GraphOhm

Final Publishable JRP Summary for SIB51 GraphOhm
Quantum resistance metrology based on graphene

Overview

The units of electricity play a key role in industrial, scientific and technological applications since the measurement of nearly all other quantities relies on them at some point. Electrical resistance is traced to the quantum standard using the quantum Hall effect (QHE, a quantum electronic effect that allows accurate realisation of Planck's constant and elementary charge). This project developed a QHE system using accurate and simple to use standards of electrical resistance based on graphene. Graphene, the two-dimensional crystal of carbon, has many extraordinary properties and characteristics which surpass those of other materials. This project paves the way to a robust, simpler to operate and cheaper, yet precise system for electrical measurements. This will benefit all NMIs, measurement services in Europe, and all industries relying on their service.

Need for the project

While quantum electrical voltage standards are widespread and easily transported, the same cannot be said for quantum resistance standards. The primary quantum resistance standards are only available at national measurement institutes (NMIs) and the resulting calibrations lose precision at every link of their long chain, which leads to a loss of time and money due to periodic recalibrations of secondary standards. Graphene exhibits the QHE at lower magnetic fields and closer to room temperature than any other material. The material could therefore help create simple and portable 'bench-top' systems which could be deployed more widely and easily than current resistance standards, including into industry. This would reduce the cost and inconvenience of the calibration chain.

The need for a better quantum resistance standard has been triggered by the fact that users of metrological services, and NMIs, cannot take direct advantage of the perfect quantum standards. Up until now the equipment needed for exploiting the QHE is very specialised and expensive and requires highly experienced staff.

A QHE system which is simpler, transportable, and provides the primary reference closer to the end user will reduce the cost and inconveniences of traditional calibration chains, constituting a real breakthrough for European and worldwide metrology. For the QHE there is now an opportunity to create such a system using graphene and widely available laboratory equipment, such as simple cryo-coolers and liquid helium dewars.

This system, when combined with compact superconducting magnets instead of large scale difficult to operate systems, would fulfil the main requirements of simplicity and transportability. Their reduced cost and complexity will allow their deployment more widely as a bench top system - into smaller NMIs, into industry, or allowing a dedicated QHE reference at the point of use.

This project addresses the improvement of the material, of methods for its reliable characterisation, the testing of the precision limits with respect to temperature, magnetic field and measurement current, as well as the development of dedicated simplified measurement equipment.

Scientific and technical objectives

In order to investigate and produce a graphene QHE resistance standard, and simplify the resistance traceability chain, the objectives were:

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European Metrology Research Programme
Programme of EURAMET

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- **Advanced fabrication methods for graphene materials and of QHE devices** to fulfil requirements in terms of homogeneity, contact resistance, size. The goal is fabrication of graphene material and devices with optimised parameters, which are stable under typical usage conditions involving repeated cool-down cycles.

  Before the project, fabrication of graphene films and of graphene devices which meet the extreme quality requirements for a QHE application had been achieved only in two research labs. The yield of production was low, just sufficient for obtaining first research results.

- **Develop procedures for precise, quantitative, non-destructive characterisation** of graphene and graphene devices combining structural, chemical and physical methods.

  The potential of graphene and its properties mean that these first two objectives have impact far beyond the scope addressed by this project.

- **Explore and understand the limits of achievable uncertainty** by precision QHE measurements on graphene under less demanding experimental requirements of temperature and magnetic field.

  This objective addresses the key challenge of the project.

- **Assess the potential of a graphene-based impedance standard** by investigating ac-losses in graphene devices and demonstrate the QHE effect at ac frequencies in graphene.

  This objective constitutes a feasibility study for an extended QHE application at ac frequencies which addresses a possible quantum standard of impedance. Impedance, and specifically capacitance, is nearly as important a quantity as resistance in industrial and technological applications.

- **Develop customised cooling and measurement instrumentation** to support the simplified use of a graphene resistance standard. This includes a non-cryogenic measurement bridge with performance similar to that of a cryogenic one.

Results

Advance fabrication methods for graphene materials and of QHE devices

The methods to grow graphene to enable it to be optimally suited for a use as a QHE device were considerably advanced in the project. One achievement is the avoidance of stripes or patches of double layer graphene which act as electrical shorts and render the material unsuitable for QHE application. They are created during the heating phase when the silicon carbide (SiC) host crystal is brought to the required 1600 – 1800 °C range where the volatile silicon atoms evaporate and leave carbon atoms behind which convert into graphene. The project found that the counterintuitive method of offering additional carbon before heating prevented the additional uncontrolled double layer growth. A European patent has been issued for this method. Another achievement is the growth of SiC-graphene on a full wafer instead of mm-sized chips as before. This opens more opportunities for the fabrication of large arrays of QHE-devices which can be used for realising a whole range of resistance values. A variant of the established SiC-graphene growth was developed in a collaborating institute and has the potential to yield material of excellent quality. Finally, the issue of having too many electrons in the graphene layer was addressed by developing a method to compensate for the electronic charge by depositing ions in a resist layer covering the graphene film.

