Phase-Change and Carbon Based Materials for Advanced Memory and Computing Devices

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Signature: .................................................................
This work is dedicated to all my Family and Friends who helped me, encouraged me
and pushed me forward through all these years of study.

Thank you.

Pei
Abstract

The aggressive scaling of CMOS technology, to reduce device size while also increasing device performance, has reached a point where continuing improvement is becoming increasingly problematic and alternative routes for the development of future memory and processing devices may be necessary; in this thesis the use of phase-change and carbon based materials as one such alternative route is investigated.

As pointed out by Ovshinsky [1, 2] some phase-change material should be capable of non-binary arithmetic processing, multi-value logic and biological (neuromorphic) type processing. In this thesis, generic, nanometre-sized, phase-change pseudo-devices were fabricated and utilised to perform various types of computational operations for the first time, including addition, subtraction, division, parallel factorization and logic using a novel resistive switching accumulator-type regime in the electrical domain. The same accumulator response is also shown to provide an electronic mimic of an integrate-and-fire type neuron. The accumulator-type regime uses fast electrical pulses to gradually crystallize a phase-change device in a finite number of steps and does not require a multilevel detection scheme.

The phase-change materials used in this study were protected by a capping layer of sputtered amorphous carbon. It was found that this amorphous carbon layer also underwent a form of resistive switching when subjected to electrical pulses. In particular, sputtered amorphous carbon layers were found to switch from an initially high resistivity state to a low resistivity state when a voltage pulse was locally applied using a Conductive Atomic Force Microscope (CAFM) tip. Further experiments on amorphous carbon vertical pseudo-devices and lithographically defined planar devices showed that it has potential as a new material for Resistive Random Access Memory (ReRam) applications. The switching mechanism was identified as clustering of the $sp^2$ hybridized carbon sites induced by Joule heating. It was not possible to reset the devices back to their initial high resistivity state presumably due to the highly conductive nature of sputtered amorphous carbon.
List of Publications

- Nanoscale non von-Neumann computing using phase-change devices - C.D. Wright, P. Hosseini. EPCOS 2012 (Poster).
• Threshold switching via electric field induced crystallization in phase-change memory devices and Neuromorphic applications - J. Vasquez, P. Hosseini and C. D. Wright. ONYX12 Meeting. May 2012 (Talk).


• Phase-change and Carbon Based materials for biologically inspired computing and data storage - P. Hosseini. UKICTPioneers2012. (Top3 Finalists Poster).
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1 Introduction
1.1 Memory: we need more, we need different

In last few decades the evolution of what is commonly known as Information Communications Technology has contributed enormously to the way people interact with each other, shaping the current society we live in like never before. Laptops, Ipods, ebooks, social networks are all products of a technological revolution that not only influence the people that are actively using them, but even those who don’t have access to them [3]. Hardware and software that are faster, more powerful and yet, most importantly, cheaper than the previous generation are driving industries and investors into finding new solutions and new technologies to offer to a wider market. Innovative products like social networks, smartphones or digital photo cameras are available to almost anyone thanks to this continuous evolution. All these technologies have a unique characteristic in common: they require a vast amount of digital memory that needs to be constantly accessed for storing and retrieving programs and data. Some interesting facts on the extent and pervasiveness of modern data storage are collected in Table 1:

Table 1 - Facts and Figures of digital data created in 2012. From [4-6]

<table>
<thead>
<tr>
<th>Fact</th>
<th>From</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 times</td>
<td>The increment in the &quot;Digital Universe&quot; between 2005 and 2020.</td>
</tr>
<tr>
<td>40%</td>
<td>The increment in spending on IT infrastructure between 2012 and 2020.</td>
</tr>
<tr>
<td>24</td>
<td>Hours of videos uploaded every minute on Youtube.</td>
</tr>
<tr>
<td>4·10^9</td>
<td>Number of videos watched every day on Youtube.</td>
</tr>
<tr>
<td>18'000'000</td>
<td>Number of songs stored on ITunes servers.</td>
</tr>
<tr>
<td>450'000</td>
<td>Number of Google servers around the world.</td>
</tr>
<tr>
<td>700</td>
<td>Billion $, total capital of the 5 industrial leaders in data storage.</td>
</tr>
</tbody>
</table>
The very essence of a general computer system is the ability to perform any appropriate task stored in its memory without having to be redesigned from scratch once a new task is required. This ability is not restricted to desktop PCs, most of the modern digital embedded systems (like an mp3 player or an eBook for example) are programmable and they also require an on board dedicated memory. Storing data is thus a complementary and necessary part of any general purpose computer system. In the semiconductor industry and in the academic research community there is a constant drive for being able to offer faster, more efficient yet smaller devices to the largest number of users possible. The consumer demand and the view of a considerable financial return is such that each player in the business has invested millions of pounds in the current state of art memory technologies. In his 1965 paper titled: "Cramming more components onto integrated circuits", Gordon E. Moore, co-founder of Intel, defined what has proven to be an extremely accurate trend in the semiconductor industry: the Moore’s Law. This law states that the density of transistors that can be inexpensively fabricated on an integrated chip doubles every 18 months. This aggressive and constant scaling of devices to smaller dimensions is fundamentally challenging for the industry but offers a considerable amount of advantages in terms of increased performance and lower cost of production. To clarify the reason behind this we bring the example of metal oxide semiconductor transistors (MOSFETs). By following three simple rules: 1) reduce lateral and vertical dimensions by k, 2) reduce the supply and threshold voltages by k, 3) increase the doping density by k, k being the scaling factor, some immediate advantages are attainable. The scaled drain current is now at $\frac{I_D}{k}$, a new gate capacitance at $\frac{C_G}{k}$, a delay time now at $\frac{T_D}{k}$ and finally and most importantly a
dissipated power now at $P_d \frac{h}{k^3}$. This simple yet powerful solution has represented the main drive force in the semiconductor industry for the last 40 years. After almost half a century since Moore’s 1965 paper, his “law” still holds true and can also be applied to many different technological sectors, some examples are the pixels-per-dollar in commercial Charge Coupled Devices (CCD) or the network capacity in fibre optics communication.

Figure 1.1 reports the increment of areal density of information over the last fifteen years for two major data storage technologies: Hard Disk Drives (HDD) and Flash Drives. As we can see the aforementioned Moore’s Law increment in storage density is evident from the fitted data of both systems. The trend is increasing over the years but an overall deceleration is showing in the timeline beyond the year 2005.

![Figure 1.1 - Moore’s Law applied to Hard Disk Drives and Flash Products. The projected increase in areal density over the next few years is decreasing for both technologies. From [7].](image-url)
Even more importantly a second deceleration is predicted for the next three years (2012 - 2015). What this trend is showing is a struggle that the HDD and Flash industry are encountering at the present time when scaling down to nanometre features. The specific reasons why this is happening will briefly be explained in the next subchapter, here we would like to point out at why this constitutes a problem. The fundamental problem is the divergence between the amount of digital memory requested from a broader number of users and the reasonably priced amount offered from an industry that is struggling to move forward in its current major technological platforms. This has forced the biggest semiconductor manufacturers association, the International Technological Roadmap for Semiconductors (ITRS), to start looking at alternatives to replace the current classes of memory devices in the near future. In the next subchapter we will briefly discuss some of the most interesting alternative to conventional memory solutions as conveniently reported in the ITRS 2010 emerging memory technology report [8].
1.2 Status and challenges of current memory technologies

Perhaps the most interesting example of multi-memory system is today's Personal Computer (PC) memory architecture, as shown in Figure 1.2.

![Memory pyramid on a general purpose computer system](image)

The Central Processing Unit (CPU) is at the top of the pyramid and the various memory system are placed at different levels based on how often they need to be accessed by the CPU. The most important thing that characterize the different memory systems is the relationship between speed and cost per bit. The CPU doesn't need all the information available all the time therefore data is wisely and systematically divided between interconnected systems at various levels so that the best relationship between cost / performance is always maintained. As an example an all-SRAM computer would technically be extremely efficient (without considering the volatile character of SRAM) but every Gbyte of memory would cost
approximately $5000 making it prohibitive for the vast majority of users. We will now discuss the current relevant memory technologies together with their characteristics and limitations.

1.2.1 SRAM

Static Random Access Memory (SRAM) is the fastest type of memory currently available on the market. It’s generally used in CPU/GPU registers or in level 1 or 2 cache memories, another common implementation is in high performance Digital Signal Processing Devices (DSP) as a buffer cache. A very simple design and sub nanosecond access speeds are the key characteristics of SRAM. Figure 1.3 shows a common SRAM cell made of 6 transistors (6 T cell). M1-4 are the complementary transistors dedicated to store a single bit, M5-6 are access devices to the bit and word line.

![Figure 1.3 - 6T SRAM cell. M1-4 are the complementary transistors used to store a single digital bit, M5-6 are access devices for the word and bit lines.](image)
One can immediately see that with SRAM, every bit stored requires 6 transistors which translates into a $84F^2$ single cell size with $F$ being the smallest feature possible with a chosen lithographic technology. The cell has therefore a considerable size and requires constant supply of energy, being a volatile memory technology. The scaling of SRAM depends completely on how far conventional photolithography can be pushed to. At the present time it is not clear if scaling beyond 16 nm node will be possible at all [9].

1.2.2 DRAM

The second level of the memory pyramid is dominated by what is known as Dynamic Random Access Memory (DRAM). The principle of DRAM memory operation relies on the storage of charge inside an integrated capacitor which can be accessed by a control device, namely a transistor. Figure 1.4 pictures a single cell DRAM with the access device and the integrated capacitor.

![Figure 1.4 - DRAM cell. An access device control the charging and discharging of a integrated capacitor. A refresh is required to avoid information loss.](image)

Charge stored between the capacitor plates is responsible for storing digital information and DRAM is another type of volatile memory. Because of current leakage the capacitor must be periodically refreshed by an external source, thus
the term "dynamic", adding to the device energy consumption. The access time for this class of memory is around tens of nanoseconds and the size has been constantly improved over the time with new devices down to $6F^2$ or even $4F^2$, the latter being the theoretical limit for DRAM cells. As fabrication technology progresses the cost per bit of DRAM modules goes down. Interestingly some of the largest computer manufacturing companies have started to sell product with Solid State Disk (SSD) memories, these drives are nothing more than DRAM modules integrated with Flash drives. Once the system is turned on, an on-chip controller transfers all the necessary files from the slow but non volatile flash drive to the fast but volatile DRAM, at low level, with none of the operating systems nor the user involved. Although the solution can be extremely interesting for specific application it is not attractive to the vast majority of users because of the high cost of DRAM memory cells. Same as SRAM it is not clear if DRAM scaling beyond 16 nm node is possible [9].
1.2.3 Flash Drive

Most current embedded and portable computing applications use Flash drive technology as their main memory system. Flash is a cheap (£/bit) system compared to SRAM and DRAM (but still more expensive than HDD) is non volatile and has capacity now exceeding tens of Gbyte on a single chip.

The operation principle of Flash memory cells relies on electrical charge stored by a floating gate sandwiched between a control gate and a semiconducting channel. Charge transfer comes from hot electron injection or Fowler-Nordheim tunneling from the semiconducting channel into the floating gate, and once stored, charge can remain stored at detectable levels up to 10 years. Since the floating gate is completely surrounded by insulating materials no refresh is needed as in the case of DRAM. The cell size varies between $8F^2$ and $4F^2$ depending on the specific type of design. An advantage of using charge to store data is the inherent multibit capability of Flash memories, transferring more or less charge to the floating gate can be easily translated into multiple stored bits (i.e. 1 cell storing 4 levels or 8 levels). The main issues with this memory technology are all related to future scalability. As the dimension of the device becomes aggressively smaller with new
node technologies, less charge can be stored. Because less charge translates into smaller energy separation between various levels in multibit cells, the Signal to Noise Ratio (SNR) goes also down to unreliable levels. As for the other memory technologies (SRAM and DRAM), It is not clear if Flash scaling beyond the 16 nm generation will be possible. A new more scalable memory solution with the same advantages of Flash drives will therefore soon be needed.

1.2.4 HDD

The Hard Disk Drive (HDD) technology has probably been the most successful memory technology constantly incrementing in terms of capacity while keeping the £/bit cost at the minimum. Invented more than 100 years ago it went through an incredible number of technological improvements (Figure 1.1 marks some of them by date), like the Giant Magneto-resistance (GMR) head whose invention lead to the 2007 Nobel prize in Physics. The enormous capacity, low £/bit cost, reliability and non volatile character made this memory the most widespread among almost every system. In this chapter we will only refer to the last generation of HDD, mostly pointing at the challenges ahead in the next decade.

