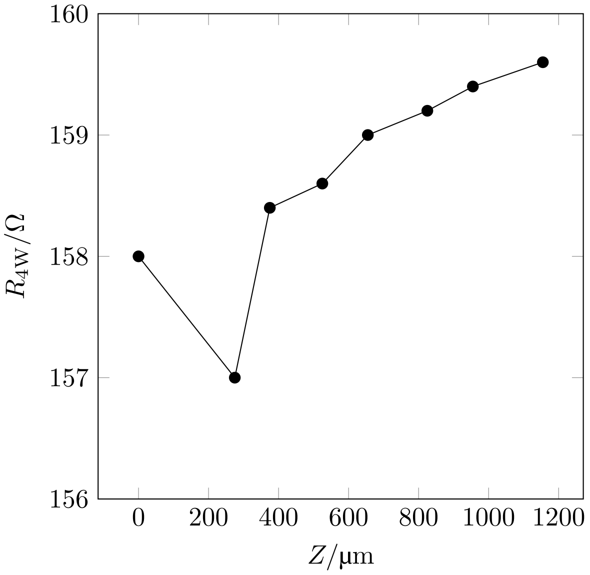

Fig. 3. 4-wire resistance measurements R_{4W} performed on the graphene sample. Error bars representing the type B uncertainty are not shown because negligible in comparison with the vertical axis range. The maximum Z for the used tips is $2.5\,\mathrm{mm}$.

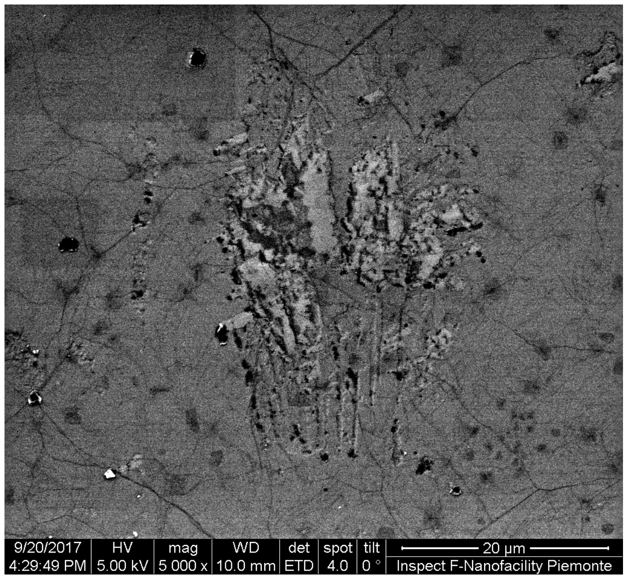

Fig. 4. SEM micrograph of one of the landing spots of the test probe tips on the graphene sample. Graphene grain boundaries and multi-layer seeds are visible as darker profiles and spots. In the center, a footprint of the probe tip is visible. Sign of shear displacement of the tip is visible in the lower part of the footprint. Lighter gray represents areas where graphene was scratched away for the support and Silicon thermal oxide appears.

check the stability and repeatability of the contacts, measuring both the probe spring displacement Z and the resulting weight, while measuring the electrical resistance. The net displacement Z of the tips springs was calculated by subtracting the displacement of the balance plate to the total probe displacement measured by the moving tool. The total applied weight to the sample (proportional to the spring force) was measured by means of the weighting scale placed under the glass slab supporting the sample. The 4W resistance R_{4W} was measured at 8 different spring Z, in the range $0\,\mu m$ to $1155\,\mu m$ (where the position $0\,\mu m$ corresponds to the probe making electrical contact with the graphene) to check whether the applied force influenced the contact quality, and to assess the damage induced by the probe on the graphene layer. The 4W resistance measured placing the probe at the center of the sample was $R_{4W} = 158.65\,\Omega \pm 0.85\,\Omega$. The type B uncertainty calculated from the measuring instrument's specifications was of the order of $0.05\,\Omega$. The small standard deviation of the measurements suggests that the effect of the spring displacement was not critical. Results of this measurements are reported in Fig. 3. The plot shows the larger change in R_{4W} occurring at small Z, up to about $300\,\mu m$, reasonably because the contact is still weak, then the readings stabilize with a slight increment up to the larger considered Z.

