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Micro-supercapacitors on silicon with superior power densities based on solid source MXenes growth

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14. ABSTRACT
Building further on the key knowledge developed during our 17IOA027, which allowed us to isolate the graphene from the SiC/Si substrate, we have established that we can obtain large -scale epitaxial graphene, and for the first time we have shown a thorough evaluation of the charge transport properties. This is a milestone for the pursuing applications of this graphene in electronics, photonics and energy.
Specifically, in the supercapacitors area, we confirm that the solid –state synthesis of MXenes has not led to notable results, indicating that this approach may be too challenging. However, we have:
1) Focused on the fundamental physical and chemical mechanisms behind the electrodes/gel electrolyte interface, which has led to the invention of an agent-free, fully in-situ functionalization of the graphene electrodes leading to greatly enhanced capacitance, Coulombic efficiency and cyclability, thanks to the addition of stable faradaic reactions sites. This work has earned a VIP mention, as well as front cover feature on Batteries & Supercaps, Wiley;

2) We have initiated an ongoing collaboration including AFRL and Sandia Nat Labs using the CINT/Sandia environmental TEM to study electrode/electrolyte interfaces; the Covid situation has slowed down this investigation, but Sandia is likely to extend the award;

3) We have shown an alternative 2D material stacking for enhanced capacitance, using a layer of MoS_2 grown on the graphene on SiC/silicon. This research is about to be published and indicates that the combination of high-quality graphene and MoS_2 as layered electrodes greatly enhances the capacitance of the supercapacitor cells. We argue that this is because the graphene offers high conductivity (unavailable in MoS_2), while the TMD material allows for a high area available for storage.

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"Micro-supercapacitors on silicon with superior power densities based on solid source MXenes growth"

Date 21st August 2020

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Period of Performance: 08 /24/2018 – 08/23/2020 (Final)

Summary:

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List of Publications and Significant Collaborations that resulted from your AOARD supported project:

a) papers already published in peer-reviewed journals:

1) L.Jiaxing, A.Mondal, D.Wang and F.Iacopi, "Graphene-based micro-supercapacitors: Recent advances and future challenges", Invited Review, Adv.Mater. Technol. 4 (1), 1800200, 2019.
This is a complete overview of status and perspectives of the broad area of microsupercapacitors based on graphene or hybrid graphene-2D materials electrodes, including progress on solid –state electrolytes.

2) N.Mishra, M.Bosi, F.Rossi, G.Salviati, J.Boeckl, F.Iacopi, "Direct growth of graphitic carbon layers around silicon carbide nanowires", Journal of Applied Physics 126, 065304, 2019.
This paper shows the first demonstration of the capability of coating SiC nanowires with graphene using our catalytic alloy method, as opposed to flat SiC surfaces. These graphene –coated nanowires have potential use in areas going from biosensing, field –emission, photonic absorbers, to energy storage materials. This demonstration also confirms the capability of this graphitization process to coat with graphene any type of 3D SiC surface, which is key for photonic applications.

3) A.Pradeepkumar, M.Amjadipour, N.Mishra, C.Liu, M.S. Fuhrer, A.Bendavid, F.Isa, M.Zielinski, H.I. Sirikumara, T.Jayasekara, D.K.Gaskill and F.Iacopi, "p-type Epitaxial Graphene on Cubic Silicon Carbide on Silicon for Integrated Silicon Technologies", ACS Appl. Nano Mater. 3 (1), 830-841, 2020.
This is the first report of electronic transport properties of epitaxial graphene on SiC on silicon via actual electrical measurements. This pioneering work was enabled by our large –scale graphene coverage and understanding of the unstable SiC/Si interface junction issue. Main results are that 1) we obtain characteristics very similar to those on bulk SiC, in particular our conductivity is very comparable 2) the graphene electronic characteristics are dominated by the interaction with the SiC surface, not by the grain size 3) we have a large p-type doping originated by charge –transfer from the oxidised SiC substrate. This all indicates that if we can control the EG/SiC interface with an appropriate intercalation to tune the charge transfer, this EG could play a key role in integrated systems

4) M.Amjadipour, D.Su and F.Iacopi, "Additive -free Activation of Redox Reactions in Quasi-Solid-State Supercapacitors with Graphitic Electrodes", Batteries & Supercaps, 3, 587 –595, 2020 (**VIP paper**; also **Invited Front Cover** and Cover Profile).
This paper follows up an invention filing (now at PCT stage) where we indicate the capability for greatly increasing the performance of graphene/ PVA-H_2SO_4 supercapacitors, by enhancing both electrochemical double-layer capacitance and redox capacitance, with no added external agent. We obtain this through an in-situ electrochemical functionalisation of the graphenic electrodes involving electrolysis reactions in the electrolyte material, inducing further oxidation hence a larger inter-layer

spacing and better wettability, promoting thus a better interlayer dispersion of the PVA and enhanced performances. The redox reactions seem to be also related to morphological properties of the electrodes. This will be further studied through our experiment planned in Sandia.