In summary, the fabrication methods have been advanced to a stage where it is now possible to grow graphene reliably and with excellent yield, avoiding or minimising the limitations previously encountered with graphene as a material for resistance standards.

Develop procedures for precise, quantitative, non-destructive characterisation

Any successful thin-film fabrication requires reliable and, ideally quick, characterisation methods to inform device making and growth. In the project, several such methods were developed or adapted for the specific needs of graphene device fabrication.

A microwave dielectric resonator system, including operating software, was designed and constructed. It enables a quick and contactless method for assessing the electrical transport properties of graphene samples. The system was designed to also be applicable to large scale and high quality graphene thin films. Using this setup, fast measurements of the sheet resistance of graphene samples were made and they greatly helped to optimise the growth processes.

Measurement results from various non-destructive scanning probe techniques (atomic force microscopy, scanning Kelvin probe microscopy) and scanning Raman spectroscopy, both with high lateral resolution, were demonstrated to be consistent with the large-scale microwave measurements. This is indispensable for a reliable characterisation on the micro-scale. To quickly assess the detrimental double-layer coverage of SiC graphene, a very simple to use contrast enhanced (but otherwise conventional) optical method was invented, which helped in solving the above-mentioned double-layer issue.

In summary, more accurate, quantitive, non-destructive characterisation procedures were developed which not only have enabled progress in the graphene film fabrication within the project, but are valuable for the emerging graphene industry well beyond the project.

Explore and understand the limits of achievable uncertainty

The key goal of the project was pushing the limits for precision QHE resistance quantisation to lower magnetic fields, higher temperatures and higher operating currents which has been achieved. En route to this success several important scientific findings were made which further highlighted the advantageous properties of graphene. Firstly, the study of hot electron effects explained why graphene supports high operating currents without losing precision, as is the case for the conventional gallium arsenide (GaAs) - based QHE materials. Secondly, the additional carbon atom layer between graphene and its SiC substrate (the same layer that has the detrimental effect of generating too many electrons) also has a positive side: it provides an extremely wide magnetic field working range. And thirdly, one of the special growth modes developed in the project produces graphene with fewer preparation steps to adjust the number of electrons, and thus is advantageous for device fabrication.

In summary, within this project five NMIs (NPL, PTB, LNE, MIKES, and METAS) using graphene devices from four fabrication lines, demonstrated a precision of graphene quantised resistance standards which matches, and partly exceeds that of GaAs-based QHE devices. This was demonstrated in a simpler to achieve range of higher temperature, lower magnetic field, and electrical current. The achieved parameter combination of 5 Tesla field, 5 Kelvin temperature, and 50 microampere of current clearly surpasses the previous best GaAs performance of 10 Tesla, 1.5 Kelvin and 40 microampere.

Assess the potential of a graphene-based impedance standard

Impedance is another important electrical unit and capacitive sensors are widely used in numerous fields of industry, technology and science, including modern touch screen devices. Its realisation by a simple-to-use quantum standard would therefore be an important advance in electrical metrology. A quantum Hall device, when operated at a frequency of 1-2 kHz, provides a direct measurement chain to the fundamental constants of Planck's constant and electronic charge. Since the measurement system is nearly the same as that for resistance, laboratories would have the advantage of needing only one quantum system for realising both quantities.

As a feasibility study, and in order to test graphene in such a scenario, QHE devices were made and design rules were developed for assessing graphene's potential as an impedance standard. In view of the 16 years of development it took to establish GaAs materials as an impedance standard it was quite amazing to discover that graphene has advantages over GaAs also under these conditions. While all details are not yet fully understood, the advantages seem to stem from the fact that operation current densities (the important quantity, as it is the current per millimetre of device width) for graphene devices can be higher than for GaAs. Consequently, for a same absolute current a graphene device can be made smaller than its GaAs counterpart.

In summary, the feasibility study of graphene as a quantum standard of impedance was very successful. It demonstrated that the development of a graphene based quantum standard of capacitance is a viable option for the future.

Develop customised cooling and measurement instrumentation

The simplified graphene quantum standard of resistance developed in this project can only fully demonstrate its advantages when the peripheral electronic measurement system in which it is embedded is also simple, allowing the combination to be more practical than current options. Therefore, the two key electronic measurement system components required to compare in future calibration services the quantised resistance of the QHE device with user supplied artefacts were also improved in the project. For the key component “magnet and temperature system” this was achieved by demonstrating quantised Hall resistance in a small cryogen-free system independent of liquid Helium supply and operating at 4 K and below 5 Tesla, dispensing with big pumped liquid Helium cryostats with large superconducting solenoid. For the other component “precision measurement bridge” a room temperature-operated, low-frequency current comparator was developed and optimised. This dispenses with a liquid Helium operated resistance ratio bridge and its superconducting quantum interference device. Using both components, a laboratory will no longer need a supply of liquid Helium and a complex superconducting measurement bridge to operate a quantised resistance standard with high precision.

