Publishable summary

The project GLADIATOR (Graphene Layers: Production, Characterization and Integration) is driven by the vision of developing an approach to the production of high quality graphene (transmittance ≤ 90%, sheet resistance ≥ 10 Ohm/sq.) both on a large scale and at a low cost. This will make this type graphene (produced by chemical vapour deposition CVD) a competitive alternative to indium tin oxide (ITO) as the electrode material used in (flexible) organic electronics.

The project has completed 12 months of its planned 42 month duration and has already achieved very promising results, in accord with its ambitious schedule. These first results are outlined below.

Large volume preparation of undoped graphene

The reliable production of (CVD) graphene is key to its future success. The GLADIATOR project has systematically assessed catalysts from different suppliers, and the process gas composition and pressure have been optimised for reproducible production of high-quality graphene. The optimum recipe has been repeated 10 times; each time the material produced was characterized immediately after growth by Raman spectroscopy. An example of such a set of measurements is given in Figure 1 demonstrating the excellent quality of that graphene across most of a 150 mm wafer (measured from centre to edge). The reliability of the CVD system has been proved by repeated, randomised use of different control recipes. Additional effort focused on a new production tool design to allow the storage of several samples without the previously required time consuming cool down phase.

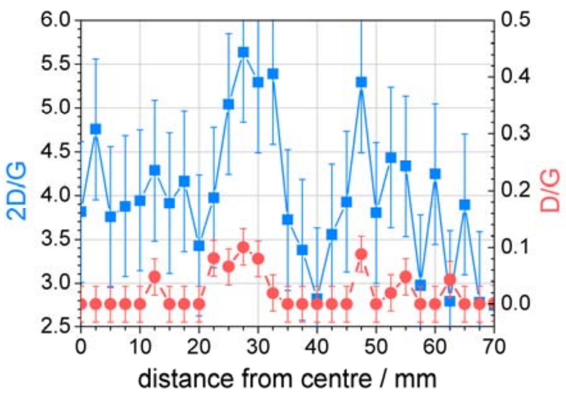

Figure 1. 2D/G and D/G distribution on a 150 mm wafer, measured with λ = 457 nm and 15 s of exposure. Data have been provided by AIXTRON Ltd.

Not only the quality of the graphene made in the CVD process is important, but also the coverage of the catalyst. Continuous progress has been achieved in the last months and a coverage of 90% is now routinely obtained (as determined by optical microscopy).

Doping to improve performance

Within this project, it will be attempted to increase the conductivity of graphene both by inserting hetero atoms during CVD growth (internal doping) and by applying dopant materials onto graphene (external doping) in order to increase the charge carrier concentration. Our main efforts so far have focused on the latter approach. For this task a variety of dopants have been screened, and the most promising candidates ($HAuCl_4$ and iodine) have been tested for long-term stability. Inserting these dopants between two monolayers of graphene resulted in low sheet resistances of 180 or 310 Ω/sq., respectively and these values were found to be stable over 4 months at ambient conditions. Once this test has been repeated at higher storage temperatures and validated with different graphene samples from the consortium, the number of graphene layers will be increased to achieve the final goal of 10 Ω/sq. at 90% of transmittance.

Resource efficient CVD production

The GLADIATOR project aims to re-use the expensive copper catalysts required by the CVD process which are currently lost during the transfer process (during which they are dissolved). Substantial progress towards this has been made: a five times reuse of a 100 mm diameter catalyst has been demonstrated, with no detrimental effect upon the graphene quality. The transfer process will be further optimized and other catalyst materials (e.g. platinum) may be investigated in order ultimately to achieve a 10-times reuse of a 150 mm catalyst.

This reuse of catalyst material is important to allow CVD graphene to be produced cheaply enough to compete in the market, and the results have been incorporated into the project's production cost model.

Robust and reliable transfer process for large sheet sizes & 'patchwork' approach

Large graphene sizes are essential for the successful commercialization of graphene, the production and transfer of large area sheets is one direct approach to address this need. However, a more efficient approach might be the connection of smaller sub-tiles to form a larger continuous area of graphene ("patchwork").

