3.1 Publishable summary

3.1.1 Project context and objectives

The concept of this project is to unlock the potential of epitaxial graphene on silicon carbide (SiC) for development of scalable electronics with the view to develop graphene-based devices and circuits with a non-conventional functionality. The strategy is to explore two promising directions of graphene-based technology: (i) the development of large-scale graphene wafers for manufacturing high-density of devices on a single SiC wafer, and (ii) the development of hybrid circuits for applications of graphene in spintronics and metrology by exploiting the flexibility for design offered by the large area of graphene on SiC.

Until recently, most impressive results on unconventional transport properties of electrons in graphene has been seen only in flakes mechanically exfoliated from bulk graphite. Although perfectly suitable for attaining a small number of high-quality structures, the exfoliation process is laborious and, thus, difficult to implement in the mass assembly of large-scale integrated electronic circuits. In contrast, in this project, we have chosen an alternative approach where graphene is grown epitaxially on silicon-carbide (SiC). Since the route towards practical exploitation of graphene on the commercial scale lies through up-scaling of prototypes to wafer-size arrays and systems, this alternative method presents an appealing direction for the development of carbon-based electronics, provided that efficient growth protocols and methods to control electron density and tailor epitaxial graphene properties by nano-structuring, better contacts, and substrates can be developed.

The scientific objectives of this project are

1. reliably produce large-area graphene with a controlled carrier density and improved transport characteristics

2. pattern graphene for applications using industrial nanostructuring and nanofabrication methods, aiming at high integration densities with a good yield of working devices

3. produce a prototype for a graphene-based Quantum Hall Resistance standard with characteristics surpassing existing silicon- and GaAs-based devices

4. develop a pilot version of spintronic devices of epitaxial graphene

In addition, our aspiration and vision for the longer term is to stimulate the rapid progress of graphene research in Europe by providing our colleagues in academic institutions and researchers in the industrial sector with graphene/SiC wafers suitable for proof-of-concept studies of electronics devices and circuits, and for a further search of new functional applications of this material. To this end, the project has a 5th objective in putting in place all prerequisits for the formation of a start-up company that will produce graphene wafers for users outside this consortium.

In this section, a summary of the progress of the project during the first two years is presented.

3.1.2 Summary of work performed and the main results achieved so far

During the first two periods, the consortium has worked on a number of problems, of which we here highlight a few:

1. epitaxial graphene growth protocol, including growth of large area (50 mm diameter) graphene and characterization of its electronic and structural integrity,
2. optimization of the SiC(0001)/graphene interface,
3. weak localization measurements as a characterization tool,
4. optimization of contacts to graphene,
5. understanding and influencing the doping of epitaxial graphene,
6. metrology: a comparison of the quantum Hall resistance accuracy achieved with our graphene devices against the current GaAs/AlGaAs standard,
7. fabrication of Hall bar arrays for practical metrology,
8. making of a spinvalve prototype and characterization of spin transport in epitaxial graphene
9. formation of a start-up company that will produce graphene wafers for users outside this consortium

For 1) the growth, we have grown graphene on three SiC polytypes 4H, 6H, and 3C. The Linköping and Erlangen methods consists of growth at elevated temperatures in Ar-atmosphere, which typically leads to n-doping with a lower electron density n~10^{12} cm^{-2} compared with other groups utilizing low temperature vacuum growth. The most reproducible single layer graphene has been obtained on the Si-face of 4H and 6H substrates, while graphene grown on 3C has been shown to be promising although further research is needed to conclude on its eventual suitability for electronics applications. For the C-face, single layer is harder to achieve. For few-layer graphene grown on the C-face with the Linköping method, we have observed island formation (stacks) without rotational disorder between planes within stacks, but relative misorientation between islands.