Figure 1.6 - Principle of operation of magnetic recording. From [10].
Figure 1.6 shows the operation principle of this technology. A magnetic media is read from and written to by a magnetic head with data being stored as a change in the direction of magnetization of a magnetic domain. The read / write head is able to generate a powerful and confined magnetic field able to flip the magnetization direction of a small portion of the media which now corresponds to a single bit, the smaller the bit addressable the highest the density can be. The industry is now coping with several difficulties in having to deal with such small bit sizes. At nanometric sizes the direction of magnetization can randomly flip, even at room temperature, due to a physical effect known as "superparamagnetism". Materials that can maintain magnetization at nanometric scales are available although if employed even higher writing fields would then be required, a solution that is not practical on real HDD. New approaches based on heat assisted recording and patterned media are therefore being developed to extend the lifetime of HDD memories for another decade or so. However, the successful commercialization of such approaches is not certain, and so once again there's a need to find a cheap substitute of secondary memory system.
1.3 Emerging Memory systems: ReRam

In the previous section we discussed how new technologies require a constantly increasing amount of digital memory which the semiconductor and HDD industry will soon struggle to deliver. This divergence between demand and availability is generated by some of the problems that consolidated memory technologies are now facing with increasing storage density. We have pointed out that new device paradigms are required that, although could benefit from it, don't necessarily rely only on aggressive scaling as the only way to improve storage density and performance. Here we present some of the most promising candidates for next generation "universal" memory systems. The term "universal" is generally intended to refer to a memory that can substitute both primary (like SRAM or DRAM) and secondary (like HDD or FLASH) systems without losing any of their respective advantages. Having to deal with a single class of memory could revolutionize computer architecture as we know it.
Figure 1.7 - Resistive Ram memories divided by switching mechanism, polarity and material impact. From [11].

**ReRam** is a broad class of emerging memory devices that use the difference in electrical resistivity between at least two stable states to store information. Figure 1.7 groups most of the classes found in the current literature.

Various switching mechanisms are responsible for the change in resistivity for different types of ReRam. In the following subchapters we will discuss some of the most commonly investigated types together with some very recently proposed ones.

### 1.3.1 Metal Oxide based memristors

In 2008 Prof. Stanley Williams' group at HP-labs demonstrated [12] for the first time the existence of the memristor, the fourth fundamental passive component theorized in 1971 by Prof. Leon Chua [13]. The memristor is a general system that
shows inertia upon the application of an external stimuli. This inertia creates a non
linearity in one of the physical properties of the system that can be seen as a
memory effect making the memristor an interesting alternative to conventional data
storage solutions. The fingerprint of a memristive device is the so called "pinched
V/I hysteresis loop" which forms when the external voltage is swung from negative
to positive values [14].

The first memristor discovered was a TiO$_2$ (titanium oxide) active layer sandwiched
between two platinum electrodes. The switching mechanism involves movement of
oxygen vacancies in the TiO$_2$ layer by means of an applied positive or negative
potential between the two Pt electrodes [15]. The resulting difference in resistivity
between the two cases is used to store information. Since this first memristor,
many other oxides have been demonstrated to possess a memristive character:
Ta$_2$O$_5$[16], HfO$_2$[17], VO$_2$[18] and many others. A big advantage of memristor
technology over the Silicon competitor technologies is the possibility of using the
so called crossbar design (as shown in Figure 1.8) were the active oxide layer is
placed between two perpendicular arrays of electrodes. This is not only simpler

Figure 1.8 - Memristor made out of Pt/TiO$_2$/Pt structure. From [15]. The boundary linking the TiO$_2$ and
the oxygen deficient TiO$_{2-x}$ could be moved by applying a voltage between the Pt electrodes. The
resulting difference in resistivity is used to store information.
than conventional (e.g. Flash arrays) designs but also allows simple 3D stacking of multiple arrays effectively reducing F by several times (one for each layer).

1.3.2 Nanoionic based memories

These new class of memories are similar in structure to the metal oxide ReRam and have an insulator material packed between two electrodes, this time made of two different metals (Metal Insulator Metal, MIM structure), although their switching mechanism is quite different. First evidences for a memristive effect in MIM structures was already seen in 1962 by Hickmott et al.[19]. Here an electrochemical process induces the migration of an active metallic electrode (made for example of Ag or Cu) toward the other inert one (usually Pt or W) when a sufficiently high (few volts in nanometric size cells) is applied between the two terminals [20]. Figure 1.9 explains the physical process superimposed over a typical cell I/V curve. The entire phenomenon is reversed by applying a potential with the opposite sign to the same structure. Prototype systems have been demonstrated with switching endurance up to $10^7$ times [21] and projected retention of 10 years at room temperature.
1.3.3 Phase-change memories

Phase-change materials will be part of this work and a more in depth presentation will be given in the next chapter. Briefly they are materials taken from the chemical family of the chalcogenides, examples are alloys of various elements such as Ge, Sb and Te (GST family) or Ag, In, Sb, Te (AIST family). Discovered in 1968 by Ovshinsky et al. [23] these compounds posses two stable and reversible phases: crystalline and amorphous, phases that have distinguishable optical and electrical properties. In optical storage technologies like DVD-RW or "Blu Ray" disk, an integrated pulsed laser system is used to switch between their different phases and information is encoded as changes in optical reflectivity. Interestingly the amorphous and crystalline phases have also very distinct electrical resistivity and
an electrical pulse can be used to switch between the two stable states making Phase-change Memory (PCM) a very attractive candidate to replace Flash memories, HDD [24] or even DRAM[25].

![Figure 1.10 - PCM switching mechanism. Electrical (or optical) pulses are employed to switch the materials between its amorphous and crystalline phase. The difference in resistivity (or reflectivity) gives the meaning to store digital information.](attachment:pcm_switching_mechanism.png)

Figure 1.10 shows a diagram of phases and their related properties. A long low amplitude excitation pulse (commonly identified as the SET pulse) favours crystallization of an initial amorphous materials while a short, high intensity pulse (known as the RESET pulse) quenches it back to the amorphous state after briefly exceeding the compound melting temperature. Commercial PCM devices are already being employed in mobile applications thanks to their low power consumption [26] and attractive scalability [27] beyond the 16 nm node. An example is the $40 Samsung GT-E2550 mobile phone that has an integrated phase-change memory chip as main memory (Figure 1.11).
1.3.4 Carbon Based Memories

Carbon Resistive Random Access Memory Materials are a new and relatively unexplored class of memories. These systems have generally a carbon based material sandwiched between two conductive electrodes. The switching mechanism is a matter of debate with different groups pointing to phase transitions [29], metal filament formation [30], graphitic layer rupture/formation [31]. A better understanding of the switching mechanism is required to further progress into the development of a usable carbon based memory. In this thesis we will concentrate on a study of the switching mechanism of the SET process using vertical pseudo-devices and horizontal planar carbon devices in a variety of different experiments. A detailed description of carbon based resistive memories is reported in the next chapter.
1.4 Additional Functionalities: beyond Von Neumann architecture

In his 1945 EDVAC (Electronic Discrete Variable Automatic Computer) report John Von Neumann defined the basis of what we recognise as today's modern computer. The EDVAC core architecture's was based on the concept of relay elements, mechanical or electrical components with discrete equilibrium states [32]. This concept of discrete, binary, states greatly simplified the physical design of the system and, as was pointed out in the report, allowed the use of the newly discovered vacuum tube, a fast electronic device, cheaper and more reliable than any other forms of conventional mechanical relay. Other prototypes of general purpose computers, like the 1946 ENIAC, were designed as base-10 calculators, with arithmetic operations processed in a more "human-like" approach. Unfortunately those solutions required complicated (for that time) technological solutions and were ultimately abandoned for the simpler binary Von Neumann architecture.

![Classical Von Neumann Architecture](image-url)
This concept lead to a system design in which computing and data storage are physically separated, a simple but limited architecture where the processor cannot execute a program faster than it can fetch instructions or data from its memory, a simplified schematic of such architecture is shown in Figure 1.12. The term "Von Neumann Bottleneck" was later coined referring to this architectural limitation [33]. While in recent years scientists and engineers have been successful in reducing the impact of the bottleneck by introducing for example cache memory and multi-core architecture, it has long been a 'dream' that practicable computing architectures might be found in which processing and storage are carried out simultaneously and at the same physical location. Such invention would give the immediate advantage of not having to move data in and out of the CPU, it would increase the speed of computation without relying on aggressive scaling technologies or higher clock rates (both proven to be challenging and eventually bound to reach an impasse in 5/10 years time). In fact as pointed out in the 2011 ITRS (International Technology Roadmap for Semiconductors) Roadmap, 'we have reached the point where the Roadmap challenges the most optimistic projections for continued scaling of CMOS'[9]. Indeed, the ITRS Roadmap highlights as one its 'Grand Challenges' the pressing need for entirely new device concepts, and in particular asks for 'A new “beyond-CMOS” information processing technology' and also recognizes that 'A non-binary data representation may be required [9]'. Phase-change based systems are potentially one way of achieving this incredibly relevant technological "dream".
John Von Nuemann, as we said, developed his computing architecture with some clear constraints in mind. He couldn't technologically afford to create something too complicated (which led to a binary system instead of a decimal one) and with too many electrical paths (or buses) between components. This simplicity was the key to the EDVAC success and from that to all the computers all the way up to our present times. It is interesting to note however that he saw an analogy between machine computing and biologically inspired computing already in his 1945 report:

"It is worth mentioning, that the neurons of the higher animals are definitely [configurable memory] elements in the above sense. They have all-or-none character, that is two states: Quiescent and Excited."[32] p.5.

"Following W.S. MacCulloch and W. Pitts (A logical calculus of the ideas immanent in nervous activity," Bull. Math. Biophysics, Vol. 5 (1943), pp. 115{133)) we ignore the more complicated aspects of neuron functioning: Thresholds, temporal summation, relative inhibition, changes of the threshold by after effect of stimulation beyond the synaptic delay, etc. It is, however, convenient to consider occasionally neurons with fixed thresholds 2 and 3, that is, neurons which can be excited only by (simultaneous) stimuli on 2 or 3 excitatory synapses (and none on an inhibitory synapse). It is easily seen that these simplified neuron functions can be imitated by telegraph relays or by vacuum tubes. Although the nervous system is presumably asynchronous (for the synaptic delays), precise synaptic delays can be obtained by using synchronous setups."[32] p.5.

The development of the EDVAC was thus a simplified version of an otherwise unfeasible biologically inspired computer. Now that the electronic industry has
moved from vacuum tubes to semiconductors the long unrealized dream of "cognitive" computing is within reach.

In the following Chapters we will unveil an unprecedented application of phase-change materials for arithmetic processing and data storage at the same physical location. This new approach will not be affected by the aforementioned Von Neumann Bottleneck setting the base for a future Phase-change Microprocessor with enhanced functionality, reduced consumption and increased performance.
1.5 Project Aim

This thesis makes a contribution that spans across various disciplines of engineering and physical science. In the first part we will discuss and later demonstrate the possibility of using phase-change material to perform novel forms of arithmetic computing. Using an accumulation based processing regime we will show how a generic PCM cell can be utilized to perform various types of mathematical operations ranging from base-n operations (where n can be arbitrarily chosen) to the implementation of many-input serial logic gates. These results are addressing a specific call of the 2010 ITRS "More than Moore" report in an effort to find different approaches for solving existing problems within the semiconductor industry mainly derived from the continuous miniaturization paradigm [34]. The ITRS paper describes what is known as the virtuous cycle of the semiconductors industry (Figure 1.13).

![Figure 1.13 - Virtuous cycle of the semiconductor industry. From [34].](image)

Reducing the size of transistors (moving to smaller nodes) allows the performance, the density and efficiency of any device to increase while reducing the costs at the same time. This virtuous cycle however is hindered by the fact that scaling beyond nodes smaller than 22 nm has enormous difficulties. In principle the technology to
achieve transistor with ultimate channel dimensions of 1 atom has already been demonstrated [35], reproduced in Figure 1.14, but these are far from being economically attractive and thus not considered for mass production applications.

![Figure 1.14 - First demonstration of a single atom transistor. From [35]. A single phosphorous atom is placed with atomic precision between two electrodes using a Scanning Tunneling Microscope forming a single dopant channel.](image)

Although semiconductor giants like Intel are heavily investing in the next generation of optical lithography system known as Extreme Ultraviolet Lithography or EUVL, many years of research are still needed for the first commercial application to be produced. Using a relatively well know technology like PCM with a different, "out-of-the-box", approach could help mitigate the pressing need of not-yet-ready scaling solutions while being able to achieve more with the technology available today.

The subsequent part of this thesis will explore amorphous carbon as a possible competitor in the new and exciting class of Resistive Random Access Memories (ReRam). Switching from silicon as the main ingredients for semiconductor devices
to new and sometimes exotic materials requires billions in investment that no company or institution is willing to make before the benefits of such new materials are clear and persuasive. After presenting a review of the available literature in the area of Amorphous Carbon Based Memories we will investigate sputtered amorphous carbon thin films for a possible beyond silicon ReRam system showing how to produce it, how to characterize it and its main interesting features.
1.6 Thesis synopsis

After the short introduction of **Chapter 1** we will continue with the following scheme:

**Chapter 2** - Here we present a review of the current state of research on phase-change and amorphous carbon based materials, mainly focusing on their respective electronic properties and memory applications.

