GRAPHENE FLAGSHIP

Graphene Core 2

Graphene Flagship Core Project 2

Horizon 2020 RIA

WP15 Production

Deliverable 15.1 'Graphene with lower than 200 ohms/square sheet resistance with 90% transparency at 265nm'.

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Due date of deliverable: M12

Actual submission date: M12

Dissemination level: CO

Funded by
the European Union

Project funded by the European Commission under Grant Agreement n°785219

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Summary

UV-LEDs today have extremely low total efficiencies and they use metal fingers/mesh with no current spreading, so any breakthrough in a UV-range transparent electrode (i.e. graphene) is desired. In this task, the goal is to develop the production method for transparent electrodes for UV-LEDs achieving 90% transparency at 265 nm and sheet resistance <200 ohm/square. There is a need to develop a manufacturing process that can fulfil these specifications and speed up the production of the material.

In order to fulfil the mentioned specifications, Graphenea has worked on different transfer processes such as wet and semi-dry processes in order to identify the most suitable one to fulfil these requirements. The semi-dry transfer process developed in WP10 (Wafer Scale Integration) has been adapted and optimized to produce multilayer graphene samples and is at the moment the most appropriate transfer process since it considerably speeds up the graphene processing. This process has been successfully implemented to transfer graphene onto relevant substrates for this application such as fused silica, single crystal quartz or sapphire. Sapphire has been selected as a suitable substrate for growing AlGaN nanowires. Crayonano has grown AlGaN nanowires on graphene/sapphire substrates using Metalorganic vapour phase epitaxy (MOVPE). The first device prototype demonstrating the concept of graphene as a transparent electrode showing light emission at 365 nm (UVA-LED), has been successfully developed, proving the feasibility of graphene as a substrate and transparent electrode for UV-LEDs.

The work carried out in this task shows a scalable transfer method of multilayer graphene for use as a transparent electrode in UV-LEDs.

We would like to highlight that the target transparency included in the deliverable (90%) is not appropriate at 265 nm since graphene has a considerably larger absorption at that wavelength as reported in W.Li et al. “Broadband optical properties of graphene by spectroscopic Ellipsometry” Carbon 99 (2016) 348-353.

Introduction

The work proposed in this task required the development of a scalable graphene transfer process on substrates suitable for UV-LEDs such as fused silica, single crystal quartz, and sapphire.

1 Graphene Transfer

In order to accomplish this, CVD monolayer graphene was synthesized in a cold walled CVD reactor (Aixtron BM) using copper foil (Cu) as A catalyst at 1000°C and at low pressures using methane as the carbon source. Prior to the growth the Cu foils were chemically pre-treated and annealed. Once the graphene is grown on the Cu catalyst, it is transferred to the desired substrate.

In the first instance, Graphenea evaluated a polymer assisted wet transfer process. Basically, consisting of using a poly(methyl methacrylate) (PMMA) supporting layer on top of graphene in order to provide integrity during the Cu etching. Different cleaning steps are applied, and the monolayer graphene is finally scooped in water onto the final substrate (fused silica, single crystal quartz or sapphire). Finally, the PMMA layer is removed by dipping it into acetone and isopropanol. Although this process resulted in a good graphene quality, the need to speed up the fabrication of graphene samples led to the pursuit of an alternative semi-dry transfer process.

A commercial thicker polymer (150microns), which allows easy handling and drying of the graphene film with a N_2 gun after the cleaning steps, was used. The etching and cleaning steps were the same as the ones used in the wet transfer process. Once the film was cleaned, the stamping of graphene on the target substrate was done using lamination (applying pressure and temperature). Since this transfer process does not involve any trapped water in between the substrate and the graphene, the resulted adhesion is much better than in the wet transfer process, which is beneficial for graphene processing. Figure 1a shows the main steps of the semi-dry transfer process.

