

SEVENTH FRAMEW

# Carbon resistive random access memory

### Rendicontazione

Informazioni relative al progetto

CARERAMM

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Sito web del progetto 🛃

Progetto chiuso

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Coordinato da THE UNIVERSITY OF EXETER

## Final Report Summary - CARERAMM (Carbon resistive random access memory materials)

Executive Summary:

The primary objective of the CareRAMM project was to research exciting new carbon-based non-volatile memory concepts. We followed two strands of work, one based around the development of amorphous-carbon (a-C) based materials and devices as an alternative/competitive/complementary approach to existing memory technologies (such as Flash, hard-disks, DRAM) and one based around graphene-oxide memories for possible use in flexible electronics applications.

In both the case of a-C and GO memories developed in CareRAMM the actual storage mechanism revolved around electrical resistive switching, i.e. the devices are electrically excited into two (or more) resistive states to store binary (or multi-level) data. Prior to the start of CareRAMM the actual physical mechanisms involved in resistive switching of both a-C and GO was not at all clear, with several alternative theories present in the literature (such as sp3/sp2 conversion, sp2 filamentation, metal filamentation, redox processes, oxygen vacancy diffusion). Furthermore, the likely limitations of a-C and GO materials for resistive switching memories, in terms of key performance parameters such as switching speed, energy, endurance (number of switching cycles achievable), maximum operating temperatures, minimum devices size etc., were not known.

In CareRAMM therefore we set out to address such important issues, setting ourselves the extremely ambitious objectives of the development of materials and device structures that are capable, ultimately, of providing (in real devices):

- sub-nanosecond switching times
- sub-10 nm feature size (switching region)
- sub-10 µW write power (~ pJ write energy)
- predicted lifetime of at least 10 years at 100 C for consumer applications
- predicted lifetime of at least 10 years at 200 C for automotive, aerospace and military applications
- · demonstration of binary and multi-level storage capability
- · demonstration of memristive-like 'additional functionality'
- demonstration of suitability of GO-based memory for flexible electronics applications

We have succeeded, via a careful programme of materials and device fabrication and characterization in meeting almost all of these objectives, some technological highlights include:

Successful fabrication of sub-10 nm a-C based devices, with sub-pJ switching energy

Operation of a-C based devices at temperatures up to 300 C

GO-based devices with 4-level storage (2 bits per cell) and endurance (#switching cycles) > 1000 on flexible substrates

GO-based devices capable of withstanding > 10,000 bending cycles and high bending radii

We have also very significantly advanced the state-of-the-art in terms of understanding resistive switching process in both a-C and GO based materials and devices. By using a combination of atomistic scale modelling and nanoscale characterisation techniques we showed that in our a-C devices switching was driven by sp2 clustering/filamentation, while in our GO devices switching was a result of reduction-oxidation processes at the interface between the GO layer and the metal electrode.

#### Project Context and Objectives:

Carbon materials offer an exciting route to future generations of high-performance, cost-effective and environmentally-friendly non-volatile data storage, suited to both conventional and flexible electronics applications. Scalability to the molecular level, sub-nanosecond switching time, ultra-low power operation, environmental stability, environmental friendliness, simple memory structures, advanced functionality, cost-effectiveness and compatibility with CMOS processing and flexible substrates are all features readily provided by carbon-based data storage materials.

CareRAMM focuses on development of next-generation data storage/memory materials via two routes: i. thin films of (sp3-rich) amorphous carbon (a-C) for the provision of high-performance non-volatile memories

ii. graphene-based materials (GO) for the provision of non-volatile memories suited to flexible electronics applications.

The storage mechanism in these materials is commonly referred to as 'resistive switching'. The exact physical mechanism responsible for this resistive switching in carbon materials is not clear, with sp2 filamentation, sp2 clustering, metal filamentation and interfacial redox reactions all being implicated in the literature for various material and electrode configurations. A goal of CareRAMM was thus be to determine the precise physical mechanisms at play, allowing us to control and exploit such mechanisms to provide for optimum memory performance. Carbon-based resistive memories should also offer the capability for multi-level storage and 'memristive-like' behaviour, allowing for the storage of more

than one bit per cell (increasing storage densities), while also providing advanced signal processing/computing-type operations (such as logic and neuromorphic computing).

There are also compelling environmental reasons that make carbon an attractive proposition; it is, for example:

- Non toxic (to persons or the environment)
- Not reliant on rare mineral extraction (and the knock-on environmental problems)
- · Expected to have relatively easy 'end of use' disposal/recycling
- Expected to offer low (total) energy of production (compared to other electronics materials)

In summary, the general aims of CareRAMM were to develop advanced carbon-based resistive switching materials for next generation non-volatile data storage applications.