**Chapter 3** - In this chapter a brief description of the experimental procedures and equipment used throughout the work of the thesis is presented.

**Chapter 4** - Here phase-change pseudo cells are used to perform novel forms of arithmetic and biologically-inspired processing. A first evidence for the contribution of the amorphous carbon capping layer in the observed memory switching is presented.

**Chapter 5** - In this chapter we describe how to produce amorphous carbon thin films using a magnetron sputtering system and their subsequent systematic characterization by Raman Microscope, Atomic Force Microscopy (AFM), Conductive Atomic Force Microscopy (CAFM) and four probe electrical measurements (for a variety of deposition and annealing conditions).

**Chapter 6** - In this chapter a series of a-C vertical pseudo-devices are electrically characterized at frequencies ranging from DC to MHz. The possibility of using a-C for an all-carbon memory system is demonstrated together with accumulator-type response for a possible future all-carbon processing and storage device.

**Chapter 7** - Using electron beam lithography a series of planar amorphous carbon devices are fabricated and electrically characterized. The transport conductions are
identified for both pre and post switching conduction and the precise region involved in memory switching imaged with nanometric resolution.

**Chapter 8** - Here, Raman mapping of micrometre sized electrically switched area of a-C together with Secondary Ion Mass Spectroscopy (SIMS) reveals the real Joule heating related switching mechanism of a-C memories. Metallic filament formation is also excluded as a switching mechanism.

**Chapter 9** - This conclusion chapter analyzes all the experimental evidence found during the making of this work giving an overview of both PCM and a-C materials for arithmetic and biologically-inspired computing and data storage.
2 Background on Phase-change and carbon based materials
2.1 Scope

In this Chapter we introduce a background on phase-change and carbon based materials from the current state of art work of the international scientific community.

Phase-change materials are first introduced and their main properties and characteristic explained to the reader. The use of such materials for beyond Von Neumann computing is proposed and a possible implementation scheme presented.

Amorphous carbon materials are then introduced together with their basic structures and properties. A review of the current work on amorphous carbon resistive memories is also presented.
2.2 Introduction to Phase-change Materials for memory applications

Phase-change materials are the key ingredients in today’s optical disk memory technologies (CD, DVD, BR). Chemically speaking they are commonly known as *chalcogenide glasses*, alloys of a chalcogen (namely elements from the group VI of the periodic table) with one or more electropositive element. The key property of interest in these materials is the possibility to switch between their two metastable states, crystalline and amorphous, using external optical or electrical pulses. In rewriteable optical disk technologies the easily detectable difference in optical contrast between amorphous and crystalline states are used to encode digital (0,1) bits along a defined track. Laser pulses with different widths and intensities can locally switch phase-change materials between their two states. Starting from a completely amorphous region a relatively long laser SET pulse heats up the material favoring local re-crystallization that ultimately leads to an area of higher optical reflectivity. When a shorter, higher in amplitude, RESET pulse hits the same spot a second time, it melts the material and forms a new amorphous region upon rapid quenching. The reflectivity is once again low and the entire optical phase-change process (hence the name) can be repeated over one million times [36]. This incredible change in optical reflectivity made such materials a rarity among those that can be thermally switched between crystalline and amorphous states. Another important aspect that made the success of these technologies is the speed at which these transitions can be induced. In commercially available semiconductor compound materials (such as IV group or III-VI group crystals) a big difference in optical contrast always requires a significant changes in the atomic arrangement of the various elements of the system. This makes an energy driven
transition from different states an inherently slow process. In phase-change materials the re-crystallization process (which has to be slower than the amorphization process) takes only few tens of nanoseconds or less [37-39]. All these concurrent requirements narrow considerably the number of materials available for commercial products. In the last few decades many compositions and different class of system have been tested and today three major classes are considered to be useful for industrial applications. The Ge$_2$Sb$_2$Te$_5$ compound is arguably one of the most investigated by the scientific community due to its incredibly high relevance in today’s modern optical data storage industry and its likely upcoming future as substitute for non volatile flash memory technology [40, 41]. A second class known as doped Sb$_2$Te alloy with doping elements made of Ag, In and Ge are commonly used in commercial DVD-RW and DVD+RW disks [42]. Recently a third class of materials with composition Ge-doped Sb has also been found [43]. In this work we will concentrate on the first class of phase-change material Ge$_2$Sb$_2$Te$_5$ commonly referred as GST.
Figure 2.1 - Typical memory cell in commercial PCM. The blue spot in the vicinity of the bottom TiN electrode represents a crystalline area (the active region) of an otherwise amorphous phase-change cell.

Although the first commercial application of phase-change materials was based on their tunable optical properties the idea of using electrical resistivity as a way to monitor the state of a cell was already introduced in 1960 by Ovshinsky et. al [23]. Recently new nonvolatile memory concepts based on resistance change in memory cells are seriously considering GST as a replacement for CMOS flash memory and potentially DRAM applications [44]. A typical commercial phase-change memory (PCM) cell is shown in Figure 2.1. Here a titanium nitride (TiN) bottom electrode is used as local heater and the temperature of the active region (depicted in blue color in Figure 2.1) controlled by applying a voltage pulse between the top and bottom electrode.
In solid state memory applications, the very high contrast of electrical resistivity (reproduced in Figure 2.2) between amorphous and crystalline phases is the key parameter used to store digital (0,1) information. A similar writing scheme applied in phase-change optical storage technologies is replicated in phase-change solid state storage technologies. A long electrical pulse increases the temperature at the interface between the TiN electrode (i.e. the heater) and the phase-change material, such an increase is commonly known as Joule heating. Even for relatively small amplitude pulses the temperature can rapidly increase to a few hundred degrees, enough for the material to crystallize from an initial amorphous phase. Depending on the specific design of the cell the region between the two electrodes might crystallize completely or only partially, as for the case of Figure 2.1 (a design commonly known as contact minimized or mushroom type PCM cell) only the area in the vicinity of the heater becomes crystalline, here depicted in blue color. The electrical resistivity of the cell is now much lower and a digital bit is securely stored.
Data is thus stored as a resistivity change in the PCM cell and there is no need for a continuous energy supply as in the case of SRAM, with great advantages in terms of power consumption. To switch the material back to its initial amorphous phase a second pulse, now with higher amplitude and shorter width is applied once again to the cell. In a classic picture the temperature reached with this new pulse is now high enough to melt the "active" volume of the material, the pulse is much shorter and, once removed, the material quenches into its initial amorphous state. The cooling speed is thus of great importance and much attention has been directed over the years on material and cell design research for more efficient thermal quenching. If the re-amorphization is successful the resistivity of the cell is back to the initial higher state and a digital 0 is now stored. For current state of art devices the entire process of crystallization to amorphization and back to crystallization is repeatable up to $10^{12}$ times [45] which is not only remarkable but also fundamental for future solid state memory applications.

Another characteristic of PCM often discussed is the stability against self re-crystallization, an important feature given by their natural crystallization kinetics. As we said previously an amorphous region of material is created upon heat quenching when a digital 0 has to be stored. Thermodynamically speaking the crystalline phase is the most stable phase of the system, the amorphous phase is metastable and will eventually re-crystallize even at room temperature if a sufficient amount of time is given to the system. This results in data loss and data retention related issues and is an obvious unwanted circumstance. During laser crystallization digital information is written in a few tens of nanosecond ($10^{-8}$ s), at the same time an amorphous bit must withstand 10 years ($10^9$ s) of retention time.
at standard room temperature. In other words the speed at which the crystallization occurs at 30°C has to be 17 orders of magnitude smaller than the same crystallization at 300°C - 500°C. Crystallization theory is the unraveling key to this remarkable phenomenon. At high temperatures (close to the melting temperature of the material) crystallization is thermodynamically favoured but the average high atomic mobility is over compensated by the small driving force for nucleation. On the opposite side, slightly above the glass transition temperature, the driving force for nucleation is high but the atomic mobility is low which results in slow crystallization. Crystallization only occurs in the region between glass transition temperature and melting temperature, where a favourable compromise exists between mobility and driving force; this is the region that memory applications are exploiting.
2.3 Phase-change Materials for arithmetic and biologically inspired computing

Using the intrinsic properties of novel materials to perform new forms of CMOS-free digital and analog computing is a relatively new field of science. In 2010 Borghetti et al. demonstrated how an array of TiO\textsubscript{2} memristors could be employed in the realization of nanoscale digital processor where computation and storage coexist in the same physical location [46]. Their discovery set an important milestone in the area of computational material science but was still relying on the implementation of simple Boolean logic functions. Hasegawa et al. proposed a solid state atomic switch showing intrinsic learning abilities without the need of software programming [47].

The use of phase-change material for novel forms of Non Von Neumann computing has been proposed theoretically in the past [1, 2, 48] and recently demonstrated using femto-second laser pulses [49]. More recently PCM cells have also shown the possibility to emulate synaptic functions of the human brain [50-52]. In this thesis we show that electronic phase-change devices are capable of performing complicated non-binary arithmetic processing and computation, including for example fast parallel factorization and fractional division. Furthermore, such computation is carried out simultaneously with storage, at the same physical location, of the computed result, leading to a particularly simple and effective form of non-von-Neumann computing. To configure a phase-change device as an arithmetic computer, we tailor the input pulse amplitude and/or duration such that the SET state is reached from the RESET state not with a single pulse (as for
normal binary memory operation) but with a pre-determined number of pulses, thus
providing a form of phase-change accumulator. A representation of such scheme is
shown in Figure 2.3. Unlike the accumulators to be found in conventional
processor architectures however, the phase-change accumulator is nonvolatile,
works directly in high-order bases, is capable of carrying out both basic (e.g.,
addition, subtraction, multiplication, division) and advanced (e.g., factorization,
fractional division) arithmetic operations, can function as a simple neuronal mimic
and can provide a form of rudimentary non-volatile logic.

The possibilities of using phase-change materials as both computing and storage
element relies in the details of crystallization dynamics in nucleation-dominated
disordered materials [48]. Applying a small amount of energy (electrically or
optically) to a localized region of this particular class of materials will generate a
variety of small, highly conductive crystalline clusters of material within its
amorphous domain. These first nuclei will be sufficiently separated in space that
the total resistivity of the cell will still be dominated by the amorphous, highly
resistive regions. If more energy is pumped into the system the crystalline domains
will start growing up to a critical dimension where the distance between them is small enough for the percolation threshold to be reached and a “total” conductive state will appear. This metallic, highly conductive, state will considerably increase the current density through the cell promoting further crystal growth until the whole cell becomes crystalline Ge$_2$Sb$_2$Te$_5$. These type of PC materials are known as nucleation-dominated. Other types of phase-change materials like GeSb behave in a very different way, they crystallize starting from a specific favorable place in the energized region and growth from that particular spot until the whole thermally excited region is transformed. These type of PC materials are known as growth-dominated. A glimpse of the difference between GST and GeSb types of crystallization can be seen in Figure 2.4; here a laser pulse was employed as energy source to crystallize similar, micrometre-sized, regions of the two materials. The laser power was cut before complete crystallization occurred revealing two different growth mechanisms. In growth-dominated material the crystallization starts always from a fixed point and growth occurs until the whole region is crystallized. By comparison the nucleation dominated GST shows several randomly distributed crystallites in the region interested by the laser pulse.
Our bio-inspired and arithmetic mechanism will exploit the nucleation kinetics of GST materials and the sudden increase in conductivity at the percolation threshold as a reliable way of assessing the state of a cell. An important distinction has to be made between this implementation of computing mechanism, which from now we will refer as *accumulation regime* and the memristive or *multilevel regime*. If we consider a phase-change cell as a state machine that moves into a consecutive state after each excitation, the electrical resistance will substantially be constant until the very last state where the percolation threshold is reached and the resistivity drops by roughly 100 times [24].

![Figure 2.4 - Difference between nucleation dominated crystallization in GST material and growth dominated crystallization in GeSb materials. From [24].](image)

![Figure 2.5 - Comparison between multilevel regime and accumulation regime computation for a generic base-6 device.](image)
Although similar (from a resistance value point of view) these are pre-percolation states are distinct since it takes different amounts of energy (i.e. different number of subsequent excitation pulses) to bring each different state in the pre-percolation region to the SET state (or to a resistance below a pre-determined decision level).