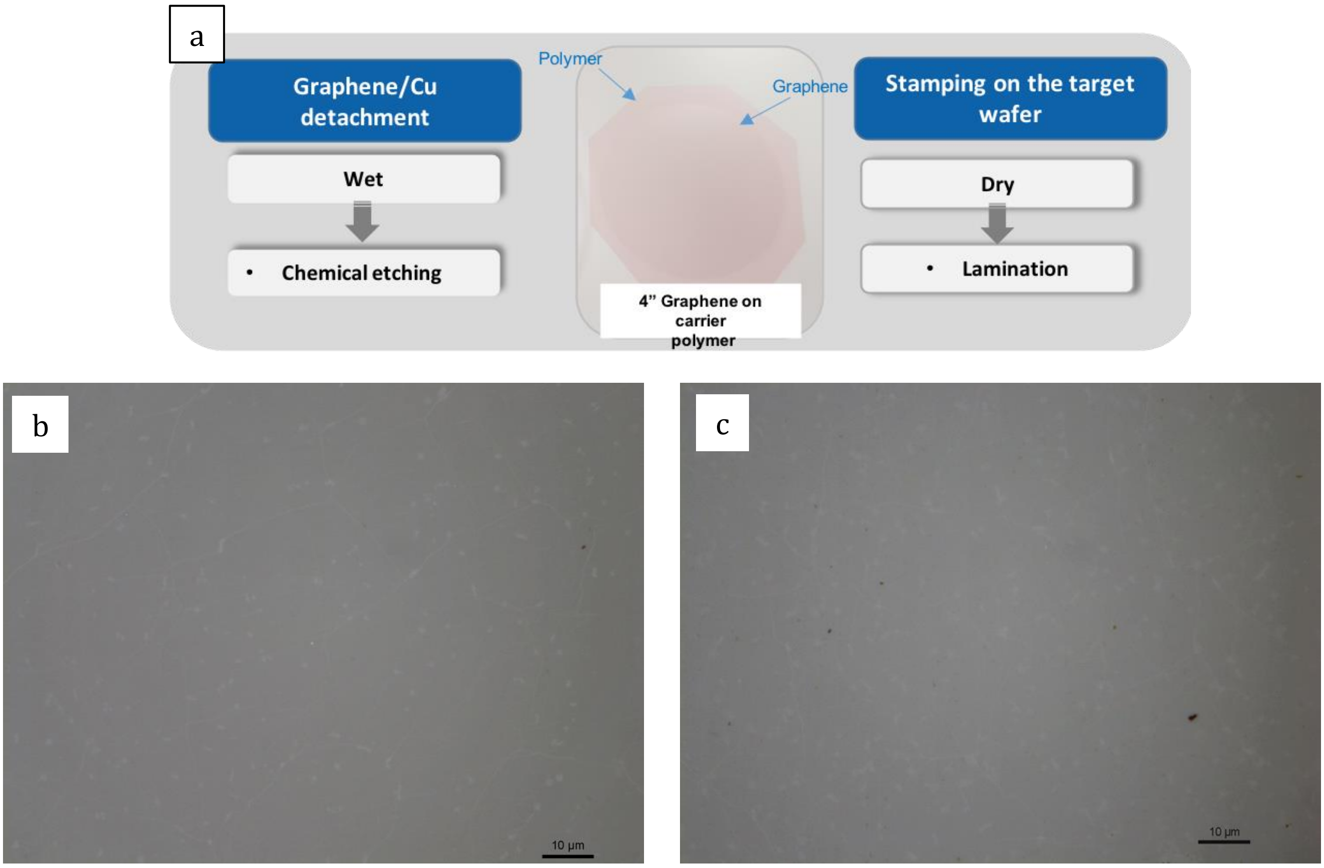
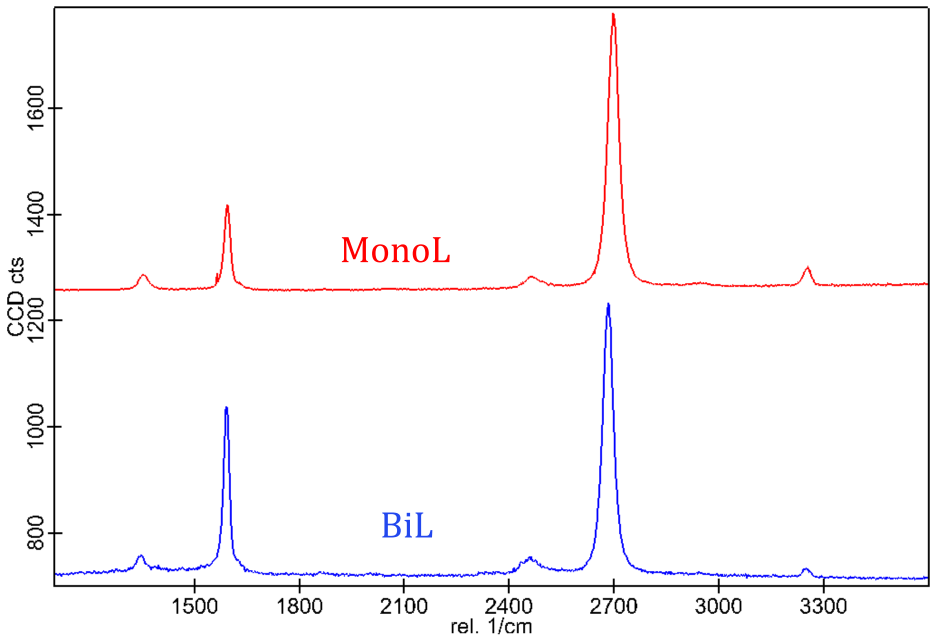