Our primary scientific and technical goals were:

- To fabricate and characterise a-C and GO films for resistive memory applications
- To determine the nature and origin of resistive switching in such a-C and GO films
- To determine the nature and role of any contact effects
- To determine the ultimate scalability dimensionally, temporally and in terms of energy of such resistive switching
- To determine the expected limits of endurance (cyclability), lifetime and operating temperatures and, in the case of GO-based materials, suitability for flexible electronics applications
- To explore 'additional functionality' (i.e. multi-level resistance and memristive properties) capabilities

To ensure we reach these goals our plan was to:

• Fabricate and characterise, both from fundamental and applications perspectives, a range of sp3 rich a-C films on Si substrates

• Fabricate and characterise, again from fundamental and applications perspectives, a range of GO films on both rigid (Si) and flexible (e.g. polyimide, PET) substrates

• Fabricate patterned 'all-carbon' based a-C based memory structures (such as graphene/sp3-rich a-C/graphene) and determine their switching mechanisms and ultimate performance limits

• Fabricate patterned GO-based memory structures on both flexible and rigid substrates and determine

their switching mechanisms and ultimate performance limits

Fabricate materials/memory structures with a range of contact materials, including pristine and doped graphene electrodes for use with a-C films and both 'inert' and 'diffusive' metals for use with GO films
Employ a range of nanoscopic characterisation tools for probing behaviour on the atomic scale (e.g.atom-probe microscopy, HRTEM with 0.05 nm resolution)

• Develop physically-realistic theoretical models and computer simulation tools to gain a proper understanding of, and explanation for, resistive switching processes and contact effects in a-C and GO-based materials, and to aid in the design and optimisation of improved materials and structures.

Project Results:

See attached Final Public Summary Report

Also see attached the more detailed Periodic Report covering the technical work and achievements during Months 19 to 36.

Please also see attached project Dissemintation List

Potential Impact:

We envisage a range of potential applications for CareRAMM related technologies, ranging from fast, high-capacity, low-power memories to the provision of new concepts in unconventional (memrisitive) computing.

The primary objective of the CareRAMM project was to research the exciting new carbon-based memory concepts and thus pave the way towards possible further development and commercialization. We followed two strands in the CareRAMM project, one based around the development of amorphous-carbon based materials and devices as an alternative/competitive/complementary approach to existing memory technologies (such as Flash, hard-disks, DRAM) and one based around graphene-oxide memories for possible use in flexible electronics applications. In terms of potential exploitation, carbon-based memories currently have much more potential as compared to graphene-oxide, primarily because GO is aimed at the flexible electronics market, but as yet there are no significant products in the flexible electronics 'space'. We therefore concern ourselves in this report to consideration of the possible exploitation of amorphous carbon based memory technology.

There is truly an explosion of data. With the multitude of digital devices around us, such as mobile phones and digital cameras, gigantic amounts of information are created every second. The emergence of social networking, sensor networks, and huge storehouses of business, scientific and government records creates an abundance of information referred to as "big data". It is estimated that the digital universe is growing at about 60 percent each year! The amount of data stored globally is outpacing the technological increase in data storage products.

Besides the need to store the significant amount of data that is being created, we have also started realizing the significant power of all this data at our disposal. "Big data" is a natural resource ready to be mined. This data enables us to understand the incredibly complex economies and societies that we are all part of. We have realized that a statistical approach based on analyzing vast amounts of information using powerful computers and sophisticated algorithms produces something similar to intelligence/knowledge.

This has brought us to the third era of computing namely, the so-called cognitive era.

For such data-centric computing, significant improvement in memory access latency and bandwidth is required. Unfortunately, this is happening at a much lower rate than increase in areal density. In particular access latency is lagging, leading to a distinct speed gap between the memory and storage side of the computing architecture. The technologies that will fill up this gap are called Storage Class Memory (SCM). SCM is a class of technology that blurs the boundaries between slow, high density storage and fast, lower density memory by combining a high speed with high areal densities in non-volatile memory.

It is expected that storage class memory will eventually cut into the market share of DRAM and Flash. It will also create its own niche market share. The worldwide revenue for NAND flash memory for 2016 is forecast to be US\$26.6 billion which is a significant share of the worldwide semiconductor revenue of \$333.7 billion.

Such a storage class memory will be very attractive to all the information technology giants such as IBM, Intel, Microsoft, Google, Facebook, Amazon etc. thus providing a strong customer base. Given the dramatic increase in data-centric workloads this interest level is only going to increase further in the future.