**Thus, we are not storing information in different resistance levels and are not using the same scheme as proposed for multi-level PCM memories [53-55] or for synaptic-like functionality [50, 56].** Indeed, a perfect accumulator would have only two-levels of resistance, above the decision level for all states from state-0 to state-(n-1) of a base-n system, and below the decision level for state-n. This distinction between the accumulation regime of phase-change devices and the multi-level regime is sometimes overlooked and the two are often confused, but they are different modes of operation and it is the former, accumulation, that makes best use of phase-change cells capability for arithmetic computing and neuron mimics. **Error! Reference source not found.** shows a comparison between the two mechanisms. Unlike in multi-level phase-change memory applications, arithmetic computing via accumulation should not require special methods to combat resistance drift. Indeed, if the low-resistance end-point state of the accumulator is the SET state, then this is essentially stable against resistance drift whereas all other pre-end-point states will over time drift upwards in resistance, actually increasing the decision ‘window’ between resistances above and below the decision level. We should also point out that, with a view to a future phase-change processor, an accumulation computation scheme does not require the use of multiple analog-to-digital converters during the readout of a stored bit (unlike the
multilevel regime) which could truly exploit the ultrafast (< 1 ns) operation of phase-change materials [39].
2.4 Introduction to Carbon materials

One of the most important functional materials in today's semiconductor industry is Silicon, a 4th group element in the periodic table. Having the ability to be tuned between incredibly different values of conductivity by both chemical and electrostatic doping has made Si the last material to radically change human history after stone, bronze and iron. Carbon is also in the same group as Si but it has an extra feature: it's much smaller atomically. In fact Carbon is the smallest element with 4 valence electrons; the cartoon in Figure 2.6 compares various atomic radii from 4th group elements. Such peculiarity leaves the electrons of carbon outer shell free to rearrange in different hybrid configurations leading to an incredible diverse family of materials in both the organic and inorganic compounds.

![Hydrogen, Carbon, Silicon and Germanium Atomic Radii Comparison](image)

Figure 2.6 - Atomic radii comparison between H, C, Si and Ge.

When two carbon atoms are close enough to form a chemical bond one of three possible configurations is bound to happen:

- $sp^3$ hybrid orbital. Every atom’s orbital forms a sigma bond with a neighbour creating a strong tetrahedral structure in which all the atoms are three dimensionally spaced with angles of 109° respect to each other. This is the case of diamond, a fully sp3 wide bandgap material, with extreme hardness, elastic modulus and optical transparency [57] (see Figure 2.7).
Figure 2.7 - Diamond, the fully sp\(^3\) bonded carbon crystal.

- \(\text{sp}^2\) hybrid orbital. In this configuration 3 valence electrons form sigma bonds with in plane neighbours while leaving the remaining electron to form weak longitudinal pi bond. The 100\% sp2 hybridized bonded carbon crystal is graphite, which has recently attract an incredible scientific attention after the discovery and isolation of graphene, a single sheet of graphite with unique and exotic electronic properties [58] (See Figure 2.8).

Figure 2.8 - Graphite, the fully sp2 bonded carbon crystal.

- \(\text{sp}\) hybrid orbital. One s and one p orbital hybridize together and form an sp hybrid, the remaining 2 valence electrons form p orbitals in the z and y direction. Although efforts have been made to create a sp hybridized solid material [59] sp orbitals are mostly observed in numerous organic compounds, like polymers for example. Acetylene is a classic example of a carbon allotrope with a sp hybrid bond, the carbon-carbon triple bond in the middle is formed by 1 sigma and 2 pi bonds (See Figure 2.9).
The characteristic layered crystalline structure of graphite was the subject of intensive scientific research and lately found able to produce more exotic nanomaterials now known as fullerenes (see Figure 2.10). The first carbon fullerene to be discovered came in 1985 when Prof. H. Kroto published the first experimental evidence of what he called C-60 or Buckminsterfullerene, a sp\(^2\) hybridized "cage" of carbon atoms with a shape resembling that of a soccer ball [60]. Prof. Kroto later received the Nobel Prize in Chemistry for the discovery of Fullerenes. In 1991 Sumio Iijima reported transmission electron microscope pictures of what was later named a carbon nanotube or CNT [61]. CNTs have since attracted considerable attention for both their peculiar electron and mechanical properties. Interestingly the charge transport characteristic of CNTs can be either metallic or semiconducting based on the chirality of the specific nanotube, with metallic tubes theoretically expected to show ballistic transport and superconductivity [62]. In 2004 Prof. Andre Geim and Dr. Konstantin Novoselov demonstrated that graphite, the fully sp\(^2\) crystalline allotrope of carbon, could be mechanically exfoliated down to a single atomic thickness (graphene) while remaining stable at room temperature and ambient pressure [63, 64]. The successive experiments confirmed the nature of the charge carriers as being massless Dirac fermions [65, 66] and the popularity of graphene quickly raised and the new science of 2D crystal materials was born. After 6 years only from its discovery the two scientists from Manchester received the 2010 Nobel prize in physics for the discovery of graphene and its unique characteristics.
Figure 2.10 – The fullerenes, a family of $sp^2$ hybridized crystalline carbon materials. Starting from left: buckyballs, carbon nanotubes and graphene are respectively a 0D, 1D and 2D arranged structures of carbon atoms now the subject of intensive scientific research thanks to their unique and exotic properties. From [58].
2.5 Amorphous Carbon materials

Between diamond and graphite, the two main crystalline forms of carbon there's a wide variety of non-crystalline or amorphous structures that can be produced by various different techniques such as ion beam deposition [67], magnetron sputtering [68-70], laser ablation [71], filtered cathodic arc vacuum [72]. Figure 2.11 (reproduced from [73]) shows the ternary phase diagram of amorphous carbon materials deposited at various sp², sp³ and hydrogen content ratio. Historically a-C was produced for the first time in 1971 by Ion Beam deposition [67]. It quickly became a key technology for the manufacturing industry thanks to its hardness, low friction properties, low deposition temperature, chemical inertness and membrane like properties [74]. A general nomenclature scheme was (although incomplete) constructed over the years as various form of a-C were discovered. To classify a carbon material one needs to know several of its structural and chemical parameters, notably:

I. The sp³ content of the film.
II. The degree of clustering of the sp² sites.
III. The 3D nature of the film.
IV. The level of doping (usually Hydrogen or Nitrogen).

A collection of dopant free amorphous carbon materials information can be found in Table 2 following the guidelines of [74].
Table 2 - Amorphous Carbon systems.

<table>
<thead>
<tr>
<th>Name</th>
<th>Sp(^3) content</th>
<th>Clustering</th>
<th>Notes</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ta-C</td>
<td>&gt;70%</td>
<td>Lowest</td>
<td>Hardness comparable to that of diamond.</td>
<td>[75]</td>
</tr>
<tr>
<td>Tetrahedral amorphous carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-C or DLC</td>
<td>10% to 70%</td>
<td>High to Low</td>
<td>Tuneable electronic and optical properties.</td>
<td>[68-70]</td>
</tr>
<tr>
<td>amorphous carbon or diamond like carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nc-G</td>
<td>&lt;10%</td>
<td>High</td>
<td>Highly disordered graphite crystal.</td>
<td></td>
</tr>
<tr>
<td>nanocrystalline graphite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Doping the material with hydrogen or nitrogen changes both its mechanical and optical properties. A set of material recipes and references reported in the international literature is reproduced on Table 3.

Table 3 - Hydrogenated and nitride amorphous carbon systems.

<table>
<thead>
<tr>
<th>Name</th>
<th>Doping</th>
<th>Sp(^3) content</th>
<th>Notes</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLCH</td>
<td>H(_2) at 40 to 60 %</td>
<td>Up to 70% (to H!)</td>
<td>Soft, low density. 2-4 eV gap.</td>
<td>[76]</td>
</tr>
<tr>
<td>Polymer like a-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DLCH</td>
<td>H(_2) at 20 to 40 %</td>
<td>Lower sp(^3) to H. Higher C-C sp(^3).</td>
<td>Harder than PLCH. 1-2 eV gap.</td>
<td>[73]</td>
</tr>
<tr>
<td>diamond like a-C:H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ta-C:H</td>
<td>H(_2) at 25 to 30 %</td>
<td>≈ 70% C-C sp(^3).</td>
<td>Hardest a-C:H. 2.4 eV gap.</td>
<td>[77]</td>
</tr>
<tr>
<td>tetrahedral a-C:H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GLCH</td>
<td>H(_2) &lt; 20%</td>
<td>Low sp(^3).</td>
<td>High number of sp(^2). High sp(^2) clustering. 1 eV gap.</td>
<td>[78]</td>
</tr>
<tr>
<td>graphite like a-C:H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-C:N</td>
<td>N(_2) at few %</td>
<td>Low sp(^4).</td>
<td>High % of sp(^2). Nanostructured at 200°C.</td>
<td>[79]</td>
</tr>
<tr>
<td>a-C nitride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ta-C:N</td>
<td>N(_2) Up to 10%</td>
<td>Sp(^3) at 80-90%</td>
<td>N(_2) doping brings clustering and sp(^3) to sp(^2) conversion.</td>
<td>[80]</td>
</tr>
<tr>
<td>ta-C nitride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Although extremely helpful in giving a general picture of amorphous carbon materials based on their average crystalline composition, Figure 2.11 doesn’t mention the fact that materials with similar composition may have very different
electronic and optical properties. Amorphous carbon system with equal number of \( \text{sp}^2 \) to \( \text{sp}^3 \) sites show a variety of electronic structures thanks to the clustering of the \( \text{sp}^2 \) sites [57]. The most important characteristics defining a \( \text{sp}^2 \) cluster is its physical size. The average cluster size can be quantitatively inferred from Raman Spectroscopy techniques which will be later discussed in Chapter 3.5. Electronic and optical characteristics of a-C materials are closely related to the clustering of \( \text{sp}^2 \) sites within the \( \text{sp}^3 \) matrix. A \( \text{sp}^2 \) hybridized orbital is composed of 3 in plane \( \sigma \) bonds and a single out of plane \( \pi \) bond. Since \( \pi \) bonds lie closer to the Fermi energy they are the ones that dictate the details of the band structure. Robertson et al. describe a model where \( \text{sp}^2 \) sites (isolated or aggregated) define the electronic properties of the material while a \( \text{sp}^3 \) backbone gives its mechanical properties (strength, hardness, etc.) [81].

![Ternary phase diagram of carbon based materials with different sp^2, sp^3 and H ratio. From [73].](image)

A relation between \( La \) (cluster size), \( \text{sp}^3 \) fraction and final "flavour" of a-C is reported in Figure 2.12 (reproduced from [74]). Starting from a cluster size of infinite dimension, as more disorder is incorporated into the system the material
becomes nc-G to a-C and finally ta-C. The sp\(^3\) fraction starts from 0% in the case of natural graphite to 100% for single crystal ideal diamond structure. As we said previously \textit{La} dictates the final electronic and optical properties of the material up to a point where the sp\(^3\) site are the vast majority of the bonds in the carbon system.

In this thesis we will focus on amorphous carbon produced by magnetron sputtering deposition following previous works and recipes from [68, 70, 82-84]. Most of these works are concentrated on a-C coating with specific application to protective layers for hard disk drive media [85, 86] thus analyzing mechanical and optical properties of various films produced with a incredible variety of deposition techniques. However, in this thesis the focus is on understanding the effect of electrical field and current density on the structure and properties of sputtered
amorphous carbon thin films, in particular in the context of their use for resistive memory applications.
2.6 Amorphous Carbon materials for novel memory applications

We introduced in the previous chapter the incredibly rich chemistry of Carbon where a single element can have a surprisingly vast number of different allotropes. Various research groups around the world have recently turned their attention to carbon based materials in an effort to use their electrical characteristics for memory applications. A summary of recent activity in this area is given in Table 4.

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>sp(^2) / sp(^3) content</th>
<th>Switching mechanism</th>
<th>Switching Type</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/DLC/SiN/W. DLC is deposited through via made on SiN</td>
<td>sp(^3) content &gt; 80% (calculated from Raman only).</td>
<td>sp(^2) filament growth / rupture.</td>
<td>UNIPOLAR</td>
<td>[87], [29]</td>
</tr>
<tr>
<td>1) Planar device Pt/C(<em>{\text{cable}})/Pt. 2) Vertical device W(</em>{\text{probe}})/C/Cr/SiO(_2)</td>
<td>100% sp(^2)</td>
<td>Graphite sheet rupture and formation.</td>
<td>UNIPOLAR</td>
<td>[31]</td>
</tr>
<tr>
<td>TiN/a-C/PtSi conductive Pt tip.</td>
<td>sp(^2) rich.</td>
<td>Clustering of sp(^2) sites by joule heating.</td>
<td>WORM</td>
<td>[88]</td>
</tr>
<tr>
<td>Pt/C+Cu/Pt Cu to C ratio = 1.5</td>
<td>Not reported.</td>
<td>Cu ion migration.</td>
<td>BIPOLAR</td>
<td>[89]</td>
</tr>
<tr>
<td>Al/TaC+N/Al N content 5%.</td>
<td>Identified as Ta-C via EELS.</td>
<td>Electron promotion.</td>
<td>BIPOLAR</td>
<td>[90]</td>
</tr>
<tr>
<td>Cu/a-C:H/Pt Ag/a-C:H/Pt Au/a-C:H/Pt</td>
<td>a-C:H with 35-60% H atoms and up to 70% hybridized sp(^3)</td>
<td>Migration of metallic ions.</td>
<td>BIPOLAR</td>
<td>[30]</td>
</tr>
<tr>
<td>1) Metal(<em>{\text{fastdiff}})/a-C/CNT/Metal(</em>{\text{fastdiff}}). 2) Metal(<em>{\text{inert}})/a-C/CNT/Metal(</em>{\text{inert}})</td>
<td>Not reported. Believed to be sp(^3) rich.</td>
<td>1) Metal ions migration. 2) sp(^2) graphitic filaments.</td>
<td>1) BIPOLAR 2) UNIPOLAR</td>
<td>[91]</td>
</tr>
<tr>
<td>Au/a-C:H+B/CrN H at 55% B at 0-5%</td>
<td>Not reported.</td>
<td>Schottky barrier lowering and tunnelling.</td>
<td>BIPOLAR</td>
<td>[92]</td>
</tr>
</tbody>
</table>

Different electrical behaviours (unipolar versus bipolar) and different switching mechanisms emerge from the current international literature available. A clear
picture of the operating principle of a-C memories and their resultant characteristics is clearly far from established. This thesis has the ambition to contribute towards a more deeper understanding of carbon based memory. Many of the research paper are pointing toward a system where metal migration is responsible for the resistive switching mechanism in a similar way to new ReRAM systems briefly presented in Chapter 1.3.2. This might not be the only possibility since a-C has already been shown to become crystalline at high current densities in vacuum.