Figure 1. (a) Description of main steps of semi-dry transfer process, (b) optical image of monolayer graphene and (c) bilayer graphene on sapphire

This process can easily produce multilayer graphene samples by completing individual transfers on top of each other. In the optical images of Figure 1, monolayer and bilayer graphene show a very good quality after transfer, with low amount of defects and residues and a total area covered >98%.

2 Graphene Characterisation

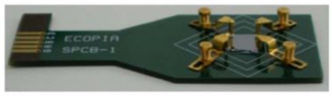
Samples of up to 2-inch wafer sizes have been produced with good quality and the process has also been tested on up to 6-inch wafers. Raman spectroscopy was used to characterise the quality and uniformity of the transfer. The values also show that no damage was induced during the transfer process, as shown in Figure 2.



Sample	Frecuency G (cm-1)	FWHM G	Frecuency 2D (cm-1)	FWHM 2D	IG/I2D	ID/IG
MonoL graphene	1596 ± 2	19 ±1	2692 ± 4	40 ± 2	0.37 ± 0.08	0.09 ± 0.05
BiL graphene	1592 ± 1	20±1	2685± 3	37± 2	0.68 ± 0.03	0.023 ± 0.004

Figure 2. Raman data corresponding to monolayer and bilayer graphene

Graphene samples were also characterised in terms of electronic properties (sheet resistance, charge carrier concentration and mobility) as shown in table 1 for monolayer and bilayer graphene transferred on sapphire. Hall measurements are performed in a van der Pauw configuration in fully-covered 1x1 cm^2 samples. For this purpose, Ecopia HMS3000 equipment is used (Figure 3), with a permanent magnet of 0.55T.



Monolayer ref.	Sheet resistance (ohm/sq)	Charge carrier den. (10^13 cm^-2)
1	496	1.814
2	482	1.944
3	517	1.955
4	513	1.978
Avg. / Std desvt.	502 ± 16	1.92 ± 0.07

Bilayer ref.	Sheet resistance (ohm/sq)	Charge carrier den. (10^13 cm^-2)
1	257	1.483
2	254	1.459
3	256	1.446
4	261	1.598
Avg./Std desvt.	257±3	1.49 ± 0.07

Figure 3. Electronic properties of monolayer and bilayer graphene on sapphire

The values obtained show how the sheet resistance decreases with the number of graphene layers, and values close to 200 ohms/sq are obtained for bilayer graphene. It is expected that increasing the number of stacked layers up to 4L values < 100 ohms/sq could be achieved. The UV-VIS analysis of the samples was performed on a Jasco V-630Bio system from 200-400 nm. In the bottom picture (Figure 4), it can be observed how the transmittance decreases with the number of layers (up to trilayer-3L has been stacked).

