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Graphene on SiC as Outstanding Functional and Structural Nanomaterial with Applications from the Nano- to the Macroscale - 154032

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14. ABSTRACT
This research project uses a novel approach to the synthesis of high-quality and highly uniform few-layer graphene on silicon wafers that is based on solid source growth from hetero-epitaxial SiC films and represents a promising avenue for a graphene technology on silicon. The current funding period involved further analysis and refinement of the comprehension of synthesis mechanisms and graphene physical, chemical, electrochemical, electrical, electronic and mechanical properties. A critical issue was identified in the SiC/silicon system that affects previous electrical and electronic evaluations of graphene. It was determined that SiC/silicon interface breaks down under high temperature anneal and/or high temperature growth, and thus leads to an effective shorting with the silicon substrate. This is a crucial understanding as it allows revision of the fundamental understanding of the p-type conduction of graphene, which is going to be a crucial issue for any research group attempting to grow graphene or III-V materials (GaN) on SiC/silicon. The research suggests that using a more robust barrier between SiC and SiC, as recently shown by Japanese researchers, provides a workable solution. This finding applies to any attempt to use SiC/silicon for harsh environment devices. Further insight into synthesis mechanisms of the catalytic alloy-mediated graphene on SiC/silicon established that oxygen plays a key role, and that this method leads to the prevalent formation of a monolayer graphene on a buffer carbon layer, which is an important factor in exceptionally high adhesion of this graphene to the substrate. It was demonstrated that graphene on SiC/silicon is a path towards high performing integrated supercapacitors, which obtained energy densities higher than state-of-the-art thin-film Li-ion batteries, and thus find application in miniaturized supercapacitors.

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

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Summary:

During our previous project, we have pioneered a novel approach to the synthesis of high-quality and highly uniform few-layer graphene on silicon wafers, based on solid source growth from hetero-epitaxial SiC films, as the most promising avenue for a graphene technology on silicon. In the current project, on the one hand we analyze and refine the comprehension of the synthesis mechanisms and the graphene physical, chemical, electrochemical, electrical, electronic and mechanical properties, while on the other hand, we explore the most promising application of this novel platform.

The main new results produced by the current project so far can be summarized as follows (see papers for details):

1. We have been able to identify a critical issue in the SiC/silicon system which affects our previous electrical and electronic evaluation of graphene. The SiC/silicon interface breaks down under high temperature anneal and/or high temperature growth, leading to an effective shorting with the silicon substrate (A.Pradeepkumar et al, APL 2016). This is a crucial understanding as it not only allows us to revise our own statement on the p-type conduction of graphene, but it is going to be a crucial issue for any research group attempting to grow graphene or III-V materials (GaN) on SiC/silicon. We also suggest that the solution is to use a more robust barrier between SiC and SiC, as recently shown by the Suemitsu group in Tohoku. This also equally applies to any attempt to use SiC/silicon for harsh environment devices.
2. We have achieved more insight on the synthesis mechanisms of the catalytic alloy -mediated graphene on SiC/silicon. We have established that oxygen plays a key role in the synthesis, and that our method leads to the prevalent formation of a monolayer graphene on a buffer carbon layer. The significance is that a) we confirm previous reports by researchers at AFRL that oxygen plays an additional catalytic role for the synthesis of nanocarbon from SiC and b) proves the presence of a buffer layer as an important factor in the exceptionally high adhesion of this graphene to the substrate.
3. We have recently demonstrated graphene on SiC/silicon as a path towards high -performing integrated supercapacitors, obtaining energy densities higher than state-of-the-art thin -film Li-ion batteries. This type of approach could be used to produce miniaturized supercapacitors faster, safer, and with longer lifetime than batteries, which can be integrated in devices from consumer (smart cards, wearable computers) to healthcare (endoscopic and implantable monitoring systems).
4. One advantage of our graphene synthesis the possibility for realizing easily graphene/SiC MEMS and plasmonic microstructures for highly superior (bio)sensing though the

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pre-structuring of the SiC solid source on silicon at the wafer -level. We have further refined our patterning capabilities for SiC and evaluated the sensing performance before coating with graphene. Our next step will be the evaluation of the structures with the graphene coating, including plasmonics. This part of our activity led to several publications including one exploring specifically the opportunity for label -free, high throughput and miniaturized biosensing. In addition to drug -screening, healthcare applications such as endoscopic and implantable sensing devices could be envisaged.