Not surprisingly several companies are exploring various candidate technologies for the realization of storage class memories. The most notable effort is by Intel and Micron who announced the arrival of a 3D cross-point memory sometime in 2016. Other prominent players in the memory market such as Samsung and SK Hynix also have strong research and developmental efforts geared towards storage class memory.

Within CareRAMM we researched the concept of carbon memory which is yet another attractive candidate to serve as a storage class memory. The main selling points of carbon memory are the following:

- High read / write speeds
- Bit addressability
- Low energy consumption

There are also some unique selling points associated with carbon memory as the following:

- Robustness (radiation hardness, retention)
- Low-cost production
- Extreme scalability
- · Ease of integration with carbon-based logical elements
- · Environmentally-friendly and sustainable raw material

The read/write speeds in the order of 10 ns or less is very attractive compared to all the competing technologies. The energy consumption of < 2 pJ is also very competitive even though this is something that could be improved on with further scaling to smaller dimension. The primary drawback so far is the relatively low endurance (# switching cycles achievable). The endurance of carbon memory devices based on DLC is on the order of hundreds of cycles which is only sufficient for storage-type (cf. memory-type) applications. Carbon memory devices based on oxygenated carbon have shown endurance on the order of tens of thousands of cycles which might make them also attractive for limited memory-type applications. Note that this endurance is substantially higher than that of the state-of-the-art flash memory technology.

However, to really serve on the memory side of storage class memory, it is necessary to improve on these endurance numbers even further.

To summarize, based on the current status of the technology carbon memory shows enormous potential to serve in the storage-end of storage class memory but is not yet mature enough to serve in the memory end of storage class memory.

In terms of dissemination activities the following is a list of CareRAMM-related publications, as at 31/1/2016:

1. Published/accepted journal papers and conference papers/presentations:

"Recent Advances in Carbon-Based Resistive Memory", W. W. Koelmans, T. Bachmann, F. Zipoli, A. K. Ott, C. Dou, A. C. Ferrari, O. Cojocaru-Mirédin, S. Zhang, C. Scheu, M. Wuttig, V. K. Nagareddy, M. F. Craciun, A. M. Alexeev, C. D. Wright, V. P. Jonnalagadda, A. Curioni, A. Sebastian, E. Eleftheriou; IEEE International Memory Workshop (IMW2016), Paris, May 2016

"Selective modification of as-grown CVD graphene on Cu by oxygen plasma for flexible electronics applications", A Alexeev et al., International Conference on Modern Materials and Technologies, (CIMTEC2016), Perugia, June 2016

"Graphene as protective coating for ultra-high storage density hard disks", A. K. Ott, N. Dwivedi, R. J. Yeo, C. Dou, U. Sassi, D. De Fazio, C. S. Bhatia, A. C. Ferrari, Graphene week 2016, June 2016, Warsaw, Poland

"Carbon based resistive random access memories with graphene electrodes", C. Dou, A. K. Ott, U. Sassi, I. Goykhman, A. C. Ferrari, Graphene 2016, April 2016, Genova, Italy.

"Graphene as protective coating for ultra-high storage density hard disks", A. K. Ott, N. Dwivedi, R. J. Yeo, C. Dou, U. Sassi, D. De Fazio, C. S. Bhatia, A. C. Ferrari, Graphene 2016, April 2016, Genova, Italy.

"Molecular-dynamics simulations of resistance switch in amorphous carbon", F Zipoli et al., MRS Fall Meeting, Boston, Nov 2015

"Contaminations and Quantification of Defects in Doped Graphene by Raman Spectroscopy", A. K. Ott, M. Barbone, M. Bruna, M.K. Ijäs, D. Yoon, U. Sassi and A.C. Ferrari, Poster presented at Graphene Week 2015, June 2015, Manchester.

"Determination of Shear Modulus and Out of Plane Young's Modulus of Layered Materials by Raman spectroscopy", S. Milana, D. Yoon, M. Ijäs, W. P. Han, P. H. Tan, N. M. Pugno, T. Bjorkman, A. Krashenninnikov, A. C. Ferrari, Talk at E-MRS conference, May 2015, Lille, France.

"Raman Spectroscopy of Defects in Doped and Chlorinated Graphene", A. K. Ott, U. Sassi, M. Bruna, G.V. Bianco, M. Losurdo, M. M. Giangregorio, G. Bruno, A. C. Ferrari, Talk at E-MRS conference, May

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"Determination of Shear Modulus and Out of Plane Young's Modulus of Layered Materials by Raman Spectroscopy", S. Milana, D. Yoon, M. Ijäs, W. P Han, N. M. Pugno, T. Björkman, A. Krasheninnikov, A. C. Ferrari, Talk at Graphene 2015 Conference, March 2015, Bilbao, Spain.

