GRaphene Golay micro-cell Arrays for a color-seNsitive TeraHertz imaging sensor (GRANT)

Erik Betz-Güttner[1*], Davide Truccolo [1], Nicola Cefarin[1], Alessandro Pitanti[2], Leonardo Vicarelli[2], Alessandro Tredicucci[2], Andrea Perucchi,[3] Giuseppe Cautero [3], Ralf Menk[3], Simone Dal Zilio [1], Marco Lazzarino [1*]

[1]CNR-IOM, SS 14 km 163.5 34143 Trieste, Italy; [2]CNR-NANO Piazza San Silvestro 12 56127 Pisa, Italy; [3]Sincrotrone Trieste , SS 14 km 163.5 34143 Trieste, Italy
*lazzarino@iom.cnr.it

ABSTRACT

The **Terahertz radiation** is a portion of the electromagnetic spectrum between microwave and infrared radiation. Despite its wide number of potential applications in many sectors such as medicine, security, quality control, telecommunications, the **lack of efficient and economic detector** and the scarcity of high-power sources has limited its implementation. Here we aim to improve a specific type of detector, the **Golay's cell,** using **advanced materials, graphene above all, and innovative microfabrication and optical detection approaches.** Our goal is to create a **new generation of Terahertz sensors**, paving the way for their use in new fields yet to be discovered.

Keywords: THz; Graphene; Golay Cell; Sensor.

1. INTRODUCTION

The TeraHertz (THz) region of the electromagnetic (EM) spectrum, consisting of waves with frequencies comprised between 0.1 to 10 THz, has a great potentiality in terms of amazing technological applications. THz has the ability to penetrate opaque surfaces — for example, scanning luggage — at much higher resolutions than currently possible with non-ionizing radiation. Many biological chemicals also have spectroscopic signatures in this range, allowing for easier identification of chemicals in biotechnology applications. Concrete, wood and other structural material are rather transparent thus allowing THz to penetrate and provide information on the aging and potential collapse of large infrastructures.

The project proposed the use of graphene and plasmonics to demonstrate an array of sensors that translate the EM power in temperature and thus into the deformation of a thin membrane that can be then detected optically using a compact-disk read-out analogy: The graphene Golay cells, GGC in short, will enable the realization of

- Portable THz inspection systems for security in uncontrolled and crowded open space
- Unmanned airborne inspection systems to control the status of large constructions such as concrete bridges, dams, etc,
- Unmanned airborne inspection systems for crop control in particular for watering, infections and maturation state

Thanks to the unique combination of micromachining technology, outstanding graphene properties and plasmonic approach the GGC will outperform existing technology in:

- Room temperature operation,
- Temperature independent performance,
- Low cost, large sensing areas,
- Spectral sensitivity.

In this paper we report on the main achievement obtained so far and in detail:

- the fabrication of GGC array
- the fabrication of the plasmonic gratings used to select provide spectral sensitivity to the GGC
- The development of alternative readout strategies.

2. STATE OF THE ART

While affordable THz laser sources are available on the market since the demonstration of the first quantum cascade THz laser by one of the authors [1], the development of affordable and low-cost THz detectors for imaging (the equivalent of the CCD for the visible light) was much slower. The bulky array of gear currently used to measure terahertz waves is clunky and expensive, making it impractical outside of a laboratory. Thus, most current multipixel THz-detector arrays are narrowband or require cryogenic temperatures [2,3] although microbolometer arrays offer great potential as they can detect large bandwidths at room temperature [4]. Alternative strategies use single pixel THz cameras in conjunction with spatial encoding masks [5], which however require a power consuming signal post processing stage. So far, the most promising approach for THz imaging relies on CMOS technology and FET plsamonic antennas which already proved sub nW/Hz NEP [6].

Terasense produces RT detectors with maximum 64x64 pixels based on electron plasma oscillation in GaAs electron gas with 1nW/Hz NEP.

In spite of the fast evolution in field of THz sensing and THz imaging both scientific and commercial, a leading technology has not emerged yet, and alternative strategies should still be developed in competition within each other to let emerge eventually a standard approach. Thermal arrays such as microbolometers show high sensitivity at RT, as low as 10pW/Hz [7].

Graphene, thanks to its outstanding physical and chemical properties, has been successfully exploited for the development of a huge number of applications in a variety of field, from physics to chemistry, from optics to biology [8], and is the natural candidate to form the flexible membrane of a miniaturized Golay cell array for THz imaging.