During the second year, growth of 50 mm diameter graphene by SiC sublimation has been demonstrated. The material has been investigated by spectrocopic ellipsometry (SE) and low-energy electron microscopy (LEEM). It is seen that the graphene films are predominantly monolayer, but with several islands of bilayers or multilayers (typically 2-3). In LEEM images of regions where SE indicates monolayer coverage, small bilayer islands are revealed. Still, the monolayer coverage is prevalent. The conclusion is that it is indeed feasable to grow large area monolayer graphene, but further optimization of the process is needed to get even higher percentage of monolayer coverage and minimize the occurance of bilayer and multilayer islands. The consortium has identified SE as a suitable method for express characterization of large-area graphene.

For 2) interface optimization, extensive work has been performed at Erlangen on intercalation of graphene on the Si-face of 6H SiC, including characterization of the influence of the buffer layer on the electronic properties of epitaxial graphene. Intercalation by hydrogen, fluorine, and oxygen leads to a conversion of the buffer layer into a graphene layer. Starting with only a buffer layer, annealing in the different atmospheres converts the buffer layer to quasi-free standing monolayer graphene (QFMLG). Hydrogen and fluorine intercalation leads to p-doping. Oxygen intercalation leads to substantial disorder and is a less promising route to monolayer formation. So far, the best method is hydrogen intercalation. The best samples had a room temperature mobility of $\mu(300\ K) = 3060\ cm^2/Vs$ at $p = 6\times10^{12}\ cm^{-2}$. This value is similar to those reported recently by other groups and therefore defines the current state-of-the-art for QFMLG.

For 3), weak localization characterization, we have carefully compared experiments with theory and obtained good agreement. This has enabled us to extract the various scattering times and lengths: intra- and inter-valley scattering and phase-breaking scattering. The temperature dependence of the scattering lengths are similar to what has been obtained in graphene flakes exfoliated onto SiO_2. This proves that the quality of epitaxial graphene is as good as graphene flakes. In addition, since epitaxial graphene has very large area, we are able to fabricate larger Hall bars than what is possible with flakes. This leads to suppressed universal conductance fluctuations which enabled us to extend our measurements to low temperature and extract the Abrikosov-Aronov electron-electron interaction correction to conductivity. It turns out that e-e interactions, quantified by a Landau Fermi liquid parameter, is reduced by the reduced phase-space scattering available for Dirac electrons.

For 4), contacts, different methods are required for the two classes of devices considered in the project: a) ohmic contacts for the quantum Hall effect and metrology, and b) tunnel barriers for spintronic devices. For a) ohmic contacts, we have shown that residues of resist from the lithographic processing can be detrimental. With current methods, we are able to achieve contact resistances of order an Ω. The best contact resistance was 0.5 Ω, which is very good for metrological applications. Occasionally, large contact resistance of the order of a few kΩ is found, which can be detrimental for quantum Hall bar arrays. By topographic characterization through various scanning probe techniques, and theoretical modeling, we have concluded that the graphene parts of these contacts (the bare graphene arm leading from the Hall bar to the large-area metal/graphene interfaces) contain bilayer stripe defects connecting the two edges of the arm. Such defects most probably cause an unwanted resistance in the quantum Hall regime and should be avoided through characterization of wafers before device fabrication and adjustments of device design. For b) tunnel contacts, a process of creating tunnel barriers of aluminum oxide has been developed.

For 5), doping, we have developed a photo-chemical gate consisting of two polymer layers: one protective layer (PMMA) and one photoactive layer (ZEP520A). When exposed to UV light, potent acceptors are created in the photoactive layer. The subsequent charge transfer from graphene leads to a lower electron density in graphene ~10^{11} cm^{-2}, or slightly below. This leads to an enhanced mobility of order 5000 cm^2/Vs at room temperature and a resulting enhanced accuracy of the quantum Hall resistance measurements, see below.

A theory of charge transfer from the substrate and the buffer layer to epitaxial graphene has been developed. Comparing theory and experiments, we have shown a strong pinning of the filling factor $\nu=2$ in epitaxial graphene with increasing magnetic field due to a magnetic field dependent doping mechanism. The resulting widening of the quantum Hall plateau and incresing break-down current at high magnetic fields is very advantageous for metrology since the signal-to-noise ratio is enhanced and the accuracy is improved.