In summary, ‘peripheral electronic measurement systems’ were developed which allow an uncompromised and simple use of the new graphene quantum resistance standards.

Actual and potential impact

This project used materials science and improved measurement precision to build stable graphene devices that can operate in relaxed conditions of higher temperature and lower magnetic field, and can be used as quantum resistance standards for the electricity community.

Dissemination activities and stakeholder engagement

Project partners presented their results at 46 international conferences and seminars, eighteen of them with an audience of more than 100, and sixteen with more than 200 participants.

The biannual Conference on Precision Electromagnetic Measurements, CPEM, is the most influential forum for research and development activities in electrical and magnetic measurements. Twenty contributions from the project were presented at the 2014 and 2016 CPEM conferences.

A GraphOhm workshop was held in Prague for project partners and stakeholders. A training course was held on the use of graphene as a QHE resistance standard, which focused on the topics most important for the user community, such as preparation of devices, their conditioning and handling, and the best measurement instrument configuration.

The following guides and information for end users is available on the project homepage:

- Guidelines on the determination of the sensitivity and calibration of ratio error of the Room Temperature Current Comparator (RTCC)
- Report on precision measurements of a graphene QHR device with the room temperature current comparator
- Guide on realisation and operation of cryocooled QHR devices
- Video demonstrating the carrier density tuning of a graphene QHR device
- Best practice guide in metrological applications of electrical microscopy to carbon materials

Contribution to standards

As project collaborators, the acknowledgement and involvement of the *Bureau International des Poids et Mesures*, *BIPM*, was valuable in ensuring maximum impact in the worldwide measurement system.

This acknowledgement is reflected in the March 2015 News article of the Consultative Committee for Electricity and Magnetism, CCEM, which states that “*Significant progress on the quantum Hall effect with graphene samples … will lead to simpler and lower cost quantum resistance standards, and in consequence to their wider use.”*

In addition, the collaboration between BIPM and the project is highlighted in a September 2015 News article of BIPM. The article says that “*In the framework of the GraphOhm EURAMET project, samples developed in a collaboration between* [project partner] *VTT and Aalto University (Finland) were measured at the BIPM, and proved suitable for calibration use in the existing setup. … (BPIM) envisage(s) being able to implement a* *much simplified transportable system for on-site QHE comparisons (operating at 4 K temperature and 5 T field). The collaboration (with both* [project partners] *PTB and MIKES) also involved the investigation of a new generation of low frequency current comparators that could form the basis of room temperature resistance bridges to accompany the new graphene reference."*

The project results were presented and discussed during workshops of the BIPM Technical Committee of Electricity and Magnetism (TC-EM) meetings. The engineering task of converting the scientific project results into new (i.e. simpler to use and commercially available) standards will be a process on a longer timescale, but it has already started at NPL, VTT, PTB, RISE and CMI.

Early impact

The outputs of this project have been taken up by several industrial companies who are developing systems that utilise the benefits of the graphene technology developed during the project.

Among these companies are:

- UK based Oxford Instruments plc, collaborating with NPL, has produced a closed cycle cooler system adapted for graphene QHE measurements which is now available.
- Swedish based company GraphenSIC, linked to Linköping University, has produced a compact low-field magnet insert for Helium dewars, including a graphene QHE device, which is now available.
- Canada based company Measurement International, cooperating with the project consortium announced production and marketing of a dedicated graphene QHE resistance standard system.

Potential impact

The improved methods for characterising graphene films have already found their way into various laboratories (e.g. Swedish based company GraphenSiC, and Spanish company Graphenea) where graphene films are grown for research or for electronics applications. The ability to measure quantum electrical resistance and impedance precisely by the end user, with a reduced length calibration chain will save money and time for end users.

Parts of such systems, like dedicated cryo-coolers are available already. Knowledge transfer programmes in national or European funding schemes have the potential to lead to a complete and standalone commercial system within the next five years.

Another important potential impact relates to the redefinition of the kilogram, which will in the future 'New SI' be based on the Planck constant h. The connection to h in a so-called Kibble-balance requires use of the Josephson and Quantum Hall Effects, and therefore the simpler to use graphene-based resistance standard will have strong impact for those future primary mass standards, which operate at very low uncertainty.

The following two patent applications have been filed:

- Procedure for producing Graphene (filed by PTB, granted as European patent EP 3 106 432 A1)
- Single crystalline gCVD-graphene growth (filed by KRISS)

List of publications

List of publications can be accessed on the Final Publishable Report, on the EURAMET publication repository or on the project homepage.

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JRP start date and duration:	1 June 2013, 36 months
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