Publishable Summary for 16NRM01 GRACE
Developing electrical characterisation methods for future graphene electronics

Overview

The overall goals of this project were 1) the development of validated protocols, to be used in the production of Good Practice Guides (GPGs), for the measurement of the electrical properties of graphene, and their implementation in order to achieve accurate and fast-throughput measurement of graphene; and 2) collaboration with international standardisation committees in order to initiate and develop dedicated documentary standards for the electrical characterisation of graphene. The project contributed towards the development of five standards from the technical committee IEC/TC113. Two of these were directly initiated by the project. Furthermore, the adoption of GPGs developed in the project and, subsequently, of such standards, has enabled industry to perform accurate measurements of the electrical properties of graphene and thereby provide customers with reliable and comparable specifications of graphene as an industrial product.

Need

Discovered in 2004, graphene, is a two-dimensional (2D) lattice of carbon atoms and is currently being extensively investigated by industry as a potential new material for electronics. However, the adoption of graphene as an electronic industrial product is limited by the inability to grow large areas of high-quality graphene with uniform and reproducible electric and electronic properties. Therefore, accurate and reproducible characterisation methods adapted to the 2D nature of graphene, both as test samples and in production lines, are crucial. But such electrical characterisation methods for graphene are presently underdeveloped; and guidelines for the proper implementation of such methods in an industrial environment are lacking. The issue has been highlighted by standard organisations such as the International Electrotechnical Commission (IEC) and the European Committee for Electrotechnical Standardisation (CENELEC), who have initiated working groups e.g. IEC/TC113 Nanotechnology for Electrotechnical products and systems. However, it is currently unclear how different approaches particularly high-throughput methods such as microwave resonant cavity methods and time-domain terahertz (THz) waves spectroscopy can be compared and mutually validated. Therefore, the European Committee for Standardisation and Electrotechnical Standardisation CEN/CENELEC has recognised, in a recent Standardisation, Innovation and Research (STAIR) survey, the need to initiate a metrology project at the European level on the issue of the characterisation of graphene and 2D atomic materials for electrical applications.

Objectives

The project aimed to develop traceable and comparable electrical characterisation methods for the electrical properties of graphene, including accurate and fast-throughput measurements. In addition, the project focussed on facilitating the uptake of such methods by standardisation bodies such as IEC/TC113. The project's specific objectives were:

1. To develop an accurate and traceable approach for the electrical characterisation of graphene through the development and comparison of different methodologies for both contact measurement and non-contact electrical measurement of its properties, with traceability to the electrical SI units. This will include the improvement of established techniques as well as the development of new methods.
2. To develop a high-throughput approach for the electrical characterisation of graphene, with the development of novel methodologies for non-contact electrical characterisations and their validation with established techniques.
3. To disseminate the metrology and methodologies established in this project in the form of Good Practice Guides (GPGs) and input to documentary standards.

4. To contribute to the standards development work of the technical committee IEC/TC113, through the initiation of and development of new written standards for the electrical characterisation of graphene based on the GPGs developed within the project.

Progress beyond the state of the art

Methods for electrical characterisations of graphene include contact methods (e.g. in-line four contact resistivity probes, S-parameter measurements on CoPlanar Waveguide (CPW) van der Pauw methods); as well as non-contact measurements (e.g. scanning probe microscopies (SPM),Scanning Kelvin Probe Microscopy (SKPM) and Scanning Capacitance Microscopy (SCM), microwave resonant cavity methods and time-domain THz waves spectroscopy). However, many of these methods pose problems in their practical application to an atomically thin material such as graphene, in terms of the verification of the underlying assumptions, traceability to the SI, and the expression of the measurement uncertainty. In particular, non-contact methods, which are suitable for high-speed characterisations in an industrial environment, are not well developed and require additional validation compared to more established contact methods. Prior to the start of the project, no inter-laboratory studies had been performed on graphene, in terms of comparing the measurements from different methods for a single property. Therefore, the uncertainty, accuracy and reliability of the measurements using either method was unknown.