Figure 2.13 – Sequence of TEM images taken from an amorphous carbon rod exposed to high density DC current. Crystallization occurs in real time, at high current densities. From [93]

Figure 2.13 (from [93]) shows a series of Transmission Electron Microscope (TEM) images taken from an amorphous carbon rod exposed to a high density DC current. Here a-C was deposited in situ via e-beam driven organic decomposition of
carbonaceous species present in the chamber. The degree of crystallization is remarkably proportional to the considerable increase in the conductivity of the rod, the whole process was recorded while observing the crystallization in real time. Bonelli et al. showed how short, high intensity, laser pulses can re-amorphize micrometre regions of a perfect graphite crystal [94]. The same laser-exposed regions were also investigated by electron diffraction techniques revealing numerous, nanometre sized, diamond cubic phase crystallites which the authors explicate as material melting followed by rapid cooling. These phenomena (similarly to conventional phase-change materials, see §2.2) may be a possible explanation for the switching mechanism of any amorphous carbon based memory.

We will address all these possibility and carry out a specific set of experiments to understand the true nature of switching mechanism.

It is important to underline that Table 4 represents a collection of research paper on memories utilizing amorphous carbon as active material. Thanks to the incredibly variety of carbon allotropes many other c-based system have been studied as next generation memory device, especially in the exciting new area of carbon fullerenes. Graphene and its numerous functionalized derivates offer an attractive and innovative option thanks to the remarkable characteristic of this novel 2D material [95-100]. Carbon nanotube systems [101-104] and C-60 buckyball thin films [105, 106] both offer other interesting possibilities which exploit their unique characteristics.
3 Methods
3.1 Scope

In this chapter we describe the experimental methods used during the realization of this thesis. A brief introduction for each technique is reported together with any relevant modification to the standard configuration that may have been implemented.
3.2 Sputtering deposition of amorphous carbon thin films

Sputtering is a powerful deposition technique, widely used for a variety of different thin film materials ranging from dielectrics to noble metals. The main advantages of sputtering over common deposition techniques such as Chemical Vapour Deposition (CVD) or thermal evaporation are the possibility to create thin films made of compounds and alloys, the highly controllable process flow and the low temperature of deposition. Sputtering relies on the generation of a plasma created using an ionized gas. This gas, usually argon or nitrogen, is let into a vacuum chamber at an ultra-low base pressure in a controllable manner, and a DC or RF potential is applied to two facing electrodes placed inside the chamber itself. The potential generates a plasma that bombards and physically removes atoms from a target of the required material, the atoms diffuse through the plasma and finally stick to the desired substrate (for example a Si wafer), accelerated by the external electrical field. A more in-depth introduction on sputtering deposition can be found in [107].

In this thesis, a six inch Nordiko deposition system with four targets and a rotating substrate holder was used to deposit a-C on silicon substrates. Both DC and RF power supplies are available making it a versatile system capable of depositing metals, semiconductors and dielectrics in a single run. A pumping system based on an initial low vacuum rotary pump stage followed by a high vacuum cryo pump stage allows the chamber to reach a pressure as low as $5 \times 10^{-7}$ Torr in a couple of hours and below $8 \times 10^{-8}$ Torr in 24 hours without the need of a load lock system. The substrate, mostly Si/SiO$_2$ in this case, sits on a steel holder as shown in Figure 3.1 (here the purple tile represents the silicon substrate). The steel plate is
constantly water cooled to 12°C, a security interlock ensures the flow to be constantly higher than 20 l/min. The various targets, which are also water cooled, are positioned underneath the rotating substrate holder (not shown) and the plasma is generated between the top and the bottom electrodes. The distance between the two is fixed to roughly 6 cm. Due to the significant size of the targets, the deposition process can be considered uniform for substrate sizes up to 4 inch in diameter. To make sure that the temperature of the deposited film does not increase more than a few degrees, a thermal adhesive was attached to the back of a substrate. The adhesive changes its colour if and when the temperature rises above 50°C. After three consecutive test depositions at 1100W DC (the highest power used in this work) the adhesive didn’t change colour. Thus, we can assume that the temperature of all our processes to be always between 12°C (the water coolant temperature) and 50°C. This direct way of measuring the substrate temperature, although less flexible, is more reliable than traditional thermocouple based methods. It's important to note that any substrate must be physically clamped to the cooling plate at all time to avoid sample overheating during deposition. Overheating generally acts as in situ annealing resulting in alterations of the expected properties of a desired film.
Before starting the deposition process a choice had to be made between different type of substrates. We chose standard silicon wafers, the most common substrate material in commercial microelectronics products. They offer a cheap, reliable and high quality platform with a standard roughness of 1.0 nm Ra or less (IDB Technologies Ltd).

Various substrate cleaning procedures were tested in this work. The most suitable procedure found consisted of three stages:

I. 15 min ultrasonic cleaning in pure acetone.
II. 15 min ultrasonic cleaning in pure isopropanol alcohol.
III. Rinse with deionised (DI) water and dry with nitrogen gun.

A simpler single step approach has also proven to be almost as good as the one above: using a lint free paper soaked in research grade methanol, the silicon tiles were gently scrubbed and dried in air. Using methanol has the advantage of leaving the substrate relatively free of residue, and this method does not require the sample to be rinsed in DI water.
In this study a solid graphite target (99.999% purity, Pi-KEM ltd) is used as carbon source, a DC power source generates the plasma. The gas flow rate is kept constant using a flow mass controller with a selectable set point (up to 200 sccm) and by regulating a throttle valve placed between the cryo pump to the main chamber. A shutter can be programmed to open and close the line of sight between the substrate and the various targets.

Different materials have different deposition rates which are dependent on deposition power, working pressure and the substrate itself. Measuring the deposition rate of each one is the first step of any process characterization. We started by putting a mask on a piece of process-ready (i.e. cleaned) silicon tiles. A fast, sharp and reliable mask was made drawing a simple line with a permanent ink marker on a random spot of the silicon substrate. At the end of the process the mask was "stripped" in acetone followed by isopropanol / DI water / nitrogen cleaning. The step in the resulting deposited film was then measured using a piezo stylus profiler (KLA Tencor).
Figure 3.2 shows how sputtering power controls linearly and directly the deposition rate of the film. The trend line doesn't intercept the axis' origin since below a certain threshold no material can be deposited, this is due to the carbon ions not having enough energy, at low sputtering powers, to reach the substrate. Figure 3.3 shows clearly how sputtering gas pressure and deposition rate are connected to each other. If the working pressure increases too much, the carbon ions will suffer from more collisions (thus having a smaller mean free path) and might eventually never reach the silicon substrate. The pressure becomes less relevant for lower pressure, values and other variables, like DC power, regain control of the rate.

$$\text{DepRate} = 0.0278 \times \text{DcPow} - 0.4487$$
Figure 3.3 - a-C Deposition Rate vs. Working Pressure

Using the linear fit equation one can precisely estimate the deposition rate at different powers.

\[
\text{DepRate} \left[ \frac{\text{nm}}{\text{min}} \right] = (0.028 \cdot \text{DCPower}) - 0.45
\]

Various metallic layers are used as electrodes, as discussed in §6.4, for experiments on a-C vertical pseudo-devices. We report below the deposition rates of their corresponding targets for 30 sccm Ar, \(1.5 \times 10^{-3}\) Torr working pressure, SiO\(_2\) substrate, 200 W DC power and 9 rpm constant substrate rotation speed:

- Pt : 7.54 nm/min.
- Ag : 17.3 nm/min.
- Ta : 4.0 nm/min.
- Ti : 3.33 nm/min.
- TiN : 1.2 nm/min for 15 sccm N and \(1.9 \times 10^{-3}\) Torr working pressure.
3.3 Atomic Force Microscopy and conductive imaging modes

In 1982 Gerd Binnig and Heinrich Rohrer, while working at IBM Zürich, released the details of the Scanning Tunneling Microscope (STM), a new type of microscope capable of imaging and manipulating conductive samples with sub-nanometre precision. This invention gave birth to a new era of nanotechnology and the inventors were awarded with the 1986 Nobel in Physics. In 1986 a similar instrument was invented by Binning, Quate and Gerber called the Atomic Force Microscope (AFM). The AFM allows imaging of any types of sample, even insulators or biological specimens, at the nanoscale using a lithographically defined tip-on-cantilever, (similar to the one in Figure 3.4), a focus laser and a quadrant photodiode.

![Figure 3.4 - A silicon AFM tip. From [108].](image)

In a typical AFM a laser beam is focused on the top surface of a small cantilever which acts as a mirror, reflecting the laser beam to the centre of a quadrant photodiode. The AFM cantilever has a lithographically defined tip at its end. The far end of the tip that ultimately interacts with the sample has a diameter of a few nanometres. Using a three-axis piezoelectric actuator, the tip is lowered and
placed in contact with a sample while the output of the photodiode is used as feedback signal ensuring that a desired set point is reached and maintained (for contact-mode imaging). The sample is being scanned in both X and Y directions and the information from the photodiode signal appropriately recorded yielding an image of the topography with nanometric resolution. Since the tip is in contact with the sample at every time this AFM mode of operation is called contact mode, and it's arguably the most common utilized mode. Contact mode operation is shown schematically in Figure 3.5.

![Figure 3.5 - Atomic Force Microscope (AFM) basic principle. From [109].](image)

Since a nanoscale contact is established in the AFM, one can obtain other information together with the topography of a sample, such as the local electrical conductivity. For such applications to be possible an electrically conductive tip is necessary, with the most common of such tips being metal coated silicon tips. More sophisticated and reliable tips, now commercially available, are made from
doped nanodiamond materials (DDESP-10, Bruker AFM), these tips withstand higher current density than metal coated tips and are less susceptible to wear.

In this work we use a phase-change continuous thin film and a conductive AFM (Innova, Bruker) to show how phase-change materials could be used as a medium for an ultra-high density storage system. This idea has recently been exploited with success in the European project "Protem" (Probe-based terabit memory - http://www.protem-fp6.org/). The principle behind the terabit system lies in using a conductive AFM tip to locally crystallize regions of a continuous, amorphous, phase-change medium via electrical pulses. In this thesis we developed a set-up capable of testing various kinds of resistive switching media with customizable pulses up to 100 MHz in frequency and ±10 V in amplitude. Figure 3.6 shows a diagram of the complete system. Two complementary modes of operation have been designed: a low frequency mode (DC to few kHz) equipped with a variable gain current amplifier (DLPCA-200, Femto), and a high frequency mode (up to 100 MHz) with no amplifying device. Access to the two modes involves changing the BNC cables between the various components, a solution kept intentionally simple to avoid any sort of attenuation or time delay between the input and output signals, thus leaving the electrical path as short as possible. The low frequency mode is used for CAFM imaging of the sample (keeping a constant voltage applied to the thin film and collecting the current via the current amplifier attached to the tip) and for I-V characterization. The high frequency mode uses a programmable function (pulse) generator (AFG3101, Tektronix) for fine control of the electrical excitation. Once pulsed (written), the bits are read back (imaged) using the CAFM, DC, mode.
A 50 Ω surface mount resistor was positioned right next to the CAFM tip module to provide a proper impedance matching between the pulse generator and the tip. A 4.7 kΩ resistor was placed in series with the phase-change sample/device and acted as current limiter, protecting the tip and the sample from any sudden increase in current during the application of a pulse (or during an I-V scan). A photograph of the finished tip holder is shown in Figure 3.7. Shielded BNC cables connect the tip to the pulse generator and to an oscilloscope. All the instruments are 50 Ω terminated.