5) A.Pradeepkumar, D.K.Gaskill and F.Iacopi, "Electronic and Transport Properties of Epitaxial Graphene on SiC and 3C-SiC/Si: A Review", Applied Sciences 10 (12), 4350, 2020.
   This is a comprehensive review of the transport properties of epitaxial graphene on silicon carbide and silicon carbide on silicon. Emphasis is put on the importance of the interfaces and their control to tune the transport in graphene.

6) P.Rufangura, T.G.Folland, A.Agrawal, J.D.Caldwell, and F.Iacopi, "Towards low- loss on-chip nanophotonics with graphene and silicon carbide: a review", J. Phys. Mater. 3, 032005, 2020.
   This review points towards the promise of the epitaxial graphene on silicon carbide combination to obtain superior light absorption and confinement, thanks to the hybridization of the plasmon polariton in the graphene and phonon-polariton in the SiC. Our technology, which allows for the synthesis of complicated shapes of any type made of graphene on silicon carbide, together with the potential for dynamic tuning of the transport in the graphene, is of great promise for metamaterials. The promise behind this work has earned us a place in the newly established ARC Centre of Excellence in Transformative Meta-Optical Systems.

b) Paper just accepted:
   1) M.Amjadipour, J.MacLeod, N.Motta, and F. Iacopi, "Fabrication of free-standing silicon carbide on silicon microstructures via massive silicon sublimation", accepted in J Vacuum Science and Technology B, Sept 2020
      We show in this work that the extent of stresses at the silicon/silicon carbide interface is so large that after patterning of the SiC, a massive sublimation of the silicon underneath the SiC/Si interface is promoted via a high temperature anneal, either in high or medium vacuum ambient. A micron-thick air gap can be formed below the SiC structures, making them suspended. Hence, the described approach can be used as a straightforward methodology to form free-standing silicon carbide structures without the need for wet or anisotropic etching and could be of great interest for devices where suspended moving parts are needed, such as micro- and nano-electromechanical systems.

c) Paper in preparation:
   1) M.Amjadipour, J.Bradford, N.Zebardastan, N.Motta, F.Iacopi, "Epitaxial graphene/MoS_2 layered electrodes for solid-state supercapacitors", in preparation for Applied Surface Science.
      This work indicates that the combination of high-quality graphene and MoS_2 as layered electrodes greatly enhances the capacitance of the supercapacitor cells. We argue that this is because the graphene offers high conductivity (unavailable in MoS2), while the TMD material allows for a high area available for storage. In addition, we show that MoS_2 on

good quality graphene tends to grow vertical crystals, such that a maximum accessible area for storage can be obtained. We argue that this approach is key in order to take advantage of MoS_2 for energy storage.

d) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

1. Dr.John Boeckl, WPAFB, AFRL, USA
    i. The close collaboration with Dr.Boeckl from WPAFB continues through the current AOARD project as well as the IC R&D on nanophotonics. I have met with Dr.Boeckl at the DSL2019 conference under a WoS (see corresponding report), where among others, we have discussed the preparation of the experiment at Sandia Labs (with Dr.Katie Jungjohann) where we will focus on the understanding in-situ of the micro/nanoscale mechanisms at the graphene electrode/electrolyte. The preparation for this TEM experiment is particularly complex and has required my post –doc Mojtaba Amjadi Pour to work with Dr.Boeckl in Dayton.
    ii. We have received an add-on travel grant from AOARD for my post-doc Mojtaba Amjadipour to carry out TEM preparation work with Dr.Boeckl's team in Dayton. The visit has taken place over 28th Oct -9th Nov 2019 (see corresponding report). A follow-on proposal to CINT, Sandia Labs, has been submitted and awarded for 2020 for in-operando environmental TEM analysis of supercapacitors. Unfortunately, so far the planned further work in AFRL and Sandia has been greatly delayed due to Covid-19 restrictions. We are in discussions for a further extension of this experiment.
    iii. The IC R&D project on graphene/SiC nanophotonics awarded to Boeckl is now in the operational phase, as an US-Australian collaboration involving AFRL, Prof. Josh Caldwell at Vanderbilt U, the Australian DST (Dr.Dennis Delic) and Prof.Iacopi at UTS. Prof.Iacopi has also obtained a DST grant through Dr.Delic to support a PhD student for 3 years (Mr.Patrick Rufangura).
2. Dr.Katheryn Jungjohann, Sandia Labs
    i. She is the TEM scientist at the Centre for Integrated NanoTechnologies at Sandia, collaborating on the experiment above under a granted project to Prof.Iacopi by the Sandia National Laboratory.