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, "Catastrophic degradation of the interface of epitaxial silicon carbide on silicon upon thermal stress", Applied Physics Letters 109, 011604, 2016.

Epitaxial cubic silicon carbide on silicon is of high potential technological relevance for the integration of a wide range of applications and materials with silicon technologies, such as micro electro -mechanical systems, wide-bandgap electronics, and graphene. The hetero-epitaxial system engenders mechanical stresses at least up to a GPa, pressures making it extremely challenging to maintain the integrity of the silicon carbide/silicon interface. In this work, we investigate the stability of said interface and we find that high temperature annealing leads to a loss of integrity. High–resolution transmission electron microscopy analysis shows a morphologically degraded SiC/Si interface, while mechanical stress measurements indicate considerable relaxation of the interfacial stress. From an electrical point of view, the diode behaviour of the initial p-Si/n-SiC junction is catastrophically lost due to considerable inter-diffusion of atoms and charges across the interface upon annealing. Temperature dependent transport measurements confirm a severe electrical shorting of the epitaxial silicon carbide to the underlying
substrate, indicating vast predominance of the silicon carriers in lateral transport above 25 K. This finding has crucial consequences on the integration of epitaxial silicon carbide on silicon and its potential applications.
In particular, related to our previous work, this finding indicates that our early interpretation wrongly attributed the presence of high p-type conduction in the graphene on SiC/silicon, whereas we now understand that that conduction was appearing because of the breakdown of the SiC/silicon interface during the graphitization anneal.

2. A.R.Kermany and F.Iacopi, "Controlling the intrinsic bending of hetero-epitaxial silicon carbide micro-cantilevers", Journal of Applied Physics 118, 155304, 2015.

We introduce a simple methodology to predict and tailor the intrinsic bending of a cantilever made of a single thin film of hetero-epitaxial silicon carbide grown on silicon. We demonstrate experimentally that a silicon carbide cantilever made of one distinct film type can be engineered to obtain the desired degree of either upward, flat, or downward bending, by selecting the appropriate thickness and cantilever geometry. A precise control of cantilever bending is crucial for microelectrical mechanical system applications such as micro-actuators, micro-switches, and resonant sensors. These cantilevers can be coated in-situ with graphene as per our earlier methods to achieve graphene/SiC composite cantilevers for sensing and actuation.

3. A.R.Kermany, J.S.Bennett, G.A.Brawley, W.P.Bowen, and F.Iacopi, “Factors affecting the f x Q product of 3C-SiC microstrings: what is the upper limit for sensitivity?”, Journal of Applied Physics 119, 055304, 2016.

We explore the f_n x Q (Hz) sensitivity parameter and thus evaluate the ultimate achievable sensitivity for micro-electro-mechanical (resonant) mass sensing. We have recently shown a f_n x Q product of 10^{12} Hz for microstrings made of cubic silicon carbide on silicon, establishing a new state-of-the-art and opening new frontiers for mass sensing applications.
In this work, we analyse the main parameters influencing the frequency and quality factor of silicon carbide microstrings and indicate that our previous result is only about a factor 2 lower than the ultimate thermoelastic dissipation limit. For fully reaching this upper limit, a substantial reduction of the defects in the silicon carbide thin film would be required, while maintaining a high residual tensile stress in the perfect-clamped strings.

4. O.Cooper, B.Wang, C.Brown, J.Tiralongo, F.Iacopi, “Towards label-free biosensing with silicon carbide: a review”, invited paper in IEEE Access 4 (1), 477- 497, 2016.