The device we are developing, is designed to have the following strengths:

- NEP better than 10nW/Hz using air as a filling gas and better than 1nW/Hz using water
- Array size up to 100x100 pixels using standard micromachining and microfabrication
- Spectral sensitivity using plasmonic filters
- Low cost fabrication using standard optics for read out.

3. PROJECT RESULTS

3.1 GGC fabrication and sealing optimization.

GGCs have been fabricated both on bulk silicon wafer and on suspended SiN membranes. The formers are intended to be filled during the fabrication step and not refillable while the latter should be filled after the fabrication and allow a larger choice of THz absorbers. Two transfer strategies have been tested, using MRI, a commercial photoresist used for nanoimprinting, and using Ti as a sacrificial layer, as already demonstrated in our lab [9].

As a reference a third strategy consisting in the transfer of a 10nm thick Ti-only membrane was tested successfully.

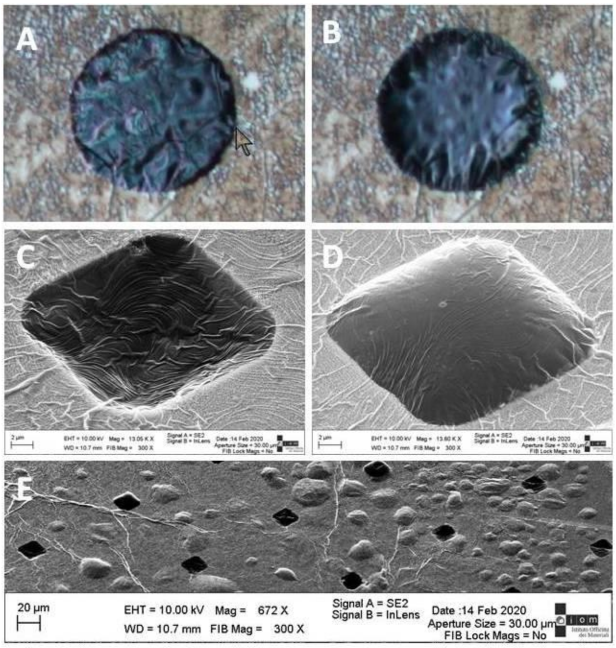

Fig. 1. A-D individual GGC membrane deposited on SiN open cells (A,B) and bulk Si closed cells (C,D), at rest (A,C) and under a pressure difference of 0.6 bar and 1 bar respectively (B,D). Figure 1E shows a detail of a large area array of GGCs.

The lowest leakage on SiN membranes were obtained by depositing a 10nm Ti/20nm Au adhesion layer on the SiN prior to the graphene transfer. These cells were able to withstand a pressure difference up to 0.6bar, which is by far exceeding the maximum pressure increase that we expect in our system to be 10Pa.

Bulk silicon cells, on the other hand, were able to withstand a pressure difference of 1bar when exposed to ultra vacuum conditions, without breaking.

Fig. 1 shows these membranes before and after the application of a pressure difference.

The response of the GGC to a thermal stimulus was first tested placing the cells on a Peltier heater. Several cycles at increasing temperature where performed showing a good reproducibility. The thermal tests, however did not allow to evaluate the response time of the systems, since the thermal inertia of the whole system, including the Peltier heater was dominating the temporal response. Fig. 2 shows the deformation of one membrane upon several thermal cycles as measured with an optical profilometer.

Finally array of membranes were fabricated with as much as 20x20 holes. Here the technological challenge consists in the production of very large defect free Graphene single layers. Layers as large as 10 mm^2 have been produced in the framework of a collaboration with the TU München. A detail of such arrays is shown in Fig. 1 E.

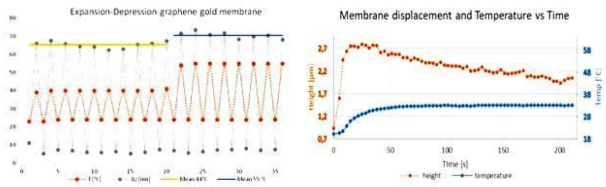

Fig. 2. The height response of a square membrane 100µm wide to a temperature variation. A cycle repetition does not affect the membrane response. B temporal stability after few minutes still shows the effect of not negligible leaks.

3.2 Raman characterization

Raman spectroscopy has been used to determine the residual stress of the graphene layer after deposition.