Figure 3.6 - The CAFM system for writing and imaging nanosized bits in a phase-change medium.
Using an CAFM tip to pass current through an amorphous carbon film creates nanometre sized regions of low resistance material. We saw in §2.5 that annealing a-C in vacuum has the same effect on resistivity, an important key point of this work is assuring that electrically induced Joule heating, during CAFM switching experiments, is in fact responsible for the increased conductivity. Raman microscopy is a powerful tool for assessing the degree of sp$^2$ clustering of the pre / post annealed bulk material (see §3.5), but it's resolution is defined by the size of the interrogating laser beam, which in our case is roughly 1 µm using a 100X lens and a collimated beam. Since a switched bit is around 20 nm to 50 nm (depending on the tip size and roughness of the film) an array of switched bits is required to achieve Raman measurable (i.e. few µm) dimensions.
To generate such an array, a pulse generator was connected to the AFM XY stage via two handshaking signals. In this operating mode the stage moves the sample to an initial point (pixel) via software, a Synch OUT signal then triggers the pulse generator to fire a user-defined pulse to both the conductive AFM tip and an oscilloscope input channel. At the same time the pulse generator sends a TTL signal to both the oscilloscope and the AFM XY stage; this signal is used as a trigger for the oscilloscope (now in single shot mode) to read the sample current and for the XY stage as a "go forward" handshaking signal. The XY stage moves to the next point (pixel) and the whole process repeats. The XY stage is set to move only a few nanometres at each stage so that an almost continuous micrometre sized region is finally switched into the higher conductivity state. Figure 3.8 shows a diagram of the entire operation. It’s important to stress that the same solutions for impedance matching and current limiting shown previously have also been
employed here. A 10x15 µm area was switched using this technique and CAFM, optical microscope and Raman mapping were used as subsequent imaging tools.

The basic sample structure for such studies is shown in Figure 3.9. A conductive mobile electrode is made from an AFM tip (DDESP-10, Bruker).

![Figure 3.9 - a-C films structure. A conductive AFM tip is used as mobile electrode to "fire and inspect" different regions of the sample.](image)

A metallic bottom electrode followed by a thin layer of amorphous carbon were sputtered on top of a 300 nm thick SiO$_2$ layer thermally grown on highly resistive Si (100) wafer. Deposition procedures and parameters are reported previously in Section 3.2. Metallic under-layers were used as bottom electrodes to focus the electric field and increase the current density generated by the tip. A qualitative difference between the two cases (with and without metal under-layer) is immediately grasped using Finite Element (FE) software and a rudimental 2D model, Figure 3.10 compares the two cases.
Figure 3.10 - 2D FE model showing the effect of 5 V DC applied to a conductive Pt tip a) without a metal underlayer and b) with metal under-layer. The color plot represents the local current density. The streamline shows the magnitude of the electric field.
Here a 2D model using the DC conductivity pack of COMSOL 3.5a was created. The values of conductivity for the materials are taken from the literature except for the a-C conductivity which was chosen to be $3.5 \times 10^2$ ohm-cm (similar to our results of §5.2). A stationary 5 V DC was applied to the top of the tip as shown on Figure 3.10. The model was solved and local values of current density are reported as colour plot while electric field magnitude is shown as streamlines. This simple FE model shows how using a back electrode should increase the current density by 3 times. To evaluate if the metallic under-layer was absolutely necessary in order to see a resistive switch, static I-V curves were taken on a number of a-C samples sputtered on a bare SiO$_2$ substrate. Typical results are shown in Figure 3.11, here for a 120 nm a-C sample on a SiO$_2$ substrate.

![Figure 3.11 - IV on a a-C sample with no metallic under-layer. No resistive switching is observed even with voltages up to ±10 V.](image)
No resistive switching is observed for voltages applied up to ±10V. A metallic under-layer is therefore necessary to exploit the functionality of amorphous carbon as resistive memory material (at least in the configuration used in this thesis).
3.4 The importance of the intermediate Ti layer

In Section 3.3 we explained the need of a bottom electrode to increase the current density necessary to switch amorphous carbon using a CAFM system. In this section we point out the importance of having a thin adhesion layer between such bottom electrode and the underlying SiO$_2$ substrate. All the samples prepared for the purpose of this thesis have an adhesion and barrier layer of 10 nm Ti used to separate the SiO$_2$ from any metallic bottom electrode. Failing to deposit the Ti layer result in several problems:

1. Naturally oxidizing metals formed a metal oxide in contact with SiO$_2$. This is explainable by thermodynamic instability at the Metal-SiO$_2$ interface. A simple reaction equation shows an excess of free energy (Gibbs energy) for the Metal not reacting with oxygen, thus bringing the $\text{MetalO}_x + \text{Si}$ as the most favourable state of the system.

$$\text{Metal} + \text{SiO}_2 \rightarrow \text{MetalO}_x + \text{Si}$$

2. Using thin oxide substrates, like a silicon wafer with 2 nm native oxide on top, and no Ti barrier produced unreliable bottom electrodes even with noble metal such as Pt. The most reasonable explanation for this is the formation of small clusters of Pt$_x$Si at the Pt-Si junction [110] that in turn forms a Si/Pt$_x$Si/Pt Schottky diode at the nanoscale.

Figure 3.12 and Figure 3.13 show a Conductive Atomic Force Microscopy (CAFM, see §3.3) conduction scan of a bare Pt electrode on top of a Si substrate with a 2 nm native oxide, bright spots are conductive spots. It’s evident that not all the film is conductive, as it should be for a noble metal; the non conductive regions
become even bigger after 72 hours from deposition. When the same Pt thickness film was deposited on a Si substrate with a 300 nm thermally grown SiO$_2$ with a 10 nm Ti barrier, almost 100% of the film was conductive as shown in Figure 3.14.

Figure 3.12 - CAFM scan of as deposited Si/Pt thin film.
Figure 3.13 - CAFM of the same Si/Pt film after 72 hours.

Figure 3.14 - CAFM scan of a Pt electrode with a Ti barrier.
The effect of the Ti barrier can also be seen in the I-V curve, as the one in Figure 3.15 for example. The film with an intermediate Ti layer between the SiO$_2$ and the Pt layer display a complete linearity from 0 V up to 3 V, in contrast with the same film deposited without using an intermediate Ti layer which show a pseudo linearity after 0.5/0.8 V with an exponential behaviour similar to standard non-ohmic contact.

![Figure 3.15 - Comparison of the I-V curves for Pt electrodes with and without a Ti barrier.](image)
3.5 Raman spectroscopy of carbon materials

To characterize the structure of samples deposited in this thesis, diffraction or spectroscopic techniques are required. X-ray diffraction (XRD) is primarily used in crystalline materials for inspection and process tuning. Unfortunately sputtered carbon doesn’t have any long range ordering, even in samples annealed up to 1300°C [111], therefore XRD is not a suitable technique for this thesis.

Raman spectroscopy can give an enormous amount of structural information, even in amorphous materials, and it’s routinely employed in studies of various forms of crystalline and non-crystalline carbon-based materials [112, 113]. The popularity of the technique comes from its ability to readily distinguish between different allotropes of carbon, it’s non-destructive, it doesn’t require any particular sample preparation process, can achieve micrometre resolution using a confocal apparatus, and recently even nanometre resolution with a so called TERS AFM system. TERS (tip enhanced Raman spectroscopy) uses a nanometre sized gold coated AFM tip to critically enhance a laser collected Raman signal via the excitation of localized surface plasmons. This highly sophisticated technique allows Raman mapping of samples with single molecule resolution [114]. A brief introduction to Raman microscopy is given here to better understand the analysed results shown in the subsequent Chapter 5.

A free atom can move in space in all three directions identified with its degrees of freedom. When $n$ atoms clump together to form a molecule, the degrees of freedom jump to $3n$ with three of them still being the Cartesian axis movement of the molecule as a single entity, three the rotational movement of the whole
molecule and the remaining $3n - 6$ the degrees of freedom that change the distance between the atoms like the length of their chemical bond and their respective angles. Since every chemical bond between atoms is elastic, these movements translate into periodic elastic motions. Classical mechanics doesn't put any constraint on the amplitude of a harmonic oscillator; quantum mechanics however shows that molecules can only exist in definite energy states. In the case of harmonic potentials these states are equidistant, while for non-harmonic potentials the distance between energy levels decreases as the energy goes up. Figure 3.16 shows the difference between the two kinds of potentials.

Figure 3.16 - Quantized energy potentials for harmonic oscillators (a) and non-harmonic oscillators (b). From [115].

The force constants of the bonds, the masses of the atoms and the molecular geometry determine the frequencies and the relative motion of the atoms [115].
Figure 3.17 shows the three normal vibrations of the water molecule, the symmetric and the anti-symmetric stretching vibrations of the OH bonds, $V_s$ and $V_a$, and the deformation vibration $\delta$. Exciting these vibrations with monochromatic light sources (and depending on their activity toward such excitations) might cause two important type of scattering events, a predominantly elastic (or Rayleigh) scattering and minor inelastic (or Raman) scattering.
Figure 3.18 - Raman scattering explanation diagram. When a molecule is excited by a coherent quantum of light an inelastic event might occur, shifting the state of the molecule to a higher (Anti-Stokes) or lower (Stokes) level relative to the pre-excitation state. From [115].

Figure 3.18 represents an inelastic (Raman) scattering event. A quantum of light with energy $h\nu_0$ excites a molecule in one of its active vibrations, the molecule
jumps to a much higher state, quickly returning to a state slightly higher \((h\nu_0 + h\nu_s)\) or lower \((h\nu_0 - h\nu_s)\) in energy than its starting point. This process emits a photon that can be captured and measured revealing the information regarding the molecule's vibrational fingerprint.

Figure 3.19 - Simplified diagram of a typical Raman Spectrometer. A monochromatic laser source is directed onto a flat sample, the refracted light is collected by a Spectrograph that uses a CCD detector to collect the Raman shifted light and transfer it to a computer for data analysis. More advanced systems have an integrated piezo-stage underneath the sample, giving the user the ability to create a spatial Raman map of specific Raman shifts on any sample. In this thesis we will use such a feature for analyzing a-C samples.
Non-organic carbon-based materials are also widely understood in terms of their Raman shift signatures. The Raman signature of single crystal diamond is a single 1332 cm\(^{-1}\) phonon mode at the centre of the Brillouin zone [116]. Graphite shows two major peaks at 1350 cm\(^{-1}\), linked to the K-point phonons of the A\(_{1g}\) symmetry, and at 1580 cm\(^{-1}\) assigned to the centre phonons of the E\(_{2g}\) symmetry [117]. In the literature they are referred as the D peak and the G peak respectively. Figure 3.20 shows graphically both phonon modes.

![Figure 3.20 - a) E\(_{2g}\) G mode. b) A\(_{1g}\) D breathing mode.](image)

Note that the D peak mode is only visible in real (i.e. not perfect) graphite crystals and it's not allowed in ideal crystals. By collecting Raman spectra of various samples deposited at different conditions an extensive range of structural properties are available to the user. One of the most important parameters that describes amorphous carbon materials is the sp\(^2\)/sp\(^3\) crystalline ratio. This gives an idea on where a particular sample stands between a fully graphite-like structure and a fully diamond-like crystalline structure. This is generally calculated from the ratio between the D peak intensity (or I\(_D\)) and the G peak intensity (or I\(_G\)) which can also give an empirical estimate of the size (L\(_a\)) of any sp\(^2\) crystalline domains using the Tuinstra, Koenig (TK) equation [116] reported here (Eq. 1):

\[
L_a = 44 \cdot \left( \frac{I_D}{I_G} \right)^{-1} \text{ [Å]} \tag{1}
\]

Eq.1
Unfortunately there are a couple of complications that have to be considered: (i) Raman spectroscopy is 50 to 230 times more sensitive to sp\(^2\) sites compared to sp\(^3\) sites because visible photons preferentially excite their \(\pi\) bonds [118]; (ii) in sputtered amorphous carbon samples there's a high degree of sp\(^2\) clustering that alters the optical and electrical characteristics of the film, giving an unrealistic measure of \(La\) [119]. Ferrari et al. gave an interpretation of sp\(^2\) clustering using a three-stage model based on the evolution of the Raman spectrum [112]. These stages are here reproduced for clarity:

**STAGE 1: from graphite to nanocrystalline graphite**

a) The G peak moves from 1581 to 1600 cm\(^{-1}\).

b) The D peak appears and \(I_D/I_G\) increases following.

c) There is no dispersion of the G mode.

**STAGE 2: from nanocrystalline graphite to a-C**

a) The G peak decreases from 1600 to 1510 cm\(^{-1}\).

b) The TK equation is no longer valid.

c) \(I_D/I_G\) tends to zero.

d) Increasing dispersion of the G peak occurs.

**STAGE 3: from a-C to ta-C**

a) The G peak increases from 1510 to 1570 cm\(^{-1}\).

b) \(I_D/I_G\) is very low or zero.

c) Dispersion of the G peak occurs.

