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

Background

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 units are traced to quantum standards of voltage and resistance, using the quantum Hall effect (QHE) for the latter. In this project a QHE system will be created which exploits unique properties of the material graphene, enabling a step-wise improvement in the dissemination of the quantum standard. This project paves the way to a robust, simpler to operate and cheaper, yet ultimately precise system for electrical measurements which will benefit all NMIs and measurement services in Europe, and all industries relying on their service.

Need for the project

The need for a better quantum resistance standard is triggered by the fact that for resistance no user of metrological services, and often not even National Metrology Institutes (NMIs), can take direct advantage from the perfect quantum standards: equipment needed for exploiting the QHE is very specialised and expensive and requires highly experienced staff. While quantum standards of voltage are widespread and easily transported, the same level of simplicity is not possible for quantum standards of resistance. Hence long chains of hierarchical calibrations are required, with the primary quantum reference only available in large NMIs. This leads to loss in precision at each chain link, and to loss of time and money due to periodic recalibrations of secondary standards.

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 quantum Hall effect there is now a first-time opportunity to create such a system: graphene exhibits the QHE at lower magnetic fields and higher temperatures than any other material, and systems become possible that use closed cycle cryo-coolers or simple liquid helium dewars. Combined with compact superconducting magnets such systems fulfil the main requirements of simplicity and transportability – eventually becoming a ‘bench-top QHE’. Their reduced cost and complexity will allow their deployment more widely - into smaller NMIs, into industry, or allowing a dedicated QHE reference at the point of use.

Scientific and technical objectives

The project will supply a new generation of robust quantum Hall devices as well as novel instrumentation, enabling a largely simplified dissemination of the unit of resistance by:

1. *Advancing the device fabrication methods to fulfil requirements of metrology in terms of homogeneity, contact resistance, variety of sizes, controlled disorder, edge structure, etc. Graphene material and devices with optimised parameters and stable under regular usage conditions involving repeated cool-down cycles will become available to NMIs.*
2. *Developing the synthetic procedures for precise, quantitative, non-destructive characterisation of graphene and graphene devices combining structural, chemical and physical methods.*
3. *Performing precision QHE measurements on graphene to test the limits of achievable uncertainty under relaxed experimental requirements of temperature above 4 K and magnetic field below 5 T.*
4. *Investigating ac-losses in graphene devices and demonstrating the ac-QHE effect in graphene and thus assessing the potential of a graphene-based impedance standard.*

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5. *Developing customised instrumentation which allows the use of graphene as an intrinsically referenced resistance standard, including peripheral, but vital instrumentation for scaling of the singular QHE value of 12.9 k Ω .*
6. *Interacting with collaborators and stakeholders to receive input from the calibration industry as well as to enable them to become early adopters of the enhanced calibration capabilities.*

Expected results and potential impact

The key outcome of this project will be new, simpler to operate quantum resistance standards and adapted instrumentation to exploit them. This will have a ground-breaking effect on the metrology landscape where it will directly impact the electricity community formed by all the NMIs and calibration laboratories by enabling them to disseminate the units ohm and farad in a simpler and quicker way.

The availability of the best imaginable standard of resistance, the fundamental constant based QHE reference, will significantly improve calibrations by shortening the calibration chains, making them more efficient and economic. A standard that is more distributed, with the primary reference available wherever and whenever it is needed, will reduce the costs and inconveniences of traditional approaches. Such improved dissemination will constitute a real breakthrough not only for calibration laboratories, but also for those NMIs which up to now cannot afford to operate the complex quantum standards.

The impact of the project will result from two developments:

- Graphene-based quantum Hall effect devices operating under strongly relaxed conditions of temperature and magnetic field, along with a technological method of fabricating them, will largely increase the user base of ultimately precise intrinsically referenced standards.
- The specific instrumentation to utilize the graphene QHE devices, differing from instrumentation exploiting traditional devices in terms of simplicity and added capability for device conditioning, will be available as well as simplified accessory instrumentation which is vital for scaling the QHE resistance from its singular quantized value to all values relevant in practice.