For 6), metrology, we have performed the most stringent test to date of the universality of the quantum Hall effect with regards to material independence by comparing the quantum resistance measured with our graphene device with the one measured with the current GaAs/AlGaAs standard device. The quantized resistance was the same in the two devices to an uncertainty of $8.7\ 10^{-11}$. In fact, the factor limiting the measuement uncertainty in these experiments was the low break down current (~100 μA) of the GaAs/AlGaAs heterostructure compared with the graphene device (~500 μA). With this accuracy, our graphene device already outperform our expectations of 1ppb which was a milestone to be reached by month 30. A description of the measurements is available as a video interview published by New Journal of Physics in connection with the scientific publication: http://iopscience.iop.org/1367-2630/13/9/093026

For 7), Hall bar arrays, we have fabricated a number of such arrays including arrays with 100 devices. The developed technology allows scaling up of the array size in a rouine manner. Initial tests demonstrate the device integrity and its readiness for metrological evaluation during the third year.

For 8), spin devices, we report successful spin injection and transport through epitaxial graphene on SiC. We have performed spin valve and spin Hanle precession measurements to extract spin transport properties. We report high spin relaxation times of 1.3 ns at room temperature, up to 2.3 ns at 4 K for epitaxial graphene on SiC(0001), which is the best achieved for any graphene type. However, a reduced spin diffusion coefficient of 2.4 cm^2/s was extracted, which leads to a modest spin relaxation length of 0.56 μm. We have performed experiments to compare spin transport in 5 different graphene materials: epitaxial graphene on SiC(0001) and SiC(000-1), exfoliated graphene on SiO_2 and h-BN, and QFMLG. We conclude that the buffer layer between graphene and the SiC(0001) substrate greatly influences spin transport. Most probably because of the presence of localized states in the buffer layer.

For 9), the start-up company, we have already formed a start-up company at Linkoping that now makes the material available for users outside this consortium.

The project has so generated 19 scientific publications and several preprints and publications under preparation, as well as a number of invited talks and poster presentations at international conferences and workshops.

In conclusion, the project is running smoothly and according to the foreseen schedule. In fact, in some parts we are ahead of schedule. In particular, the achieved quantized resistance precision one order of magnitude better than 1ppb is indeed very promising. The material is now available for users outside the consortium through the start-up company at Linkoping.

3.1.3 Expected final results and their potential impact

Our ambition is that the progress in the technological part of this project will generate a solid high-quality material base for the ready-to-expand European effort in graphene R&D. Hopefully, the European Union will be able to coordinate a revolution in ultra-fast, lower power and, potentially, quantum enhanced electronics and communications based on the work in this project. This will strengthen competitiveness of the European nanoelectronics industry through generic development of graphene science and technology, generating exploitable intellectual property and eventually creating new jobs in new and existing high-tech industries.

The project also addresses practical issues of applications of graphene in micro- and nanoelectronics. It does this by mastering nano-structuring technologies, design of innovative devices, and by better understanding of their performance. On the forward-looking side of fundamental science, the impact will be achieved by developing deep understanding of fundamental charge and spin properties of graphene on its own (both on the macroscopic and nanometer scales) and in combination with other materials (magnetic and non-magnetic metals), and by developing the device base for measurements of extreme precision. We plan to use the successful completion of the proposed case studies on the fundamental science side of this project (spintronics and quantum Hall effect metrology) to convincingly advertise the newly manufactured material to scientists and electronics engineers, and, thus, attract new European groups into the field of research in graphene and graphene-based electronics.

Already at this point, we have achieved outstanding metrological precision of the quantum Hall resistance. In fact, the precision measurements are at present limited by the small break-down current of the GaAs/AlGaAs reference system. This shows that graphene has the potential to surpass semiconductors as the material choice for quantum metrology. This could become one of the first real applications of graphene.

Project website address: www.ConceptGraphene.eu