Fig. 2 shows three spectra taken on the supported membrane (position 1) on a defect on the suspended membrane (position 2), and on a good quality position of the same membrane (position 3). The data show that the supported graphene is highly defective compared with the suspended one, as indicated by the 2D peak. The defect is instead caused by an anomalous presence of TiO_2, as indicated by the two Raman peaks at 440 and 610 cm^{-1}. The position of the graphene peaks is not shifted indicating the absence of residual stress.

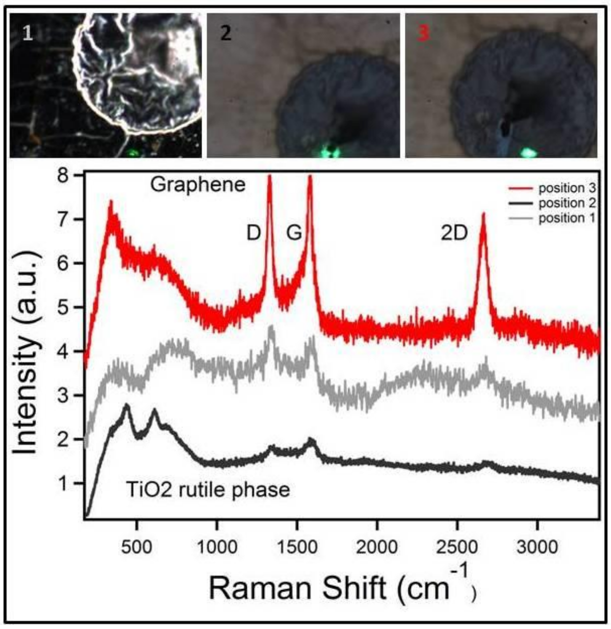

Fig. 3 . Raman spectra obtained with a 523nm laser excitation on Ti/Gr suspended and supported membranes.

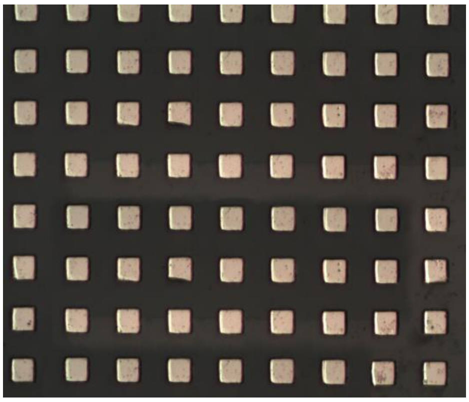

Fig. 4 Optical micrograph of a plsamonic grating which will be used to select the THz radiation.

3.3 Plasmonic grating fabrication

Plasmonic filters for THz radiation have been fabricated getting inspiration from the work of F. D'Apuzzo *et al.* [10]. The positive photoresist SPR 220 1.2 was spin coated on the SiN membranes then an array of square-shaped holes was fabricated with direct laser writer technique. A Cr/Au (10/100) bilayer was evaporated on the substrate and after lift-off process the desired array of gold squared pillars was obtained.

Fig. 4 shows a detail of the fabricated gratings.

3.4 GGC under THz radiation

A set up for testing the GGC stationary and steady state response under different THz irradiation, was assembled on the TeraFermi beamline at the Italian Free Electron laser – Fermi. Fig. 5B shows the set up during the first testing.

Unfortunately, due to the CoViD outbreak the tests were delayed due to restrictions in laboratory occupancy.

3.5 Reading approach

We envisaged two alternative strategies for the parallel read-out of the GGC response: capacitive and optical.

For what concerns the capacitive approach the major challenge is the precise alignment of the electrode array with the GGC graphene membrane. To overcome this problem during the tests we fabricated a specific AFM probe (see Fig. 5A) for which the distance with the membrane can be controlled with nanometric precision without losing the planarity. However the tests are still in progress.

For what concerns the optical response, we adopted a self-mixing approach which consist in measuring the interference between a laser light and its reflection inside the laser optical cavity. This measurement has showed in the past a z-sensitivity better than 100pm [11], therefore it could detect the smallest variation of the GGC membrane. As a preliminary result, in fig. 5B we display a profile of a Peltier-heated GGC membrane.

