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Graphene on SiC as Outstanding Functional and Structural Material for Applications from the Nano- to the Macro-scale

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14. ABSTRACT
The PI has had excellent results for this grant award. The current grant is a follow on to a previous grant to the PI. With this grant, the PI has been able to 1) understand the fundamental mechanism by which the SiC/silicon substrate used for graphene synthesis is electrically unstable and 2) implement a strategy to electrically isolate the synthetized graphene and to ensure the devices incorporating the graphene on SiC/silicon are electrically insulated from the substrate, and thus technologically viable. As a result the PI has been able to observe a graphene with sheet resistance varying in the few thousands ohms/sq, with a rather smooth behavior over a large range of temperatures (from 75K to around 500K), which is an expected graphene characteristic and directly comparable to epitaxial graphene properties on bulk SiC as published by the De Heer group. This is a first for graphene grown on SiC/silicon, and this result is able to confirm the large -scale coverage obtainable using our catalytic alloy synthesis.

As a direct result of the grant, the PI has had 6 peer reviewed journal articles, 1 edited book, and one edited book chapter. The PI also collaborates directly with a researcher in the Materials and Manufacturing Directorate at Air Force Research Lab along with many other DoD researcher (NRL) and US university PIs.

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Final Report for AOARD Grant 17IOA027

"Graphene on SiC as outstanding functional and structural nanomaterial for applications from the nano- to the macroscale"

Date 22nd May 2018

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Period of Performance: 04 /21/2017 – 04/20/2018

Summary:

During our previous projects, we have introduced and further refined a pioneering approach to the synthesis of monolayer graphene directly on silicon wafers, based on solid source growth from hetero-epitaxial SiC films. The work supported by 17IOA027 has led to a pivotal point, which is the 1) understanding of the fundamental mechanism by which the SiC/silicon substrate used for graphene synthesis is electrically unstable and 2) the implementation of a strategy to electrically isolate the synthetized graphene and to ensure the devices incorporating the graphene on SiC/silicon are electrically insulated from the substrate, and thus technologically viable.
Thanks to this advance, we have been able to observe a graphene with sheet resistance varying in the few thousands ohms/sq, with a rather smooth behavior over a large range of temperatures (from 75K to around 500K), which is an expected graphene characteristic and directly comparable to epitaxial graphene properties on bulk SiC as published by the De Heer group.
This is a first for graphene grown on SiC/silicon, and this result is able to confirm the large -scale coverage obtainable using our catalytic alloy synthesis.

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

a) papers published in peer-reviewed journals:

1) A.Pradeepkumar, N.Mishra, A.R.Kermany, J.J.Boeckl, J.Hellerstedt, M.S.Fuhrer, F.Iacopi, "Response to "Comment on 'Catastrophic degradation of the interface of epitaxial silicon carbide on silicon at high temperatures'" [Appl. Phys. Lett.109, 196101 (2016)]", 109, 196102, 2016.
2) A.Pradeepkumar, K.D.Gaskill, F.Iacopi, "Electrical challenges of epitaxial 3C-SiC on silicon", accepted in Mat.Sci.Forum 2017.
3) A.Pradeepkumar, M. Zielinski, M. Bosi, G. Verzellesi, D. K. Gaskill, F. Iacopi, "Electrical leakage phenomenon in heteroepitaxial cubic silicon carbide on silicon", accepted in Journal of Applied Physics, May 2018.

The papers above are all part of the work of understanding of the electrical properties of the complex SiC/silicon heterojunction, topic of my PhD student A.Pradeepkumar. The first paper is a response to a comment from our Griffith ex-colleague Prof.Dimitrijev, arguing that the Griffith SiC on silicon did not show the electrical instabilities that all of the other SiC on silicon material were reported to possess in our previous APL publication. In our response, we show that this issue is universally present in all of the material we analysed from different suppliers world-wide, including Griffith. The only difference is that the Griffith material shows this problem only after an anneal, since the heteroepitaxy is performed at low temperature in their case.

The second paper is from the proceedings of the International Conference on Silicon Carbide and Related Materials (ICSCRM) 2017, held in Washington DC. The paper was presented by the student, supported through this AOARD grant to attend the conference and visit NRL, and it indicated that the leakage between physically separate SiC structures on silicon is unavoidable when using doped silicon substrates, but can be drastically reduced using highly resistive silicon, and further, entirely suppressed when a deep recess is etched in the silicon between the SiC structures (several microns).

Finally, the third paper has just been accepted for publication in the Journal for Applied Physics, and illustrates for the first time the basic mechanisms at the origin of the SiC/silicon p-n junction breakdown. This issue had been known in the community for a long time, but never fully understood. We now explain that the problem is due to the large amount of C atoms diffusing interstitially in the silicon substrates, generating mid-bandgap traps for the hole majority carriers in p-silicon. Also, interstitial carbon is responsible for residual leakage when using highly -resistive silicon. Nevertheless, we show in this work an approach to suppress in-plane leakage between SiC structures, which is also crucial for the application of graphene devices grow on SiC/Si substrates.

4) Z.H.Khan, A.Oechsner and F.Iacopi, “Mechanical and Electromechanical Properties of Graphene and their Potential Applications in MEMS”, topical review, J.Appl.Phys.D, 50 (5), 053003, 2017.

   This paper reviews predicted and experimental properties of graphene for application in micro and nano-electromechanical systems. A section of this paper covers literature studies of piezoelectric properties induced in graphene (graphene is not a piezoelectric material by nature). This work has attracted the interest of researchers of the local DST, Maritime Division for potential applications of 2D materials in sonar systems.