Progress towards achieving the scientific and technical objectives to date is as follows:

1. *Advancing the device fabrication methods to fulfil requirements of metrology in terms of homogeneity, contact resistance, variety of sizes, controlled disorder, edge structure, etc.*

- Graphene growth has been continued and intensified, using the method of thermal decomposition of SiC at Linköping university and of chemical vapour deposition at KRISS.
- The SiC based growth method has been started, and first batches of SiC-graphene were grown. In parallel the optimization of device processing aiming at improved fabrication methods for Hall-bars and electrical contacts, as well as the development of more convenient technology for electrical tuning of charge carrier density are progressing. This addresses one of the key features of an improved future graphene resistance standard since the desirably low magnetic field of operation is proportional to carrier density.
- The study of the nature of defects in polycrystalline graphene (PG-CVD) and their impact on the QHE is reported in a paper submitted to Phys. Rev. Lett.
- A better understanding of graphene growth on the C-terminated face of SiC (C-face growth much more difficult than Si-face growth, but mobility of graphene is higher) was achieved.
- A graphene tunneling device was fabricated, where CVD graphene was encapsulated with h-BN. The characteristics of tunneling spectra under magnetic field showed the Landau level splitting quite clearly up to $n=15$.

- A method to grow single crystalline h-BN on Cu substrate was developed, implying a possibility of epitaxial growth of h-BN.
- The quality of epitaxial graphene growth was improved.
- A new growth variant for graphene on SiC was developed. It produces only a very low fraction of bilayer graphene, known for its detrimental effect on Hall quantization. A patent application for this new method has been filed.
- Hexagonal boron nitride (*h*-BN) was successfully synthesized on Cu foils and verified by Raman spectroscopy. Synthesis of graphene on the *h*-BN substrate was performed and confirmed by Raman spectroscopy and SEM imaging. The transfer of the *h*-BN/graphene sandwich onto a Si wafer and fabrication of Hall devices are in progress.
- The square resistance of a SiC graphene device was tuned to about 10 k Ω using a combination of UV irradiation, heating and NH₃ treatment at ambient temperature. Precision measurements of the doping-controlled epitaxial graphene Hall device were performed using the CCC resistance bridge.
- The behavior of ohmic contacts of a p-type Hall device was studied during repeated cool down. The contact resistance increased gradually above 200 Ohms and exhibited strong magnetic induction dependence. This interesting behavior was never observed in GaAs samples and it is still under investigation.
- A method for adjustment of carrier concentration in SiC graphene QHR devices using chemical and photochemical gating was developed. Application and test of such treatment in BIPM allowed tuning the device to achieve a dissipation free QHR plateau. An agreement with a conventional GaAs reference of a few parts in 10⁹ was found at relatively moderate experimental conditions ($B = 8$ T, $T = 1.3$ K and 40 μ A measurement current).

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

- Various characterization measurements of the material were performed and fed back to the growth groups.
- A study of the influence of bilayer graphene stripes and patches was published.
- A new alternative method for carrier density tuning by corona discharge was developed.
- A method for structural analysis of CVD-grown graphene using liquid crystal texture was published: Structural properties of graphene such as grain boundary structure, orientation and single layer orientation in multilayer graphene were visualized using a liquid crystal texture method.
- A non-contact microwave cavity method to measure graphene resistivity was developed.

3. *Performing precision QHE measurements on graphene to test the limits of achievable uncertainty under relaxed experimental requirements of temperature above 4 K and magnetic field below 5 T.*

- Measurement uncertainties in the few parts in 10⁹ regime with non-exfoliated graphene were demonstrated in four additional partner-NMIs (MIKES, PTB, METAS, LNE) and one collaborator NMI (NIST). The material used was either acquired from collaborators, or grown in the institute.
- Perfect quantization of the Hall resistance in graphene to within one part in 10⁹ over a 9-Tesla-wide magnetic field range at 1.4 K was demonstrated, using a measurement current of 20 μ A. Graphene grown

at the Centre de Recherches sur l'Hétéroépitaxie et ses Applications (CRHEA) on SiC with a new variant of the commonly used method was employed in these measurements. An agreement with a GaAs reference device within 4 parts in 10^{10} was demonstrated in those measurements.

