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14. ABSTRACT

The absence of a band-gap and the lack of an adequate synthesis method of high quality graphene on silicon substrates have held back the applications of graphene in electronics and integrated micro- and nano-systems. This research pioneers 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. Using a Ni/Cu catalytic alloy high-quality, uniform bilayer graphene directly was realized on silicon wafers, at temperatures compatible with conventional semiconductor processing. The highest ever reported doping for graphene (approx. 10^15/cm^2), which also corresponded to record low sheet resistance was observed using this process. The p-type “metal” sheet is grown in-situ on silicon substrates, with processes fully compatible with semiconductor industry and its conduction is unmatched by any classical metal of only 1 nm thickness. This densely intercalated graphene bilayer offers both electrical and mechanical (adhesion) reliability, largely overlooked so far but both essential to qualify for any use in nanodevices. The extremely high doping may open a new area of basic physics investigation. The research illustrates how exceptional properties of the catalytic graphene on silicon substrates can advance a wide spectrum of practical applications ranging from efficient metal replacement at the nanoscale for MEMS/NEMS to miniaturized devices for on-chip energy storage.

15. SUBJECT TERMS

Graphene, Processing, Electronic Materials, Mechanical Properties, Adhesion

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Final Report for Grant AOARD-14-4045
"Understanding the Fundamental Properties of Transfer–Free, Wafer-Level Graphene on Silicon and its Potential for Micro- and Nanodevices"

16th June 2015

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Abstract:
The absence of a band-gap and the lack of an adequate synthesis method of high quality graphene on silicon substrates have held back the applications of graphene in electronics and integrated micro- and nanosystems. 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. Using a Ni/Cu catalytic alloy we realized high-quality, uniform bilayer graphene directly on silicon wafers, at temperatures compatible with conventional semiconductor processing. We demonstrated the highest doping ever reported for graphene (~ 10^{15} at cm^{-2}, in the same order of magnitude as the carbon atoms in graphene), also corresponding to record -low sheet resistances. This p-type "metal" sheet is grown in-situ on silicon substrates, with processes fully compatible with semiconductor industry and its conduction is unmatched by any classical metal of only 1 nm thickness. This densely intercalated graphene bilayer offers both electrical and mechanical (adhesion) reliability, largely overlooked so far but both essential to qualify for any use in nanodevices.

These findings, in particular, the extremely high doping, may open a new area of basic Physics investigations. On the technology side, we indicate how the exceptional properties of the catalytic graphene on silicon substrates can advance a wide spectrum of practical applications ranging from efficient metal replacement at the nanoscale for MEMS/NEMS to miniaturized devices for on-chip energy storage.

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

a) papers published in peer-reviewed journals:
   1) F. Iacopi, N. Mishra, B.V. Cunning, D. Goding, S. Dimitrijev, R. Brock, R.H. Dauskardt, B. Wood and J.J. Boeckl, "A catalytic alloy approach for highly uniform graphene on epitaxial SiC on silicon wafers", Invited Feature Paper, J.Mater.Res.30(5), 609-616, 2015.

   Here we introduced a novel approach to the synthesis of high-quality and highly uniform few-layer graphene on silicon wafers, based on solid source growth from epitaxial 3C-SiC films. Using a Ni/Cu catalytic alloy, we obtain a transfer-free bilayer graphene directly on Si(100) wafers, at temperatures potentially compatible with conventional semiconductor processing. The sheet resistance of the graphene is about 25 ohms/square, unprecedented for bilayer graphene. The exceptional conduction qualifies this graphene as a metal replacement for MEMS and advanced on-chip interconnects with ultimate scalability.

This paper was highlighted on the on the website and the Materials 360° newsletter of the Materials Research Society.

b) conference presentations:

1) B.V. Cunning, N. Mishra, M. Ahmed, A.R. Kermany, D. Goding, S. Dimitrijev, J.J. Boeckl, R. Brock, R.H. Dauskardt, F. Iacopi, "Patterned few-layer graphene through self –aligned graphitization of silicon carbide on silicon", Diamond and Carbon Materials 2014, Madrid, Spain, 7-11th September 2014.

2) F. Iacopi et al., "Highly uniform graphene on SiC on silicon wafers and perspectives as metal replacement", invited at the 4th International Symposium on Graphene Devices (ISGD-4), Seattle, WA, USA, 21st -26th September 2014

3) M. Ahmed, M. Khawaja, M. Notarianni, B. Wang, D. Goding, B. Gupta, J.J. Boeckl, A. Takshi, N. Motta, S.E. Saddow, F. Iacopi, "Porous SiC/graphene on silicon for on-chip supercapacitors", ECS 227th Meeting 2015, Chicago May 24-28, 2015.

c) manuscripts submitted but not yet published:

1) F. Iacopi, T. Gould, J.J. Boeckl, N. Mishra, D. Goding, B.V. Cunning, B. Wood, R.E. Brock, R.H. Dauskardt, S. Dimitrijev, "Graphene as a p-type metal for ultimate miniaturization", arXiv http://arxiv.org/abs/1503.06253 (submitted to Adv Mater, April 2015)

   Here we report macroscopic sheets of highly conductive bilayer-graphene with exceptionally high hole concentrations of ~10^{15} cm^{-2} and unprecedented sheet resistances of 20-25 ohms/square over macroscopic scales, and obtained in-situ over a thin cushion of molecular oxygen on a silicon substrate. The electric and electronic properties of this specific configuration remain stable upon thermal anneals and months of exposure to air. We further report a complementary ab-initio study, predicting an enhancement of graphene adhesion energy of up to a factor 20, also supported by experimental fracture tests. In addition to providing exceptional material properties, the growth process we employed is scalable to large areas so that graphene's outstanding conduction properties can be harnessed in devices fabricated via conventional semiconductor manufacturing processes. We anticipate that the approach will provide the necessary scalability and reliability for future developments in the graphene nanoscience and -technology fields, especially in areas where further miniaturization is hampered by size effects and electrical reliability of classical conductors.

2) 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", submitted, March 2015.

   Graphene has been shown to perform extremely well as a material for charge storage in macroscopic supercapacitors. 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.

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

1) The collaboration with Dr.J. Boeckl from AFRL has strengthened further. One student from the F. Iacopi lab, Neeraj Mishra, has worked 1 month at the WPAFB/Wright State University on TEM of graphene with Dr. Boeckl, while Dr. Boeckl has visited Griffith for 2 weeks in July 2014 and will be back in July 2015. As a result from this collaboration, 1 joint paper has been published, 2 are submitted and 2 more are being prepared.

2) Also the collaboration with Prof. Dauskardt in Stanford has strengthened, leading to joint publications and joint supervision of a student at Griffith. The student will be working on fracture testing of graphene .

3) Specifically on feasibility of energy applications, which derived naturally from our synthesis method, collaboration was started with Prof. Nunzio Motta at Queensland University of Technology, and Prof. Stephen Saddow, University of South Florida (see submitted paper)

4) Collaboration has also started with Dr. J. Caldwell from NRL on the optical and plasmonics properties of our graphene

5) Finally, recently, collaboration with Prof. Michael Fuhrer from Monash University has recently started, regarding the synchrotron light analysis (XPS and ARPES) and low temperature transport characteristics of our graphene.