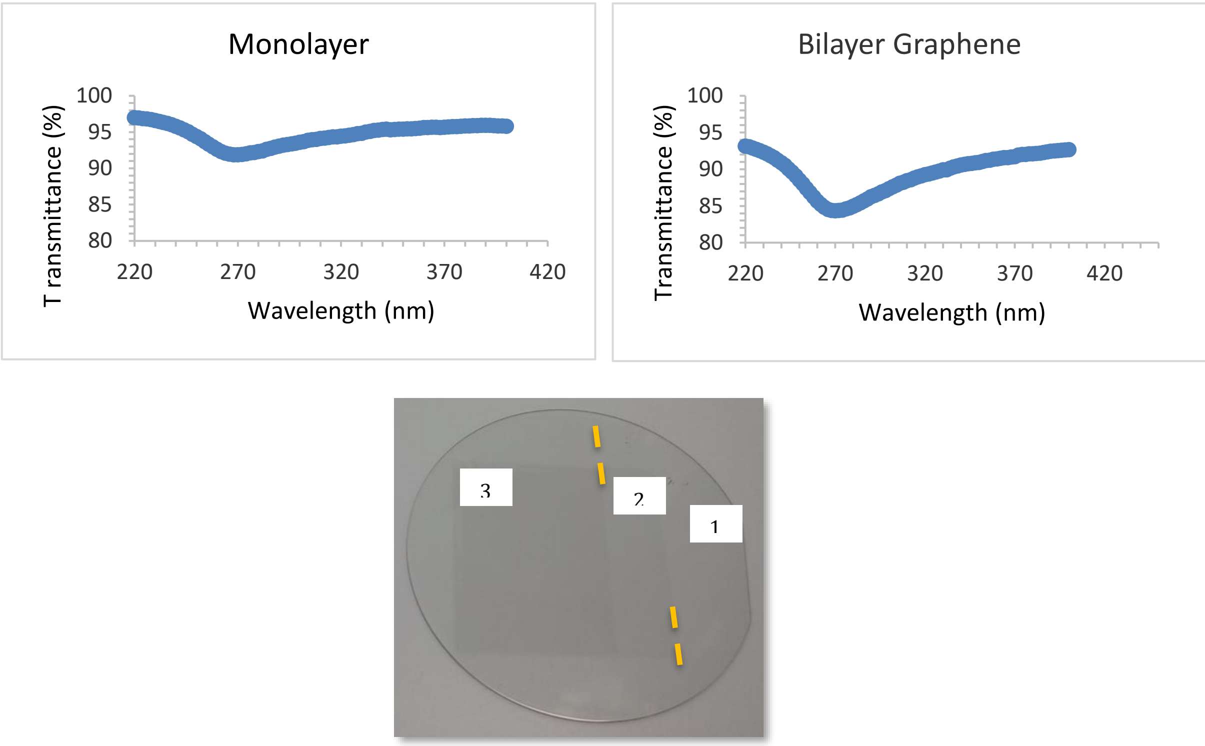


Figure 4. Transmittance of monolayer and bilayer graphene on fused silica. Picture showing multilayer graphene stacked up to 3-layers

The transmittance at 265 nm of a monolayer and bilayer are 92% and 85% respectively. As can be shown in the spectra there is a strong absorption rate at 265 nm, probing that the values in the deliverable were not reasonable. This is further backed up by Figure 5, extracted from W.Li et al. "Broadband optical properties of graphene by spectroscopic Ellipsometry" Carbon 99 (2016) 348-353.

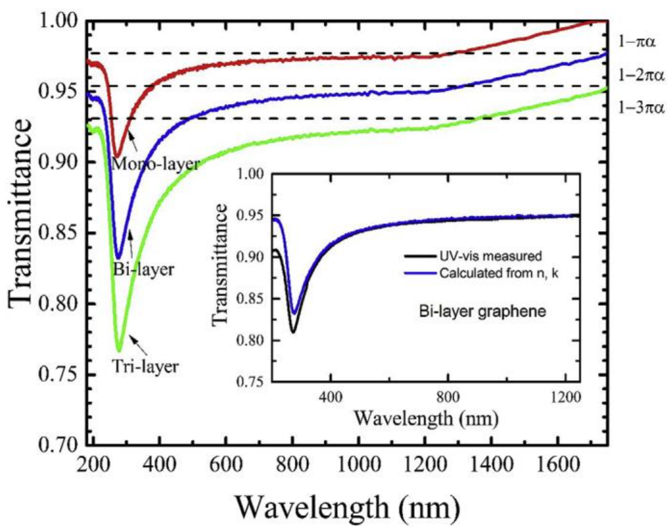


Figure 5. Calculated transmittance of mono-, bi- and tri-layer CVD grown graphene. Inset shows the comparison of measured and calculated transmittance for bi-layer grown graphene.