After the electric measurements, SEM micrographs were acquired to assess the damage produced by landing the test probe on the sample. The footprint of one of the tips, after reaching the maximum Z is shown in Fig. 4. The scratched area is about $20\,\mu m \times 20\,\mu m$, which is reasonably of the order of the round tip footprint itself. Moreover, at least two different types of damage can be observed: i) areas where graphene was pealed away, in the center of the landing spot (insulating thermal Silicon oxide appears brighter in SEM micrographs), and ii) a few linear shear scratches, at the bottom of the spot probably due to lateral movement of the probe tip. The R_{4W} increment in plot of Fig. 3 could be ascribed to the increasing damage produced by the unavoidable lateral displacement of the probe. This and other similar tests (e.g. repeatability of the contacts by raising and landing repeatedly the probe on the same spots) suggested that mechanical contacting on monolayer graphene sheets on rigid supports was a viable method to be used in standardized protocols, also considered that commercial test probes already available on the market could be directly employed for the task by most laboratories.

VI. CONCLUSION

The laboratory exploration of new concepts based on original ideas is absolutely valuable for the scientific progress, nevertheless, standardization is fundamental to bring scientific advances into production. The presented new standards IEC TS 62607-6-7 and IEC TS 62607-6-8 for the electrical characterisation of CVD graphene can contribute to the establishment of shared good practices and standardized measurement protocols respectively in research labs and industry.

VII. ACKNOWLEDGEMENTS

The work has been done within the Joint Resarch Project EMPIR 16NRM01 GRACE – Developing electrical characterisation methods for future graphene electronics. This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

VIII. *

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Electric field effect in atomically thin carbon films, Science 306 (5696) (2004) 666–669.

[2] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, et al., Large-area synthesis of high-quality and uniform graphene films on copper foils, Science 324 (5932) (2009) 1312–1314.

[3] P. Bøggild, Research on scalable graphene faces a reproducibility gap, Nature Communications 14 (1) (2023) 1126.

[4] L. Callegaro, C. Cassiago, A. Cultrera, V. D'Elia, D. Serazio, M. Ortolano, M. Marzano, O. Kazakova, C. Melios, F. Raso, et al., Grace: Developing electrical characterisation methods for future graphene electronics, in: 2018 Conference on Precision Electromagnetic Measurements (CPEM 2018), IEEE, 2018, pp. 1–2.

[5] IEC, Geneve, Switzerland, IEC TS 62607-6-10:2021, Nanomanufacturing - Key control characteristics - Part 6-10: Graphene - Sheet resistance: Terahertz time-domain spectroscopy.

[6] IEC, Geneve, Switzerland, IEC TS 62607-6-7:2023, Nanomanufacturing - Key control characteristics - Part 6-7: Graphene - Sheet resistance: van der Pauw method.

[7] IEC, Geneve, Switzerland, IEC TS 62607-6-8:2023, Nanomanufacturing - Key control characteristics - Part 6-8: Graphene - Sheet resistance: in-line four-point probe.

[8] IEC, Geneve, Switzerland, IEC TS 62607-6-25, Nanomanufacturing - Key control characteristics - Part 6-25: Two-dimensional materials - Variation of doping concentration: Kelvin probe force microscopy.

[9] A. Cultrera, A. Fabricius, A. Catanzaro, L. Callegaro, Good Practice Guide on the electrical characterisation of graphene using contact methods, Accepted by EURAMET as deliverable for 16NRM01 EMPIR GRACE, https://arxiv.org/abs/2007.13348, 2020.

[10] A. Catanzaro, A. Fabricius, A. Cultrera, O. Kazakova, Good Practice Guide on the electrical characterisation of graphene using non-contact and high-throughput methods, Accepted by EURAMET as deliverable for 16NRM01 EMPIR GRACE, https://arxiv.org/abs/2007.14047, 2020.

[11] A. Cultrera, D. Serazio, A. Zurutuza, A. Centeno, O. Txoperena, D. Etayo, A. Cordon, A. Redo-Sanchez, I. Arnedo, M. Ortolano, et al., Mapping the conductivity of graphene with Electrical Resistance Tomography, Scientific Reports 9 (1) (2019) 10655.

[12] C. Melios, N. Huang, L. Callegaro, A. Centeno, A. Cultrera, A. Cordon, V. Panchal, I. Arnedo, A. Redo-Sanchez, D. Etayo, et al., Towards standardisation of contact and contactless electrical measurements of CVD graphene at the macro-, micro-and nano-scale, Scientific Reports 10 (1) (2020) 3223.

[13] IEC, Geneve, Switzerland, IEC TS 62607-6-21:2020, Nanomanufacturing - Key control characteristics - Part 6-21: Graphene - Elemental composition, C/O ratio: X-ray photoelectron spectroscopy.

[14] IEC, Geneve, Switzerland, ISO/IEC Directives part 1, Procedures for technical work, 2022.

[15] F. Smits, Measurement of sheet resistivities with the four-point probe, Bell System Technical Journal 37 (3) (1958) 711–718.

[16] L. J. van der Pauw, A method of measuring the resistivity and hall coefficient on lamellae of arbitrary shape, Philips Technical Review 20 (1958) 220–224.