Various transfer techniques have been investigated by the consortium including the classical etching transfer, electrochemical transfer based on hydrogen evolution, and a novel electrochemical transfer exploiting controlled oxidation and reduction of copper at the copper-graphene interface. The project is now concentrating on this latter technique. The previous average delamination time with this technique of 7.5 ± 2.5 h for a complete 100 mm wafer has already been lowered by an order of magnitude, and further improvement is expected.

Regarding patchwork efforts, a characterization model system has been set up in order to answer questions such as the significance of crystal orientation, number of overlapping edges, presence of wrinkles, substrate roughness, etc. and how these affect the final patched large sheet. First results which will help to understand the patchwork performance are expected in the first quarter of 2015.

Real-time graphene production process control

Both the optical and electrical properties of graphene have to be monitored for later graphene manufacturing and integration in products at low cost. Thus, a combined system consisting of Raman spectrometer and ellipsometer is currently under development, which will be integrated in a 150 mm CVD tool to monitor *in situ* the growth of graphene. The challenge will be here to record information with sufficient signal/noise ratio because of the small solid angle available for the optical components, and the high temperature and large temperature changes of the chamber. The prototype development for the CVD tool, including both spectrometer systems, is expected to be finished by summer 2015.

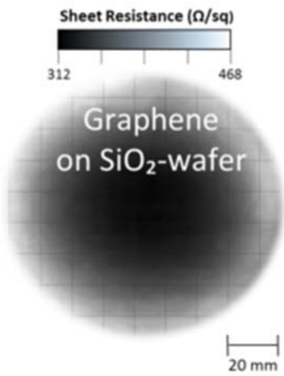

Figure 2. Sheet resistance map based on eddy current measurements of graphene with an diameter of 100 mm. Data have been provided by Suragus GmbH.

In addition, the quality assessment of the electrical properties after graphene transfer on to the target substrate will be performed by eddy current measurements. In order to properly investigate the sheet resistance also at high values, the eddy current sensor architecture and its sensitivity have had to be modified. The first measurements by the modified eddy current instrument of graphene samples from consortium members have been successfully completed.

It is planned to validate the results of the novel optical and electrical characterisation methods against other characterisation techniques in the future.

Clarifying the health risks of graphene

In order to assess the health-hazard potential of graphene related materials, both its toxicity and potential (particle) exposure has to be investigated. Since a large amount of powder material is needed to perform *in vitro* and *in vivo* experiments, reduced graphene oxide (small and large size) and graphene oxide have been used as proxies for CVD graphene in these investigations (because graphene produced by CVD process can currently not be provided in multi-gram scale).

In the first three months, an *in vitro* study has been conducted in a murine lung epithelial cell line to test for acute toxicity. This analysis included the assessment of cell death and DNA damage by exposing the cells to the graphene materials for 24 h at different doses (1–200 µg/ml). Since no significant effect on the cell viability and DNA could be observed, doses for the *in vivo* study were set to reflect the pulmonary deposition after 1, 3 and 9 working days at the exposure limit for carbon black (our reference material).

These *in vivo* tests are currently being completed and will help to draw conclusions about the toxic potential of graphene related materials, which is essential to ensure the future safe handling of graphene itself and products that make use of graphene.

Hydrophobic polymer foils allowing durable flexible organic devices

Highly conductive and transparent graphene could be the key material to lower the market barrier to flexible organic electronics. However, excellent barrier properties of the substrates with water vapour transmission rates lower than 10^{-5} g/d×m^2 are still needed for sufficiently long device lifetimes. Since many transfer processes of graphene include aqueous process steps, a polymer foil will be developed which is adjusted to the needs of graphene. As a starting point the polymer foil PET is coated with an inorganic silica film (d < 200 nm) and subsequently the surface will be additionally modified to achieve a water contact angle of 125° in order to improve the adhesion of graphene for later integration steps.

Currently different layer architectures and material systems are being experimentally investigated to isolate the most promising approach. Continuous progress has also been made in reducing the thickness of the final laminate in order to allow a smaller bending radius (useful for roll-to-roll processing and flexible devices).

More information and further details about the participating partners can be found on the project website www.graphene-gladiator.eu. For direct questions, please contact info@graphene-gladiator.eu.