3. Dr.Josh Caldwell, ex NRL, now Vanderbilt U, USA
    i. Partner in the IC R&D nanophotonics project, with Dr.Boeckl and Prof.Iacopi

4. Dr.Kurt Gaskill, recently retired from NRL, USA
    i. Dr.Gaskill is jointly supervising a PhD student in my group, Ms.Aiswarya Pradeepkumar, who is completing her thesis on the electronic properties of graphene on SiC/silicon. Dr.Gaskill continues to be a valuable collaborator in the area of graphene transport, and will visit again UTS in October 2019.

5. Dr.Matteo Bosi and Dr.Giancarlo Salviati from CNR, Italy
   Their collaboration has enabled our work on SiC nanowires, as well as further experiments on SiC on silicon, which they grow in-house. Further collaborations with them are expected in the area of photonics and biosensing.

6. Industry
   i. Dr.Zielinski from NovaSiC and CNRS (France), is continuing to collaborate with us on the growth of 3C-SiC and graphene. Further focus on the growth of SiC on SOI and SOS, as well as on intrinsic silicon will be further explored as key for supercapacitor and MEMS devices, as well as high frequency applications of graphene.

e) Updates regarding professional appointments for the lead CI Prof.Iacopi
   1. At UTS, where I am Full Professor in Electronics and head of the Integrated Nanosystems Lab (2 post-docs, 2 PhD students and 2 undergraduate students), I have stepped down from the management of the Communications and Electronics Discipline to become **Chief Investigator in the recently awarded ARC Centre of Excellence in Transformative Metaoptical Systems (TMOS**, https://tmos.org.au/). This Centre, comprising 15 CIs from 5 Australian Universities, has been awarded $34.9M for the next 7 years under the leadership of Prof.Dragomir Neshev at ANU. This appointment will allow my group to establish a long-term research in metaoptics and nanophotonics based on epi graphene on silicon carbide, and to continue the long-standing collaboration with AFRL and DST.
   2. I have been appointed in 2018 as member of the **Electronic Materials Committee of the IEEE Electron Device Society**, led by Prof.Paul Berger from OSU https://eds.ieee.org/about-eds/governance/technical-committees/electronic-materials-committee
   3. I have been appointed in 2019 as **representative for the IEEE EDS to the International Roadmap for Devices and Systems**, IRDS https://irds.ieee.org/, where I will be particularly active in the Emerging Research Materials chapted. The IRDS replaced the ITRS a couple of years ago, when Moore's Law ceased to be the only driver for electronics.
   4. As of Dec 2019, I am also the Founder and Chair of the IEEE Electron Devices Society Chapter in New South Wales https://site.ieee.org/nsw/electron-devices-society/
   5. I continue being a member of the **Awards Committee of MRS** (David Turnbull Lectureship).
   6. I have also continue as **Associate Investigator in the Centre of Excellence for Future Low-Energy Electronic Technologies**, FLEET, http://www.fleet.org.au/, led by Prof.Michael Fuhrer at Monash University.

DD882: As a separate document, please complete and sign the inventions disclosure form. If no inventions, put N/A in boxes 5 a/b.

Inventions update from 17IOA027 and 18IOA052:

- "Electrical isolation structure and process", F.Iacopi and A.Pradeepkumar, PCT/AU2018/050999, filed on 13 September 2018.

- "A solid state supercapacitor and a process for producing a solid-state supercapacitor", F.Iacopi, M.Amjadipour, D.Su and PCT/AU2020/050812, filed on 6th August 2020.