"Contaminations and Doping in Defected Graphene by Raman Spectroscopy", A. K. Ott, M. Barbone, M. Bruna, M.K. Ijäs, D. Yoon, U. Sassi, A.C. Ferrari, Poster presented at Graphene 2015 Conference, March 2015, Bilbao, Spain.

"Multi-wavelength Raman Spectroscopy of Amorphous Carbon for Resistive Switching", A. K. Ott, P. Hosseini, C. D. Wright, A. C. Ferrari, Poster presented at Joint European Workshop on Non-Volatile Memories, November 2014, Forschungszentrum Jülich, Germany.

"Diamond-like carbon based metal-insulator-metal structures for resistive memories", C. Dou, A. K. Ott, U. Sassi, M. Barbone, A. Katsounaros, M. Bruna and A.C. Ferrari, Poster presented at Joint European Workshop on Non-Volatile Memories, November 2014, Forschungszentrum Jülich, Germany.

"Raman spectroscopy of layer breathing modes of multilayer graphene", S. Milana, D. Yoon. M. Ijäs, W. P. Han, P. H. Tan, N. Pugno, A. C. Ferrari, June 2014, Gothenburg, Sweden.

"Raman Spectroscopy of Graphene and Related Materials", Keynote Rank Conference, Windermere, Sept 14

"Amorphous carbon and graphene oxide based resistive memories", C.D.Wright et al., Joint European Workshop on Non-Volatile Memories, Peter Gruenberg Institute, Forschungszentrum Julich, Nov 2014

3. Other publications acknowledging CareRAMM funding:

F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, V. Pellegrini, Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. Science 347, 1246501, 2015.

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M. Bruna, A. K. Ott, M. Ijäs, D. Yoon, U. Sassi, A. C. Ferrari. Doping dependence of the Raman spectrum of defected graphene. ACS Nano 8 (7), 7432-7441, 2014.

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Jiang-Bin Wu, Xin Zhang, Mari Ijäs, Wen-Peng Han, Xiao-Fen Qiao, Xiao-Li Li, De-Sheng Jiang, Andrea C. Ferrari, and Ping-Heng Tan. Resonant Raman spectroscopy of twisted multilayer graphene. Nature Communications 5, 5309, 2014.

Zhe Jiang, G. E. Bonacchini, Daniel Popa, Felice Torrisi, A. K. Ott, Valentin J. Wittwer, David Purdie, and Andrea C. Ferrari. Graphene saturable absorber power scaling laser. CLEO:2014, OSA Technical Digest (online) (Optical Society of America, 2014), paper JTu4A.67.

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Roman Sordan and Andrea C. Ferrari. Gigahertz Multi-Transistor Graphene Integrated Circuit. Electron

Devices Meeting (IEDM), 2013 IEEE International, IEDM13, 2013.

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3. CareRAMM articles in preparation:

"The effect of nitrogen implantation on the resistive switching properties of diamond-like carbon films for non-volatile memory applications", V. K. Nagareddy, A. K. Ott, T Tsvetkova et al., in preparation (2016)

"Fabrication and nanoscale patterning of graphene oxide using in-situ plasma oxidation of CVDgraphene", A Alexeev et al., in preparation (2016)

"Multi-level, ultra-fast, ultra-scalable, ultra-flexible, non-volatile graphene oxide memories", V K Nagareddy, M Barnes, F Zipoli et al., in preparation (2016)

"High-temperature non-volatile amorphous carbon memories", P Hosseini, A K Ott et al., in preparation (2016)

"Effect of Si-incorporation on the resistive switching properties of amorphous carbon memories", T Bachman, A K Ott, T Tsvetkova et al., in preparation (2016)

"Modelling of the resistive switching process in amorphous carbon and graphene oxide materials using a rate equation approach", A Alexeev, T Bachman et al., in preparation (2016)

"Understanding the switching mechanism in amorphous carbon memory devices", O. Cojocaru-Mirédin et al., in preparation (2016)

"Ab-initio modelling of resistive switching in amorphous carbon memories", F Zipoli et al., in preparation (2016)

"Optimized performance of tetrahedral amorphous carbon based resistive memory devices with graphenebased electrodes", C. Dou, A. K. Ott, U. Sassi, I. Goykhman, A. Katsounaros, D. Yoon, X. Chen, J. Wu, A. Lombardo, A. C. Ferrari, in preparation (2016)

"Graphene: An Emerging Protective Overcoat for Magnetic Storage Technology " N. Dwivedi, A. K. Ott., R. J. Yeo, U. Sassi, D. DeFazio, G. K. Gueorguiev, A. C. Ferrari, C. S. Bhatia, in preparation (2016)

List of Websites: www.careramm.org

## Documenti correlati

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