3 LED Fabrication

Crayonano carried out AlGaN nanowire growth by MOVPE on monolayer graphene samples transferred onto different substrates. Single layer graphene was used as a growth substrate and transparent conductive electrodes for an ultraviolet light-emitting diode, where high density self-assembled GaN/AlGaN nanowires are grown as the light emitting structure using metal organic vapor phase epitaxy (MOVPE).

LED structures were processed through photolithography to create Ni/Au contacts to the p-GaN top-part of the nanowires and Au-contacts to graphene in a flip-chip configuration, making it possible to do electrical and optical characterizations to measure the device performance (Figure 6). I-V characteristics of the LED device show good diode behaviour with a low turn-on voltage ~3V, with a negligible Schottky barrier and rectifying behaviour of up to 10^5.

Room temperature electroluminescence measurements show a GaN related near bandgap emission peak at 365 nm (UVA) with no defect-related yellow emission.

This first proof-of-concept device demonstrates that graphene can be used as a functional substrate and electrode that now will be used to develop AlGaN nanowires/graphene UVC LEDs (< 280 nm) for sterilization and disinfection purposes.

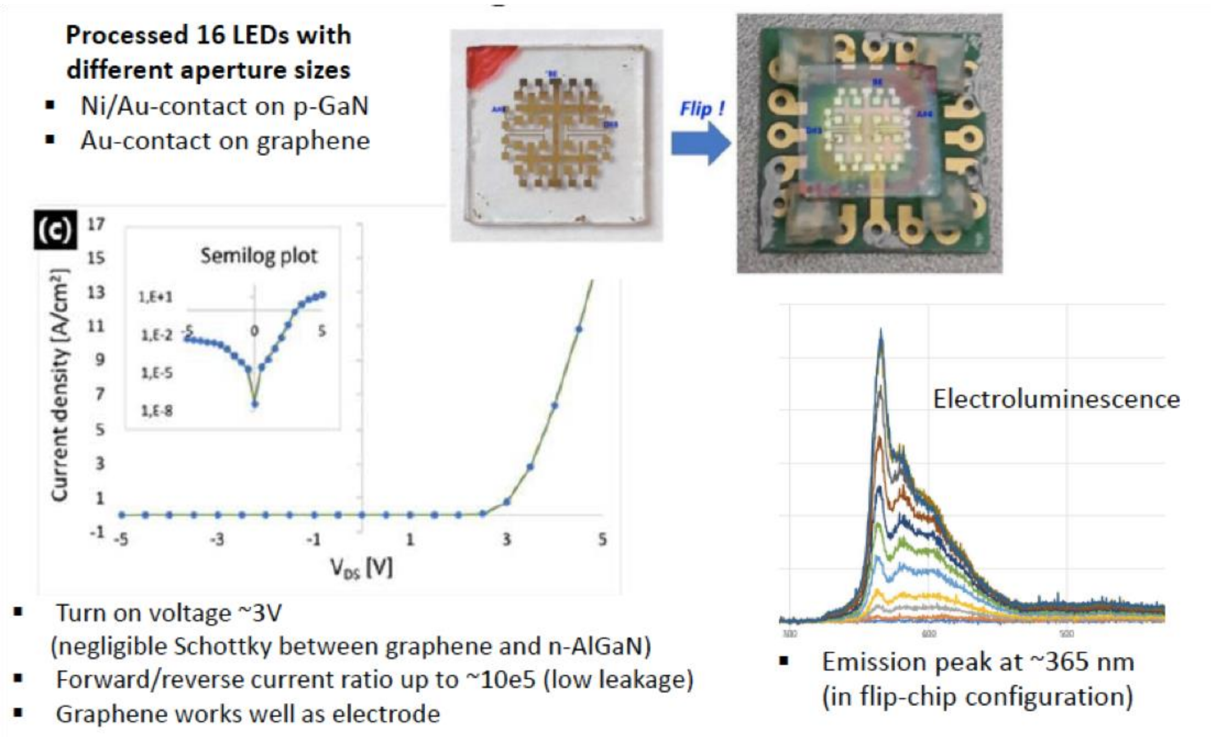


Figure 6. First proof of concept device

Conclusions

The work carried out shows a scalable transfer method of multilayer graphene with low sheet resistance and high transparency for use as transparent electrodes in UV-LEDs. In addition, the feasibility of graphene as a transparent electrode for UV-LEDs was successfully proven by fabricating the first device prototype.