Recent innovation in microelectrical-mechanical systems (MEMSs) and plasmonics-based technologies has opened up perspectives for label-free sensing of biological and chemical analytes. Label-free sensing would enable increased sensitivity and miniaturization capabilities for biosensing devices.
Silicon carbide is a semiconductor material that happens to possess ideal properties for augmenting both the MEMS/nanoelectromechanical systems and the plasmonics routes. It has remarkable chemical and biological inertness resulting in a high degree of biocompatibility, as well as pronounced mechanical resilience.
In addition, it is an effcient (low loss) plasmonic metamaterial. Its cubic polytype can be grown on silicon wafers, allowing easy micromachining into building blocks for sensing devices, scalable to large volume production. Finally, silicon carbide is an ideal starting material for a controlled, wafer-scale growth of graphene, offering an additional wealth of excellent properties for nanosensing. The combination of all of these capabilities makes silicon carbide an outstanding material platform for the realization of label-free, analyte-specific, and highly sensitive biochemical molecule detection systems. These technologies will open exciting horizons in terms of high throughput, efficient drug screening, and early pathogen detection.

5. N.Mishra, J.Boeckl, N.Motta and F.Iacopi, “Graphene growth on silicon carbide: a review”, Phys. Status Solidi A, 1–13, 2016.

We review here, the enormous scientific and technological advances achieved in terms of epitaxial growth of graphene from thermal decomposition of bulk silicon carbide and the fine control of the graphene electronic properties through

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intercalation. Finally, we discuss perspectives on epitaxial graphene growth from silicon carbide on silicon, a particularly challenging area that could result in maximum benefit for the integration of graphene with silicon technologies.

6. M.Ahmed, M.Khawaja, M.Notarianni, B.Wang, D.Goding, B.Gupta, J.J. Boeckl, A.Takshi, N.Motta, S.E.Saddow, F.Iacopi, “A thin film approach for SiC–derived graphene as an on-chip electrode for supercapacitors”, Nanotechnology 26, 434005, 2015.

Graphene has been shown to perform extremely well as a material for charge storage in macroscopic supercapacitors. Carbon-based supercapacitors are lightweight devices with high energy storage performance, allowing for faster charge-discharge rates than batteries. However, this performance has not been exploited in full for on-chip energy storage, due to the lack of a suitable fabrication process.
Utilizing in a useful fashion the extensive pitting caused by the use of Ni only (not alloyed with copper), we have designed a nickel-assisted process to obtain graphene on SiC/Si wafers with low sheet resistance and a highly enhanced surface area. As stand-alone electrodes in supercapacitors, these transfer-free graphene-on-chip samples show a typical double-layer supercapacitive behaviour with gravimetric capacitance of up to 65 F g^{-1}.
These results are extremely promising for further development of miniaturized energy storage systems, and may open numerous opportunities for fully autonomous micro-systems such as sensors for harsh environments. (A patent was filed under CI Iacopi’s previous AOARD grant, now at PCT stage)

7. B.Wang, M.Ahmed, B.Wood, F.Iacopi, “A perspective for all-solid-state supercapacitors on silicon”, Applied Physics Letters 108, 183903, 2016.

Building upon our first paper above, we present here an example of all-solid state supercapacitors on silicon for on-chip applications, paving the way towards energy supply systems embedded in miniaturized electronics with fast access and high safety of operation. We present a nickel-assisted graphitization method from epitaxial silicon carbide on a silicon substrate to demonstrate graphene as a binder-free electrode material for all-solid-state supercapacitors. We obtain graphene electrodes with a strongly enhanced surface area, assisted by the irregular intrusion of nickel into the carbide layer, delivering a typical double-layer capacitance behavior with a specific area capacitance of up to 174 μF cm^{-2} with about 88% capacitance retention over 10 000 cycles. The fabrication technique illustrated in this work provides a strategic approach to fabricate micro-scale energy storage devices compatible with silicon electronics and offering ultimate miniaturization capabilities.

b) Edited books

1. "2D Materials, semiconductors and semimetals", edited by F.Iacopi, J.J.Boeckl and C.Jagadish, Elsevier, published in July 2016.