5) N.Mishra, J.J. Boeckl, A.Tadich, R.T. Jones, P.J.Pigram, M.Edmonds, M.S. Fuhrer, B.M. Nichols, and F.Iacopi, “Solid source growth of graphene with Ni-Cu catalysts: towards high quality in-situ graphene on silicon”, J. Phys. D: Appl. Phys.50, 095302, 2017.

   In this work we hypothesize the mechanisms by which our solid source growth of graphene mediated by a thin Ni–Cu alloy leads consistently to a monolayer graphene, being to-date the best quality monolayer grown on epitaxial silicon carbide films on silicon.

   We conclude that (1) the oxidation, amorphisation and silicidation of the silicon carbide surface mediated by the Ni, (2) the liquid-phase epitaxial growth of graphene as well as (3) the self-limiting graphitization provided the molten Cu catalyst, are key characteristics of this novel synthesis method. In addition, the liquid -phase nature of this epitaxial process guarantees a higher -quality growth even on highly - defective templates like the SiC on silicon.

6) M.Ahmed, B.Wang, B.Gupta, J.J.Boeckl, N.Motta, F.Iacopi "On-silicon Supercapacitors with Enhanced Storage Performance", Journal of The Electrochemical Society, 164 (4) A638-A644, 2017.

   In this paper we point out how to improve the efficiency of few -layers graphene electrodes for supercapacitors and achieve a maximum accessible area for ion exchange, which is a typical limitation of stacked 2D materials. We use a repeated graphitization strategy using a nickel catalyst on epitaxial silicon carbide films on silicon to obtain a few-layers graphenic nanocarbon electrodes with prominent edge defects, facilitating the intercalation between multiple graphenic sheets while maintaining overall a high electrode conductivity. This work sets a path that can potentially be extended also beyond graphitic carbon to encompass other 2D materials like MXenes, which are expected to be very promising materials as electrodes for supercapacitors.

b) Edited books
   1. "Growing graphene on semiconductors", edited by N.Motta, F.Iacopi and C.Coletti, PanStanford Publishing, 350 pp, ISBN 9814774219, May 2017.

   This is the first book that comprehensively reviews the progress of direct synthesis of graphene onto semiconductor substrates such as silicon carbide and silicon.

c) Book chapters
   1. "The significance and challenges of direct growth of graphene on semiconductor surfaces", N.Mishra, J.Boeckl, N.Motta and F.Iacopi, in "Growing graphene on semiconductors", edited by N.Motta, F.Iacopi and C.Coletti, PanStanford Publishing, Singapore, 2017.

d) Unpublished work:
   There are a number of findings generated during this period that are still awaiting publication, as the respective studies are still ongoing:
   a. coverage of graphene on SiC/silicon and its relation to graphene adhesion and tribological properties (in collaboration with Prof.Dauskardt in Stanford and Prof.Carpick in U of Pennsylvania)
   b. electrical transport characteristics of graphene on SiC/silicon

e) 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 has continued throughout the past year, resulting in the co-authorship of several of the above -listed papers. Dr.Boeckl has been part of a new beamtime at the Australian Synchrotron in Melbourne, joined by my post-doc Neeraj Mishra for the analysis of graphene on grown on SiC(111) and SiC(100). Dr.Boeckl has also visited at UTS in Aug 2017, and is since a few months, Adjunct at UTS.

ii. Also the IC R&D project on graphene/SiC nanophotonics awarded to Boeckl is being finalized as an US-Australian collaboration involving AFRL, Prof. Josh Caldwell at Vanderbilt U, the Australian DST (Dr.Dennis Delic) and Prof.Iacopi at UTS.

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

3. Dr.Kurt Gaskill, NRL, USA
   i. Dr.Gaskill is jointly supervising a PhD student in my group, Ms.Aiswarya Pradeepkumar, who is focusing on the electronic properties of graphene on SiC/silicon.
   ii. Dr.Gaskill has visited early 2017 at UTS, while Ms.Pradeepkumar has visited NRL in the occasion of her attendance of ICSCRM 2017 in sept 2017 in DC The exchanges and collaboration have led to joint publications.

4. Prof.Robert Carpick, USA
   i. A collaboration with Prof Carpick was prompted by the interest in studying the tribological properties of the graphene grown on SiC/silicon. Samples have been exchanged and data is being generated for the first time in this area.

5. Prof.Yury Gogotsi
   i. One of the WoS has supported a scientific meeting among myself, Dr.Boeckl and Prof.Gogotsi at Drexel, Philadephia. Prof.Gogotsi is the discoverer of the MXenes class of 2D materials. While MXenes are still a relatively novel class, research in this area is growing exponentially due to the possibility for tailoring properties by using different M-X combinations and different number of layers. Since all of these materials are now solution -based, Prof.Gogotsi was interested in exploring the translation of our solid-state growth approach from graphene to MXenes, which will be the topic of our current AOARD application.

6. Dr.John Vanvelzen and Dr.Scott Foster, DST Maritime Division, Edinburgh, SA, Australia

   The researchers from the Maritime Division of DST expressed interest in understanding whether graphene (or other 2D materials) could be potentially used for augmenting sonar systems. This has led to a small exploratory grant to my group in this specific area.

7. Industry
   i. NovaSiC (France), with major business the polishing of SiC wafers as well as the growth of heteroepitaxial 3C-SiC on silicon, has been engaged in a collaboration to identify solutions to the leakage at the heteroepitaxial junction. Growth of SiC on SOI and SOS, as well as on intrinsic silicon has been explored. This learning will be particularly useful for interdigitated supercapacitor structures.

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