Sputtered amorphous carbon resides in Stage 2 of the amorphization trajectory. This three stage model gives a fairly accurate description of incredibly large types of amorphous carbon, from perfect graphite crystal to ta-C. It also shows how
following the amorphization trajectory in the opposite direction (i.e. ta-C transformed into graphite crystals) gives an hysteresis loop on the $I_D/I_G$ and G position tables as reported in Figure 3.21. Ferrari et al. also compared XRD and EELS (Electron Energy Loss Spectroscopy) data with Raman peaks collected from various published works in the literature and proposed a different equation to that of Tuinstra and Koenig for predicting the size of crystalline clusters within an amorphous carbon material (Eq. 2):

$$\frac{I_D}{I_G} = C'(\lambda) \cdot L_a^2$$

Eq. 2

with $C'$ (514nm) being 0.0055. The authors concluded that visible Raman spectroscopy is not a sufficient tool for extracting the correct sp$^2$/sp$^3$ ratio for carbon samples with high degree of sp$^2$ clustering, like sputtered a-C. Nevertheless visible Raman is still widely used and, together with additional measurement techniques, helps identify structural differences between carbon materials deposited at various conditions.
In this thesis we use a commercial Raman Microscope (Renishaw) equipped with a 532 nm laser and moving stage. A typical Raman spectrum for a-C films produced in this thesis is shown in Figure 3.22. Raw data is shown in blue, fitted G and D peaks are shown in green and violet respectively, red is the total sum of the fitted curves. There is still some controversy in the literature regarding which fitting functions best describe the measured points. Gaussian functions are usually employed when the G peak FWHM remains smaller than 50 cm\(^{-1}\), in our case the value is always bigger than 140 cm\(^{-1}\) so a different fitting protocol is needed. In these cases the majority of research groups use a Lorentzian fit for the D peak and a Breit-Wigner function (BWF) fit for the G peak (which has been proven theoretically to be more descriptive of the physical structure of the film [73]). For completeness these two functions are here reproduced:
\[ y = y_0 + \frac{2A}{\pi} \cdot \frac{w}{4(x-x_c)^2+w^2} \]  \hspace{1cm} \text{Eq.3}

\[ y = y_0 + \frac{H \left(1+\frac{(x-x_c)}{qw}\right)^2}{1+\left(\frac{(x-x_c)}{w}\right)^2} \]  \hspace{1cm} \text{Eq.4}

\( y_0 \) : constant.
\( A \) : area between function and x axis.
\( w \) : full width at half maximum (FWHM).
\( x_c \) : peak center.
\( H \) : function height.
\( q \) : asymmetry coefficient.

Eq. 3 shows a Lorentzian function and Eq. 4 a typical BW function. Using an iterative automated fitting program (ORIGIN Pro) all these parameters are extracted from the raw data.

Figure 3.22 - Raman profile of 50W DC deposited a-C after 30 min annealing @ 800°C.
Using a Raman microscope with a built in motorized stage also allows the reconstruction of spatial Raman map based on shifts from a fixed peak property (intensity, frequency shift, FWHM and more). A few hours are necessary for a typical area to be scanned with sufficient resolution. The Raman system only captures the profile for each point, giving a single text file as output for the entire process. To create an image a first script in Matlab was created with the purpose of separate the text file into separate files, one for each point. A batch process in OriginLab was created to fit every single Raman profile taken from each point (now divided in one text file per point) into the two D and G peaks. We have already discussed the meaning of these two peaks in this chapter. The information characterizing each peak was copied by the batch program into a final spreadsheet. The spreadsheet was saved as text file and a Matlab script finally created an output image based on these values.
Secondary Ion Mass Spectroscopy (SIMS) is a powerful technique used in elemental mapping of a wide variety of samples. A SIMS system uses a focused beam of charged ions, usually made by ionizing a gas of Ar, Cs or O, to bombard the surface of a sample. These ions are known as primary ions, they force several particles (such as secondary electrons and photons) and impact generated ions (known as secondary ions) to leave the surface of the sample. In SIMS the secondary ions are collected through a mass filter and analyzed using a mass spectrometer. There are different types of mass spectrometers, but their main purposes is the same; to precisely identify the collected ion (together with its concentration) linked to the element that composes the sample [120]. A diagram of the basic concept behind SIMS is shown in Figure 3.23.

SIMS is a destructive characterization technique since the primary ions slowly sputter the sample while the mass spectrometer is analyzing its composition. By keeping track of the ion concentration as a function of time, a depth profile of the composition of any sample, such as thin films, can be easily obtained.
As discussed in §1.3.2 atomic and/or ionic migration is the switching mechanism of various different Metal Insulator Metal (MIM) ReRam systems. In ReRam studies, SIMS can be used to directly probe the structure of a thin film helping identify what causes a voltage induced (for example) switching in conductivity. In [121] for example, the role of oxygen vacancies as switching mechanism of Pt/TiO2/Pt ReRam was identified using a SIMS system.

In this thesis a SIMS system available at CERAM ltd (UK) to compare the possible differences in elemental composition of switched and un-switched regions of amorphous carbon thin films. In §8.5 we show that no difference is discernible between the two regions, excluding metal (or any other element) migration as a possible reason for the observed voltage pulse induced switching observed in our amorphous carbon thin films.
3.7 Amorphous carbon planar devices fabricated by Electron Beam Lithography

Planar devices made of amorphous carbon with platinum electrodes were fabricated using Electron Beam Lithography [122]. An EBL system employs a beam of electrons to create patterns on a resist-coated substrate in UHV. Once the desired pattern has been created a chemical developer is used to selectively remove all the regions exposed to the e-beam during the writing process. Thermal evaporation or sputtering deposition can then be used to fill the trenches in the resist created by EBL; a final rinse in acetone (stripping/lift off step) removes all the residual, unwanted resist leaving the desired pattern in the deposited material. In this work we used a NanoBeam nB4 EBL system.

Figure 3.24 - a-C planar device design. "D" is the distance separating two electrodes and "w" the width.
A schematic of the design for the type of a-C devices used in this thesis is shown in Figure 3.24. Electrodes and carbon layers were deposited in two steps: first depositing the electrodes then following with the carbon layer. This leaves the interface between the carbon and the metallic electrodes 'open' for post-switching optical or CAFM inspection. A whole silicon wafer was used as starting substrate and 64 groups of 6 cells were fabricated for a total of 384 devices on a single wafer. Each group has a different size width of planar electrodes \((w)\) and a different separation distance between two electrodes \((d)\), ranging from 200 to 1400 nm. Before obtaining the final results here reported a series of test runs were conducted for beam dose calibration. Finding the best dose in our particular case was essential in order to achieve nanometre-sized feature on some of the devices. The complete steps to fabricate the devices are reported in Table 5, while examples of fabricated devices are shown in Figure 3.25 and Figure 3.26.

Figure 3.25 - Finished wafer of planar devices. The wafer is characterized by 64 group of devices. Each visible "square" on the wafer is a single group of 6 planar devices.
Table 5 - a-C planar devices process flow.

<table>
<thead>
<tr>
<th>Step Number</th>
<th>Process</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>Clean SiO2 wafer with acetone / isopropanol / DI water / nitrogen.</td>
<td></td>
</tr>
<tr>
<td>2)</td>
<td>Spin resist on SiO2 wafer. Bake resist.</td>
<td>200 nm PMMA, 950K a4 at 3000 rpm. 15 min bake at 175˚C.</td>
</tr>
<tr>
<td>3)</td>
<td>EBL to pattern electrodes from premade CAD file.</td>
<td>80kV, 8.75 nA, 10 C/m², using proximity correction with small feature at 7 C/m².</td>
</tr>
<tr>
<td>5)</td>
<td>Sputter electrodes.</td>
<td>First 7 nm Ti with 30 sccm Ar, 1.5E-3 torr, 200W DC, 9 rpm, 2 min. Second 40 nm Pt with 30 sccm Ar, 1.5E-3 torr, 200W DC, 9 rpm, 5.3 min.</td>
</tr>
<tr>
<td>6)</td>
<td>Strip residual PMMA. Rinse and clean.</td>
<td>Strip in acetone</td>
</tr>
<tr>
<td>7)</td>
<td>Spin resist on SiO2 wafer. Bake resist.</td>
<td>200 nm PMMA, 950K a4 at 3000 rpm.</td>
</tr>
<tr>
<td>8)</td>
<td>EBL to pattern carbon layer from premade CAD file.</td>
<td>80kV, 4 nA, 10 C/m², using proximity correction with small feature at 16 C/m².</td>
</tr>
<tr>
<td>10)</td>
<td>Sputter Carbon layer.</td>
<td>40 nm a-C -&gt; 30 sccm Ar, 1.5E-3 torr, 50W DC, 0 rpm, 40 min.</td>
</tr>
<tr>
<td>11)</td>
<td>Strip residual PMMA. Rinse and clean.</td>
<td>Strip in acetone</td>
</tr>
<tr>
<td>12)</td>
<td>Cut wafer in separate device. Rinse and clean.</td>
<td>Use any PMMA to protect wafer while cutting with diamond saw.</td>
</tr>
<tr>
<td>13)</td>
<td>Bond devices to various mounts.</td>
<td><em>Figure 3.27 a picture of the ambient pressure mount is found.</em></td>
</tr>
</tbody>
</table>
Figure 3.26 - Single group of 6 devices cut ready to be bonded.
3.8 Electrical measurements test-systems for a-C planar devices

Two different electrical test systems were prepared in order to study the memory switching mechanism of amorphous carbon devices at different ambient conditions. For both cases special device mounts were constructed using custom made PCBs and gold plated chip carriers. The PCB were equipped with 50 Ω matching resistors and 4.7 kΩ current limiters, to enable high frequency measurements and current protection for the devices at all time. Figure 3.27 shows a picture of a ready-to-test mount, with a single group of 6 devices installed for ambient pressure experiments. A four-point probe system (with environmental chamber) was used to make the connection between the instrumentation and the sample mount. Some of the experiments were carried out in inert atmosphere using an overpressure of nitrogen gas in the sample chamber while the electrical measurements were done.
A second type of sample mount featured a micro HDMI plug embedded on the PCB, allowing a device to be electrically tested in ultra-high vacuum and transferred to the CAFM for a further study without touching the sample at any time. The standard HDMI cable has an excellent high frequency transfer characteristic, together with a high number of addressable wires.

Figure 3.28 - Sample mount for electric measurements in ultra high vacuum.

Figure 3.28 shows a picture of the aforementioned sample mount ready to be tested in vacuum. The vacuum chamber prepared for the measurement can be found in Figure 3.29.
The vacuum chamber pumped down to roughly $10^{-6}$ Torr by a combination of rotary and turbo pumps, the base pressure is being monitored using a standard Penning gauge. Five feed-through BNC cables allow connection to the sample mount of Figure 3.28. A heating tape was wrapped around the chamber to help degassing of the sample and the chamber before starting any experiment. Samples were normally degassed for 2 days at a maximum temperature of 100°C, any higher temperature would possible induces changes in the structure and properties of the a-C sample, and therefore best avoided.
3.9 GST pseudo-device preparation

In this thesis, as already mentioned in §2.3, phase-change materials and devices were also investigated, in particular for the possible application in arithmetic processing. In this respect, phase-change "pseudo-devices" were fabricated, made from a continuous, wafer sized thin film of Ge$_2$Sb$_2$Te$_5$. These structures, although different from real mushroom cell type phase-change devices, have a similar switching characteristic and are considerably easier to fabricate. The continuous Ge$_2$Sb$_2$Te$_5$ films were prepared in collaboration with Plarion ltd. (http://www.plarion.com/) and were successfully employed in various research projects [123-125]. A schematic diagram of the final phase-change pseudo-device is shown in Figure 3.30.

![Schematic of the phase-change 'pseudo-cells' and method of contacting the top electrode using a CAFM (conducting diamond) tip.](image)

Figure 3.30 - Schematic of the phase-change 'pseudo-cells' and method of contacting the top electrode using a CAFM (conducting diamond) tip.
The lower a-C layer is prepared to be highly conducting \((\sigma \geq 10^2 \, \Omega^{-1} \cdot \text{m}^{-1})\) and in combination with a Ti layer provides the bottom electrode. The top a-C layer provides environmental protection for the GST and is also conducting, but less so than the bottom a-C layer \((\sigma \approx 50 \, \Omega^{-1} \cdot \text{m}^{-1})\). Using standard Electron Beam Lithography (NanoBeam nB4 system) an array of metallic electrodes was patterned on top of the GST wafer. Each electrode is separated from the others by 5 µm. These arrays were patterned on PMMA resist (200 nm of 950k:a4) and deposited by magnetron sputtering using the same system described in §3.2. The electrodes were initially made using 5 nm thick Cr and 15 nm thick Au. This solution has proven to be inadequate since pure gold has a melting point of 1064°C, not enough to support the high temperatures reached by the CAFM tip during I-V testing or pulsed-writing experiments. The final version of our pseudo-devices therefore uses top electrodes made of 15 nm Pt over a 5 nm Ti adhesion layer. Figure 3.31 shows a tapping mode scan of a random region of the processed GST wafer.