This is the first comprehensive book on 2D materials, covering the most recent progress and advances for Dirac materials, to transition metal dichalcogenides, to phosphorene, their theory, synthesis and properties as isolated materials and stacked, plus a preliminary outlook on device applications.

c) manuscripts not yet published
   1. N. Mishra, J.J. Boeckl, R.T. Jones, P.J. Pigram, A. Tadich, M. Edmonds, M.S. Fuhrer, B.M. Nichols, and F. Iacopi, "Solid source growth of graphene from silicon carbide with a catalytic alloy and role of oxygen", in preparation for submission to Nanoscale, August 2016.

   We investigate the mechanisms of the alloy-mediated catalytic approach for the direct growth of uniform graphene on silicon substrates, via solid source growth from epitaxial silicon carbide films. Raman spectroscopy measurements consistently show an ID/IG band ratio as low as ~0.2 over large areas, indicating that the graphene obtained through this method is the highest quality graphene to-date grown in-situ on silicon substrates. We describe the main steps behind the graphene synthesis on the basis of extensive morphological and structural analyses as well as depth-dependent chemical profiles. We conclude that oxidation and amorphization of the silicon carbide surface are crucial intermediate steps towards the liquid –phase epitaxial growth of graphene. Note this paper may still differ from its final submitted version.

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. Under the current grant, my PhD student Neeraj Mishra has visited Dr.Boeckl at WPAFB for a second time in January 2016 (2 weeks) to work on the TEM of graphene on SiC/Si. Some of the results of this work were published in the APL manuscript by Pradeepkumar et al, 2016.
      ii. PI Iacopi and Dr.Boeckl have submitted a joint ARC Discovery project, pending outcome, on a Tunnel-FET concept based on a graphene/silicene junction.
      iii. Dr.Boeckl and PI Iacopi have submitted a joint proposal for beamtime at the Australian Synchrotron, which has been awarded for November 2016. This capability will enable further understanding of the nature of the buffer layer and intercalation in our system.
      iv. Joint work has led to 3 newly published manuscripts and 1 jointly edited book for Elsevier

   2. Dr.Josh Caldwell, NRL, USA
      i. Dr.Caldwell has visited Griffith after his invited talk at ISGD5 in July 2016, chaired by PI Iacopi in Brisbane. We have discussed preliminary optical results from the exchanged graphene on SiC/silicon samples. We are getting close to having a full description of the dielectric function of the system, necessary to evaluate the plasmonic and phonon-polariton responses.

   3. Dr.Kurt Gaskill, NRL, USA
      i. Dr.Gaskill has visited PI Iacopi's group as well after ISGD5 in July. Dr.Gaskill is external advisor for the PhD student Aiswarya Pradeepkumar, so

the visit was used to discuss electrical measurements of graphene and plans for the PhD student.

4. Dr.Barbara Nichols, Adelphi, ARL, USA
   i. PI Iacopi has met Dr.Nichols during MRS Fall in Boston to discuss sample exchange and characterization. Her Raman measurements are now part of a paper in preparation.
   ii. Dr.Nichols and Dr.Madan Dubey have contributed a chapter in the forthcoming "2D Materials, semiconductors and semimetals", edited by F.Iacopi, J.J.Boeckl and C.Jagadish, Elsevier, published in July 2016.

5. Prof.Reinhold Dauskardt, Stanford, USA
   i. Further adhesion and fracture testing of graphene are undergoing. My PhD student Zulfiqar Khan, for whom Dauskardt is external advisor, is going to visit Stanford for 2 weeks in August 2016, supported by this grant.

6. Prof.Nunzio Motta, QUT, Australia
   i. This long -standing collaboration has been extended to the area of integrated energy storage, we share the supervision of a PhD student at QUT (graphene on nanostructures), and Motta's group is involved in the synchrotron study proposal by Boeckl and Iacopi.

7. Prof.Michael Fuhrer, Monash, Australia
   i. The collaboration with the Fuhrer group has led to the clarification of the SiC/Si interface issue, plus the synergies among PI Iacopi-Gaskill (NRL)-Fuhrer will lead to further join work on electronic properties of 2D materials.

8. Industry
   i. Preliminary talks with NovaSiC (France) may lead to a collaboration on the improvement of the SiC/Si barrier and maybe the supercapacitors
   ii. Preliminary interactions with Lockheed Martin (USA) indicated potential interest in the energy storage project

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