During its lifetime, the project has made considerable efforts in progressing beyond the state of art. Implementation of both contact and non-contact/high-throughput methods have been designed and developed by the project partners. Furthermore, extensive validation of the methods has been carried out by providing traceability to the SI for contact methods. Internal and mutual comparisons have been used for this and they have demonstrated a good compatibility. Overall, a thorough validation has been achieved through the inter-laboratory comparison, also methods such as; vdP in controlled conditions; enabled the determination of the effects of environmental conditions during storage and in-measurement. For methods providing a spatial resolution, a direct comparison of the electrical conductivity maps was carried out. The outcomes of these investigations have been reported in detail in a dedicated measurement protocols, through peer-reviewed publications, and two Good Practice Guides.

Results

1. *To develop an accurate and traceable approach for the electrical characterisation of graphene through the development and comparison of different methodologies for both contact measurement and non-contact electrical measurement of its properties, with traceability to the electrical SI units.*

Inital set of 45 diced samples on quartz were distributed to partners. Both contact and non-contact measurement techniques for conductivity, mobility and carrier concentration were been performed, under different evironmental conditions. Methods included confocal optical microscopy and Raman spectroscopy to assess the uniformity of the structural properties of the samples; van der Pauw measurements were used to assess conductivity, mobility and carrier density, and SKPM, was used (in air and under vacuum), to assess the dependence of the measurement outcome on the environmental conditions. The Electrical Resistance Tomography (ERT) technique was applied during graphene characterisation for the first time. It was also used to obtain spatially resolved conductivity maps with a contact, traceable method. Then, the outcome of the measurements and the performance of the different measurement systems were compared.

For the van der Pauw and ERT measurements comparison, the sensitivity functions of van der Pauw were considered. Results indicated good agreement of the average sample conductivities, taking into account the measurement uncertainty and the significant dependence of the electrical parameters on the environmental conditions. When using a reference material (pyrolitic graphite) for appropriate calibration; the SKPM method provided the highest spatial resolution. All in all there was good agreement with the van der Pauw measurements in the same environmental conditions. Additonally, characterisation with closed microwave resonant cavity had been carried out on different types of graphene (e.g. CVD on Quartz and epitaxial on SiC). Optimised coplanar waveguides for microwave measurements have also been designed. This objective was fully met.

2. *To develop a high-throughput approach for the electrical characterisation of graphene, with the development of novel methodologies for non-contact electrical characterisations and their validation with established techniques.*

The samples from Objective 1 have been measured with THz spectroscopy as a high-throughput method. The measurement outcomes were compared with those obtained from traceable methods, in particular van der Pauw and ERT. The results of this comparison have shown to be in good agreement. In particular, the comparison between THz and van der Pauw, provided that a proper THz map average with sensitivity functions of the vdP is performed, shows a good match between average sample conductivities. The comparison between THz and ERT showed, in addition to the average sample conductivities, a very good correlation between the spatial distribution of the conductivity. THz spectroscopy and van der Pauw measurements were also performed on entire graphene/Quartz 4-inch wafers at different steps of the graphene transfer process to assess the effect of the transfer polymer on conductivity. Furthermore, THz spectroscopy was applied, and compared with the van der Pauw method, to graphene/PEN and graphene/PET samples cut from 4" wafers. A subset of graphene samples was also characterised with an open inverted microwave resonant cavity, suitable for measurements on large-area samples and a high-throughput characterisation with movable motorised sample holder. Lastly, the measurement outcomes from all methods were collected in an international comparison report. The different measurand definitions related to the different methods required careful consideration during the data treatment, when considering the concept of "average" conductivity. The compatibility of the results thus validates the measurement protocols related to novel methodologies. Therefore, this objective was fully met.

3. *To disseminate the metrology and methodologies established in this project in the form of GPGs and input to documentary standards.*

The measurements performed in Objectives 1 and 2 were documented as measurement protocols, from which two GPGs were written and mutually reviewed by the project partners. Both published on the project's website and submitted to IEC/TC 113. The technical committee acknowledged the documents as valid inputs to new documentary standards. In addtion, the GPGs were then distributed to the stakeholder committee and advertised by IEC on their social media channels. This objectieve was fully met.