- Perfect quantization of the Hall resistance in graphene to within one part in 10^9 over a 10-Tesla-wide magnetic field from 3.5 T, temperatures as high as 10 K, or measurement currents as high as 0.5 mA were demonstrated. Graphene grown at the Centre de Recherches sur l'Hétéroépitaxie et ses Applications (CRHEA) on SiC with a new variant of the commonly used method was employed in these measurements. An agreement with a GaAs reference device within 8.2 parts in 10^{11} was demonstrated in those measurements.
- The study of a graphene device made from graphene grown by CVD of propane/hydrogen on SiC at CRHEA was continued. The large Hall bar ($100 \times 420 \mu\text{m}^2$) of electron density $1.8 \times 10^{11} \text{ cm}^{-2}$ and mobility $9400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ had been patterned in the Laboratoire de Photonique et Nanostructures (CNRS). Results on this device were published in Nature Nanotechnology (R. Ribeiro-Palau *et al*, Nature Nanotech., 10, 965 (2015)).
- The Quantum Hall Effect was realized in two types of closed cycle refrigerators and the influence of noise was studied. The possibility to realize the Quantum Hall Effect with an uncertainty below a few parts in 10^8 also outside NMIs and without an external supply of liquid helium was shown.

4. Investigating ac-losses in graphene devices and demonstrating the ac-QHE effect in graphene and thus assessing the potential of a graphene-based impedance standard.

- In the part of the project focused on graphene's potential for QHE ac-metrology, a new special sample holder together with newly established high resolution measurement of magneto-capacitance and loss-factor opened the way for precise characterisation of graphene's ac properties.
- First precision ac-resistance measurements on SiC-graphene were made (using material from collaborator Aalto university as well as from PTB).
- The great potential of SiC-based graphene devices as a precision impedance standard was proven by demonstrating negligible magnetic field dependence and unexpectedly small frequency dependence in AC-QHE measurements, using devices from two different sources.
- A 20 ppb uncertainty at 2 kHz of a digitally assisted impedance bridge was demonstrated.
- The AC-QHE results were independently confirmed using a novel kind of measurement bridge.
- The bridge needed to make AC measurements of the longitudinal resistance R_{xx} was developed and partially tested. A full test will be performed when a fully operational graphene device is available.

5. Developing customised instrumentation which allows the use of graphene as an intrinsically referenced resistance standard, including peripheral, but vital instrumentation for scaling of the singular QHE value of 12.9 k Ω .

- In the project tasks dealing with specific instrumentation for simpler exploitation of graphene quantum Hall systems, dedicated low-carrier density GaAs devices were made as a bridging technology before suitable graphene devices are available. This allowed proceeding with instrumentation development and testing without waiting for the maturity of large scale graphene Hall bar fabrication. Finally, first tests with a prototype of a current comparator working at room temperature were made. The validity of the concept was confirmed.

- A ratio deviation as small as 10^{-9} of a low frequency current comparator (LFCC) of nominal value 1:1 in the frequency range 0.143 Hz - 0.722 Hz was demonstrated.
- Fabrication of an optimised version-B of a low frequency current comparator (LFCC-B) was completed and testing of the optimised design was started.
- An agreement between two LFCCs (from MIKES and BIPM) at 10:1 ratio within 2 parts in 10^9 at 1 Hz, and 7 parts in 10^9 at 0.5 Hz was demonstrated.
- An agreement between those two LFCCs at 129:1 ratio was demonstrated within 8 parts in 10^9 at 0.5 Hz using modified BIPM bridge electronics in comparison measurements of a 100 Ω resistor with a graphene-based QHR.

6. Interacting with collaborators and stakeholders to receive input from the calibration industry as well as to enable them to become early adopters of the enhanced calibration capabilities.

- Successful growth of SiC-graphene commenced in a partner-NMI (PTB) and in a collaborator NMI (NIST).
- The project progress was presented at the meeting of CIPM's Consultative Committee for Electricity and Magnetism (CCEM).

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