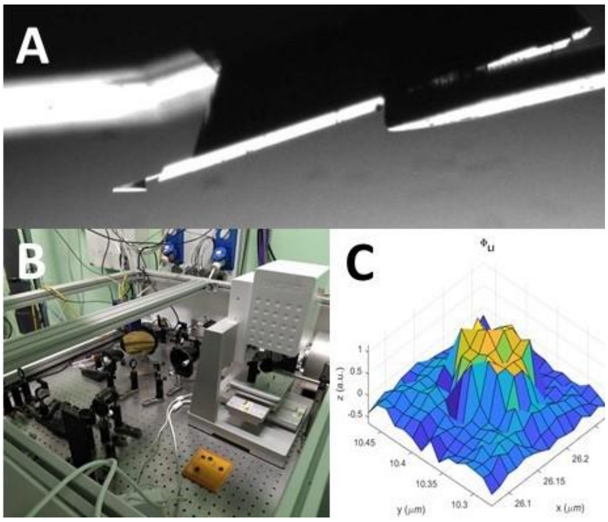

Fig. 5 . A: optical image of a cantilever used to measure the GGC deflection with the capacitive read-out. B: the set up installed at the TeraFermi beam line at the Fermi Free electron laser. C: height profile of a GGC membrane obtained by self-mixing interferometry.

4. FUTURE PROJECT VISION

4.1. Technology Scaling

Before the end of the year TRL 3 will be reached with the experiment planned at TeraFermi already rescheduled. By the end of the first semester of 2021 also the read-out electronic will completed and the device will be validated using lab equipment. This will be obtained still in the framework of attract phase 1, with internal resources.

The next stage will be the demonstration of TRL5. According to the results of the previous phase the best read-out scheme will be selected. The groups at Elettra e CNR-NANo Pisa will be deeply involved in this activity. The fabrication of reliable and large area GGC will be tackled by designing and outsourcing the implementation of an automated graphene-transfer tool. For the fabrication part we will benefit of the collaboration with a local company active in lithographic systems, ThunderNIL S.r.l. For the transfer tool, several companies could contribute. We will also need the reliable production of large and defect free graphene layer. As already highlighted in the report, the quality of commercial graphene is rather low and we will involve prof. Sebatian Günther from TU München.

The reach of TRL-7 will be fulfilled through mounting a compact system on an unmanned airborne vehicle (a drone) and obtaining images through a Wi-Fi connection. This task will require a further step of miniaturization and automation, as well as the integration in the system of a THz source. A suitable Wi-Fi connection will be designed with the help of Adants S.r.l. a company based in Padova specialized in smart and low consumption Wi-Fi communication. The THz sources will be devised by the CNR-NANO unit, a world-leader in the design of THz lasers and THz systems.

4.2. Project Synergies and Outreach

Beside the partners indicated above (namely **TU-München, ThunderNIL S.r.l and Adant Srl)**, we plan to take advantage of the already well-established connections within groups of the intra ATTRACT THz alliance (established on a meeting in Pisa on December 17, 2019). The activity will take full advantage of the experience behind the research groups of the T-**CONVERSE** and **ROTOR** projects for the sensor development especially in term of noise control and sensitivity. The **HYPERTERA** project will provide a significant support in the development of alternative optical read-out methods. An extremely valuable contribution will be provided by the **TACTICS** project which will provide an immediate application of the THz hyperspectral imaging to industrial applications, and thus help to define the best demonstration of the TRL6 – TRL9.

Dissemination will be one of the key activity in the phase 2, following the positive experience made in phase 1 with the intra ATTRACT THz alliance which was stopped by the CoViD outbreak. In particular we will organize joint conferences and schools focused on THz science and application. Following our recent experience as project leader of a large EU project on nanotechnology (Interreg ITA-SLO, nanoregion) we will realize video pills and short movies on the application of THz technology in everyday life. A dedicated YouTube channel will be created.

4.3. Technology application and demonstration cases

The application of the Grant results, namely light and portable THz colour camera to installed in remote control airborne vehicles are exemplified, but limited to the following:

- *Health, demographic change and wellbeing*

Control of failures in large building such as dams and railroad and motorway bridges, to prevent dramatic events as Genoa Morandi bridge collapse.

- *Food security, sustainable agriculture and forestry, marine and maritime and inland water research, and the Bioeconomy;*

Crop control, in particular evaluating the amount of water into plants and fruits, in order to provide the right amount of irrigation, thus saving water and increase agriculture efficiency without chemistry or genetic manipulation.

Forest control, monitoring the number of dead trees, the humidity of the undergrowth, preventing wood fires and invasions of tree parasites

- *Secure societies - protecting freedom and security of Europe and its citizens.*

Check people in large public events for hidden guns and knives, in order to prevent terroristic attacks.

4.4. Technology commercialization

One of the partners of the phase 1, Elettra, has an industrial liaison office branch that already commercializes sensor and detectors for an overall yearly turnover of more that 2M/€. The project partnership will be enlarged to some private companies; moreover some members of the *intra ATTRACT THz alliance* are also privately owned organization and companies.