4. *To contribute to the standards development work of the technical committees of IEC/TC113 and CENELEC WS SGRM, through the initiation of and development of new written standards for the electrical characterisation of graphene based on the GPGs developed within the project.*

This objective was fully met. Outside of the project, the CENELEC WS was disbanded and all standardisation activities were transferred to IEC. This was done to ensure consistency of standards and to prevent the same topics being addressed by both organisations. Thereafter, the GRACE consortium established a strong connection with IEC/TC 113 by means of a C-liaison. The Category C liaison organisations have the right to participate as full members in an IEC working group or project team so experts from this liaison can act as the official representative of an organisation. This enabled GRACE consortium members to become project leaders in the IEC TC 113 WG8 (Graphene related materials) which gave them, access to a shared platform with the other IEC experts which was utilised to raise awareness of and provide regular updates on the project's progress. Subsequently, IEC/TC 113 acknowledged the project's outputs in a detailed report submitted to EURAMET-MSU. During its lifetime, the project directly supported the following five standards in the IEC/TC 113 work programme:

- 62607-06-04: Nanomanufacturing - Key control characteristics - Part 6-4: Graphene - Surface conductance measurement using resonant cavity (Development of Ed. 2.0)
- 62607-06-07: Nanomanufacturing – Key control characteristics – Part 6-7: Graphene material – Sheet resistance: van der Pauw method (New Project)
- 62607-06-08: Nanomanufacturing – Key control characteristics – Part 6-8: Graphene material – Sheet resistance: In-line four-point probe (New Project)
- 62607-06-10: Nanomanufacturing – Key control characteristics – Part 10: Graphene film – Sheet resistance: Terahertz time-domain spectroscopy (New Draft towards Ed. 1.0)
- 62607-06-25: Nanomanufacturing – Key control characteristics – Part 6-25: Two-dimensional materials – Doping concentration: Kelvin Probe Force Microscopy (Technical input).

The GRACE Good Practice Guides were also distributed within the IEC/TC 113 and will be discussed further at the next meeting of IEC/TC 113 in October 2020.

Impact

The project has prepared 12 open access peer-reviewed papers (10 have been published and 2 have been submitted to journals for publication. The scientific outcomes of the project have also been presented at 27 conferences and events, giving focus to the status of graphene standardisation and its contribution to the commercialisation. Key events have included: 9th annual Recent Progress in Graphene and Two-dimensional Materials Research Conference (RPGR2017), Graphene2018, GraphChina 2018 and 2019, the 15th International Conference on Nanosciences & Nanotechnologies, CPEM 2018, Graphene Week 2018 and

2019, E-MRS 2020 and various other conferences and workshops. Substantial scientific outreach was also delivered to the general public through mainstream media.

Impact on industrial and other user communities

The project stakeholder committee consisted of 12 members from 7 countries. The inaugural meeting of the stakeholder committee took place during the mid-term meeting of the project which was organised in concomitance of the Graphene Week conference, 10-14 September 2018 in San Sebastian, Spain. A second stakeholder meeting was held on May 2019 in Madrid, Spain. In addition, a “industry friendly workshop” was held on September 2019 in Helsinki, Finland within the Graphene Week and at the Graphene Industrial Forum 2020.

The GPGs produced during the project, will help industrial end users in the practical implementation of different methods for the electrical characterisations of graphene and as part of the project’s research such methods will be tested under industrial environmental conditions. The GPGs content has been presented to the stakeholder community at the stakeholders' events above listed. In order to incorporate the needs of industrial end users, input from the project’s stakeholders committee was taken into account during the drafting process.

Several companies have expressed interest in the exploitation of the techniques developed in the project. LG Electronics Inc.- Materials & Production engineering Research Institute and the National Institute for Standards and Technology (NIST) are already using the project’s Conductivity mapping by Electrical Resistance Tomography facility for the characterisation of CVD and epitaxial graphene samples (respectively).

Impact on the metrology and scientific communities

The project’s GPGs were based on the measurement protocols developed by the consortium. These protocols include descriptions that can enable scientific users to understand and implement the electrical characterisation methods, and explain how to express a measurement uncertainty, check the assumptions underpinning the method, and validate it. The content of these protocols has been disseminated by presentations at scientific workshops and conferences, and during the project mid-term meeting and the stakeholder meetings. Two major training events were organised by the consortium in connection with international meetings and conferences: a "Joint Workshop of IEC/TC 113 and EMPIR project 16NRM01 GRACE on the electrical characterisation of graphene - Meeting for stakeholders" (Madrid, May 2019), and the workshop "GRACE — Methods for the Electrical Characterisation of Graphene" (Helsinki, Sept. 2019).

Furthermore, the project partners addressed the issues related to the comparability of results achieved with different measurement methods for the electrical characterisation of graphene. An interlaboratory comparison study confirmed the reliability of the implementation of the different methods for the electrical properties of graphene measurement, in particular for non-contact and high-throughput methods.

Impact on relevant standards

At the IEC/TC113 committee meeting held on November 2017 in Shenzhen, China, the project was presented to the working group dedicated to graphene. IEC/TC113 has accepted from the consortium the drafts of four potential new technical specifications, that are now at various stages of consideration and approval by the Committee. Additionally, project consortium provided regular updates on the project’s progress; in particular on the drafting process of the validated measurement protocol; at relevant IEC/TC 113 meetings. A further discussion of the inputs provided by GRACE will take place at the next IEC/TC 113 meeting planned for October 2020. Also, presentations of the project and its results were given to the EURAMET Technical Committee on Electricity and Magnetism (TC-EM).

Longer-term economic, social and environmental impacts

In the longer term, the project outcomes will contribute to legislation related to graphene and its specifications as an industrial product, at the European level. The high-throughput methods developed in the project; will lead to improved industrial characterisation, quality and efficiency; which will have an impact on the whole graphene supply chain, from producers to end-users. The development of enhanced products based on graphene will also have a positive impact on energy efficiency of lighting and electrical energy storage. Furthermore, applications of graphene are predicted to be viable for healthcare monitoring; the potential toxicity of graphene-based products is closely related to their long-term stability, that could be monitored with the methods developed in this project.

List of Publications

[1]. Melios, Christos, et al. "Detection of Ultralow Concentration NO_2 in Complex Environment Using Epitaxial Graphene Sensors." *ACS sensors* 3.9 (2018): 1666-1674. https://doi.org/10.1021/acssensors.8b00364; https://arxiv.org/abs/1808.09776

[2]. Whelan, Patrick R., et al. "Electrical Homogeneity Mapping of Epitaxial Graphene on Silicon Carbide." *ACS applied materials & interfaces* 10.37 (2018): 31641-31647. https://pubs.acs.org/doi/10.1021/acsami.8b11428

[3]. Melios, Christos, et al. "Water on graphene: review of recent progress." *2D Materials* 5.2 (2018): 022001. https://arxiv.org/abs/1804.09518; https://arxiv.org/abs/1804.09518

[4]. Panchal, Vishal, et al. "Confocal laser scanning microscopy for rapid optical characterization of graphene." *Communications Physics* 1.1 (2018): 83. https://www.nature.com/articles/s42005-018-0084-6

[5]. Cultrera, Alessandro et al. "Mapping the conductivity of graphene with Electrical Resistance Tomography." Scientific Reports 9 .1 (2019), 10655. https://doi.org/10.1038/s41598-019-46713-8

[6]. Marzano, Martina et al. "A correlation noise spectrometer for flicker noise measurement in graphene samples." Measurement Science and Technology 30.3 (2019). https://doi.org/10.1088/1361-6501/aafcab

[7]. Melios, Christos et al., "Towards standardisation of contact and contactless electrical measurements of CVD graphene at the macro-, micro- and nano-scale," Scientific Reports, 10, 3223 (2020) https://doi.org/10.1038/s41598-020-59851-1

[8]. Fabricius, Alexandra, Catanzaro, Alessandro and Cultrera, Alessandro (Ed.), "Electrical characterisation of graphene using contact methods", (2020), ISBN: 978-88-945324-0-1. https://iris.inrim.it/handle/11696/63312; https://arxiv.org/abs/2007.13348

[9]. Fabricius, Alexandra, Cultrera, Alessandro, and Catanzaro, Alessandro(Ed.), "Electrical characterisation of graphene using non-contact and high-throughput methods", (2020), ISBN: 978-88-945324-2-5. https://iris.inrim.it/handle/11696/63314; https://arxiv.org/abs/2007.14047

[10]. Cultrera, Alessandro and Callegaro, Luca, "A Simple algorithm to find the L-curve corner in the regularisation of ill-posed inverse problems", IOP SciNotes, 1, 025004 (2020) https://doi.org/10.1088/2633-1357/abad0d

Project start date and duration:	1st July 2017, 36 months	
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Internal Funded Partners: 1 INRIM, Italy 2 CEM, Spain 3 NPL, UK	External Funded Partners: 4 das-Nano, Spain 5 Graphenea, Spain 6 ISC, Germany 7 UoM, UK 8 VDE, Germany	Unfunded Partners:
RMG: -		