The enlarged consortium will define a commercialization strategy as soon TRL 5 level is reached

4.5. Envisioned risks

The main risk stem in the poor reliability of commercial graphene. In spite of the huge visibility that this material had on the media, the graphene production technology is still problematic, and commercial graphene is still defective and degrades fast.

Our mitigation strategy is twofold. We will involve in the project a collaborator at TU-München who is obtaining excellent results in producing large area defect free graphene single and multilayers. We are testing alternative materials: we already demonstrated the fabrication of Golay cells covered with a 10nm thick Ti layer; a collaborator of ours, Virgilio Mattoli from IIT-Pisa also produces ultra-thin polymeric films that could be used as a replacement of the graphene if this would demonstrate unreliable.

4.6. Liaison with Student Teams and Socio-Economic Study

The *intra ATTRACT THz alliance* organized a session at the THz-Bio 2020 9th International THz-Bio Workshop, which, because of the onset of the CoViD outbreak was postponed to March 14 – 19, 2021. The school was targeting mainly undergraduate and PhD student and the Attract staff was involved in this activity.

Similar initiative, more traditional schools as well more interactive hackathon will be organized by the consortium also in collaboration with the attract team.

I particular topics like "innovative application in everyday life of GGC technology" will be addressed.

Satellite schools on optics and graphene technology will also be organized.

Finally, an international school on "THz science and application in the developing countries" will be promoted in collaboration with the International Center for Theoretical Physics ICTP in Trieste.

Contribution from the schools as well as interviews with the consortium scientist and socio-economical experts will be regularly uploaded on the project YouTube channel.

5. ACKNOWLEDGEMENT

Authors thank: Paul Leidinger and Sebastian Günther from TU München for providing high quality, large surface, and low defect density graphene monolayers and bilayers; Damian Svetin and Dragan Mihailovic for providing access to the direct laser writing tool

This project has received funding from the ATTRACT project funded by the EC under Grant Agreement 777222

The access to the DLW tool at Jozef Stefan institute Ljubljana (SLO) received support from the ITA-SLO interreg project "NanoRegion"

7. REFERENCES

[1] Rüdeger Köhler, Alessandro Tredicucci, Fabio Beltram, Harvey E. Beere, Edmund H. Linfield, A. Giles Davies, David A. Ritchie, Rita C. Iotti & Fausto Rossi 2002 Terahertz semiconductor-heterostructure laser Nature 417, 156–159

[2] Escorcia, I., Grant, J., Gough, J. & Cumming, D. R. S. (2016) Uncooled CMOS terahertz imager using a metamaterial absorber and pn diode. Opt. Lett. 41, 3261–3264 (2016).

[3] Rogalski, A. & Sizov, F. (2011).Terahertz detectors and focal plane arrays. Opto- Electron. Rev. 19, 346–404

[4] Amanti, M. I., Scalari, G., Beck, M. & Faist, J. (2012).Stand-alone system for highresolution real-time terahertz imaging. Opt. Express 20, 2772–2778.

[5] Stantchev, R.I., Yu, X., Blu, T., Pickwell, Mac Pherson, E. 2020 Real-time terahertz imaging with a single-pixel detector Nat. Comm. 11(1),2535-2542

[6] Khatib, M., Perenzoni, M. 2018 A Low-Noise direct incremental A/D converter for FET-Based THz imaging detectors Sensors (Switzerland) 18(6),1867

[7] Aleksander Sesek, Andrej Zemva, Janez Trontelj 2018 A Microbolometer System for Radiation Detection in the THz Frequency Range with a Resonating Cavity Fabricated in the CMOS Technology : Recent Patents on Nanotechnology 12, pp 34 – 44

[8] Zhu, Y., et al. 2010 Graphene and graphene oxide: Synthesis, properties, and applications. Advanced Materials 22(35), pp. 3906-3924

[9] A Matruglio, M. Lazzarino, S. Dal Zilio 2016 Contamination-free suspended graphene structures by a Ti-based transfer method Carbon 103 305-310

[10] F. D'Apuzzo at al. 2015 Resonating Terahertz Response of Periodic Arrays of Subwavelength Apertures Plasmonics 10:45–50

[11] L. Baldacci, A. Pitanti, L. Masini, A. Arcangeli, F. Colangelo, D. Navarro-Urrios & A. Tredicucci, Thermal noise and optomechanical features in the emission of a membrane-coupled compound cavity laser diode, Sci. Rep. 6, 31489 (2016)