![Image](image.jpg)

Figure 3.31 - a) array of Pt dot on top of GST wafer, scale is 1.5 µm. b) zoom on a single dot, scale is 200 nm.
For electrical measurements on pseudo-devices, a conductive diamond CAFM tip (DDESP-10, Bruker AFM) was used to make electrical contact to the Ti/Pt patterned electrode. Thus, the complete electrical test system used with the pseudo-devices is shown in Figure 3.32 and Figure 3.33. This system allows the use of relatively fast pulses (<200 ns) of variable and controlled amplitude, while also allowing for the resistance of the pseudo-device to be measured at DC after the application of each pulse.

Figure 3.32 - GST pseudo-device and CAFM electrical test system.
The electrical linearity of the CAFM tip was checked before and after each set of pulsing experiments by measuring an I-V response with the tip placed in contact with a gold test standard. We found no difference in the I-V response of the tip on the gold standard film before and after any of the measurements performed on our phase-change devices (typical before and after curves are shown in Figure 3.34), confirming that any switching observed was not due to some non-linearity introduced by a damaged or altered tip.
A tapping mode compatible cantilever was employed in positioning the diamond conductive tip right on the top of a specific electrode without damaging the tip or the electrode itself. The AFM controller was then instructed to switch to contact mode, establishing a reliable electrical contact at a constant pressure. Once in contact, a computer-controlled function generator switched systematically between resistivity measurement, using a low voltage, low frequency triangular wave, and single-shot pulsing at different amplitudes. During the pulsing mode, the bottom electrode of the cell is redirected to ground leaving the shortest possible electrical path for the high frequency signal. A time delay of 2 seconds was left between each pulse to avoid any potential thermal effects on the outcome of the arithmetic processing experiments (see Chapter 4) and to leave enough time to the system to read reliably the resistivity of the pseudo-cell. The complete set up made of a function generator, an oscilloscope and the PC used to save the data were controlled by a script written in LabView.
4 Phase-change memory devices for beyond Von Neumann computing
4.1 Scope

In this Chapter we show how phase-change memory devices can be used to perform novel forms of arithmetic and biologically-inspired computing.

We start by writing various bits in a continuous phase-change medium using a conductive AFM tip and a standard pulse generator; the diameter of the bits are shown to be as small as 20 nm.

We then use a phase-change pseudo-device to perform novel forms of arithmetic and biologically-inspired processing.

Finally we show the first evidence for the amorphous carbon capping layer contributing in the observed memory switching.
4.2 Demonstration of an ultra-high density data storage system using a phase-change medium and a CAFM

The phase-change thin films used in this thesis were prepared by Plarion (UK), and successfully employed in various past research projects [123-125]. In Figure 4.2 we show a conductivity map of a small portion of our phase-change sample where an I-V curve was made (in DC mode CAFM) prior to imaging the area. The I-V curve itself is reported in Figure 4.1.

Figure 4.1 - Single I-V curve in DC mode. The resulting change in the local conductivity of the region was later imaged using a CAFM and reported in Figure 4.2.
Figure 4.2 - CAFM image (left) of a single switched region of our phase-change sample. The size of the written bit is 20 nm, made using a brand new diamond conductive tip in DC CAFM mode (I-V shown in Figure 4.1). A line scan through the written bit is also shown (right).

Figure 4.2 shows a CAFM image of a portion of phase-change sample after applying an I/V curve through the tip to locally switch a small, nanometre sized region, to the crystalline state. The small circle visible in the center of the picture represents the switched region with increased conductivity. Compared to its amorphous phase, Ge$_2$Sb$_2$Te$_5$ has a much higher conductivity in the crystalline phase (as discussed in §2.2). The crystallization process is induced by the voltage rising above a certain threshold (3.6 V for this particular sample) causing a drastic increase in current followed by the local heating of the medium above its crystallization temperature. It’s important to note that even though the conductivity of the region was increased, the physical topography of the sample is unaffected (see Figure 4.3). The rigid amorphous carbon capping layer avoids undesired topography changes due to the well known increase in density that a phase-change material undergoes during the crystallization process.
Writing a nanometre sized bit was possible thanks to the remarkable sharpness, when new, of the diamond conductive tips (DDESP-10, Bruker). These tips have an effective contact area of 40 nm. After a few scans and write cycles however, the tip quickly becomes larger and the resolution decreases with it. Figure 4.4, for example, shows some more I-V switched regions made with a slightly less sharp (used) tip. Here the diameter of the I-V switched regions are larger compared to the first isolated bit of Figure 4.2, incorporating more grains and being of an irregular shape. Sharper and more reliable conductive PtSi type tips were designed during the ProTeM project [126, 127] but for this thesis we used diamond conductive probes (DDESP-10, Bruker) for their superior reliability.
In Figure 4.5 we show the results of bit writing tests using the high frequency mode (described in §3.3), with rectangular pulses of 4.5V amplitude and 175 ns width. As we can see, the diameter of the dots has more than doubled (from 20 nm to 50 nm) compared to Figure 4.2, this is because of a now even bigger, worn, tip.
An important point to consider here is the difference in read current amplitudes between the various switched dots of Figure 4.5. All the bits were switched with similar type of pulses but, as seen in Figure 4.5, the read currents from the switched regions are not exactly the same. This is most likely caused by the electrical contact between the tip and the medium being slightly different at each "firing" point, which is dependent on the size of the tip, the roughness of the medium, the direction of scanning, etc. The contact resistance between a CAFM tip and any conductive medium can vary between several orders of magnitude and such a variation is undesirable for reliable and repeatable measurements. In §4.3 we shown how to avoid these contact resistance changes by creating an array of predefined electrodes on the top of our sample. We call the resulting ‘Tip-Pt dot-PC sample’ stack a "pseudo-device", and it’s this pseudo-device that we use to demonstrate the arithmetic computing capabilities of phase-change memory type devices.
4.3 Computing cell characterization

In order to avoid uncertainties due to a varying tip / sample contact resistance we patterned our continuous media with an array of identical Pt spherical dots (see §3.9 for details on preparation), using the CAFM tip as a mobile electrode to contact the top of such dots. The first step is to characterize these pseudo-devices with standard near DC mode I-V curves.

A near DC I-V curve of a pseudo-device, as measured by the CAFM, is shown in Figure 4.6. This curve carries vital information about our phase-change sample; in particular the threshold voltage ($V_{th}$), 3.6V in this case. Different layer configurations and GeSbTe stoichiometry would give different $V_{th}$. For our purposes $V_{th}$ is a key parameter in cell characterization. When we apply input pulses with an amplitude greater than this threshold (assuming typical pulse durations in the hundreds of nanoseconds range), the cell switches into the higher conductivity state (SET state) with a single pulse, as in standard memory operation. However, if we reduce the input pulse amplitude (while keeping the duration constant), the number of pulses required to reach the SET state increases.
Figure 4.6 - Static I-V on a phase-change pseudo-device. The voltage threshold is roughly 3.6 V. The three arrows indicate how the I-V curve evolves in time.

By choosing appropriately the pulse amplitude and duration (here we used a full-width-half-maximum (FWHM) pulse width of 100ns see Figure 4.7 for an example) we can tailor the number of pulses required to completely switch a pseudo-device. As an example, we report the effect of four different pulse amplitudes on various devices with the same structure (Figure 4.8). As we can see, a voltage pulse of 3.96 V (thus bigger than 3.6V), brings the resistivity of the cell below the selected threshold of 275 kΩ in a single pulse, as expected. Three pulses are needed when reducing the amplitude to 3.37 V while with 3.17 V six pulses are needed and so on. One can immediately see that the higher the number of pulses desired to switch a device, the higher needs to be the precision in controlling the voltage pulse.
We now fire consecutive pulses with various amplitudes and record the number of pulses required to switch a cell to a high conductivity state (or more simply to push the resistivity below our selected threshold level of 275 kΩ). Figure 4.9 shows the aforementioned collection of points; a clear trend emerges with lower amplitudes requiring more pulses to switch a cell into its crystalline phase.

Figure 4.7 - Standard pulse shape for the results of Figure 4.8 to Figure 4.15 as taken from a digital scope.
Figure 4.8 - Different pulsing amplitudes have different effects on the cell resistivity. Smaller amplitudes (compared to $V_m$) lead to more pulses required to switch a single cell.

Figure 4.9 - Pulse amplitude vs. number of pulses required to switch a cell.
4.4 Addition operation

After characterizing the phase-change pseudo-devices we now demonstrate how the pulsing scheme can be used to perform an addition operation, directly in base-10, using the accumulator response of Figure 4.10. For example, to perform the sum \(3_{10} + 4_{10}\) we started with the cell of Figure 4.10 in the amorphous (RESET) state and applied (3.12V, 100ns FWHM) pulses equal in number to the first addend (three pulses in this case), thus leaving the phase-change accumulator in state-3 (as shown in Figure 4.10). We then applied (identical) pulses equal in number to the second addend (four further pulses in this case), causing the base-10 accumulator to move on to state-7.

![Figure 4.10 - Base-10 addition using accumulation regime computation. The result is readily stored in the same cell used for computation.](image)

The phase-change cell thus carried out the addition \(3_{10} + 4_{10}\) and simultaneously stored the result, since the cell resides in state-7. To access the result of the sum we applied identical input pulses until the cell reached its low-resistance state (i.e.
state-10), with the complement (to the base) of the number of pulses needed revealing the result; three pulses were needed in this case, so the answer to 
\((3_{10} + 4_{10})\) is, as expected, \(7_{10}\). Should the result of an addition exceed \(9_{10}\), then the base-10 accumulator is reset, a carry forward recorded, and the process continued until the required number of pulses have been inputted to the accumulator (for example \((7_{10} + 6_{10})\) would lead to the cell being reset once, so a carry forward of one, with the accumulator left in state-3).
4.5 Subtraction operation

We now experimentally demonstrate a simple and reliable way to perform electronic subtraction using nanoscale phase-change accumulator cells. Here we choose to work in base-6 (demonstrating the flexibility of the phase-change arithmetic computing approach), so that input pulse amplitude and duration is tuned to yield base-6 accumulator responses of the form shown in Figure 4.8. To perform subtraction we use two cells (both working as base-6 accumulators) and the fact that the difference between two numbers is the same when a common number is added to each of the numbers in the subtraction.

Figure 4.11 - Subtraction using accumulation regime computation with phase-change memory devices. Two cells scheme is here demonstrated.
Specifically here we performed the subtraction \((3_6-1_6)\), using the following steps:

a. First we input pulses equal in number to the minuend \((3)\) to Cell A.

b. then we input pulses equal in number to subtrahend \((1)\) to Cell B.

c. next, we applied further pulses to Cell A until the resistance of Cell A fell below the decision level (three pulses were needed here - Figure 4.11).

d. finally we inputted to Cell B an identical number of pulses to that needed in stage (c.) (i.e. three pulses). At the end of this process the result of the subtraction is stored in the final state of Cell B; here Cell B was in state-4.

To access the result we count the number of additional (identical) pulses we need to apply to Cell B until its resistance falls below the decision level; here two pulses were necessary (see Figure 4.11), yielding the correct result. Thus, we have experimentally carried out the base-6 subtraction \((3_6-1_6) = 2_6\), using two base-6 phase-change accumulators and re-casting the subtraction as \((3_6-1_6) = (3_6+3_6) - (1_6+3_6)\). (Note that if we swapped the roles of Cells A and B in the above subtraction method, re-casting the subtraction as \((3_6+5_6) - (1_6+5_6)\), the final result would be stored in Cell A and accessed as the complement to the base of the number of pulses needed to take Cell A below the decision level; this provides algorithmic consistency with the addition method described earlier, which may be useful in practical systems.

Note that since multiplication can be implemented by sequential-addition, and division by sequential-subtraction, it is clear that we can also carry out multiplication and division, directly in high-order bases, using nanoscale phase-change accumulators. Indeed, it is possible to carry out division directly using a
single phase-change accumulator (as was previously demonstrated, albeit optically and on the tens-of-micron size scale [49]), rather than by a two-cell sequential subtraction approach. In this alternative, single-cell division 'algorithm' we use the divisor to define the number of pulses required to reach the decision level, rather than the base, inputting to the accumulator pulses equal in number to the dividend, re-setting each time the decision level is passed to reveal the quotient, with the reminder stored in the cell end-state (see Ref. (18) for details). While such an approach to division is attractive in terms of efficiency, with only a single cell being needed and division being performed directly rather than by successive subtractions, the necessity to re-configure the accumulator (in terms of the number of pulses required to switch the cell) for each divisor encountered is not attractive for general computation. However, this method of division is well suited to parallel factorization, as explained in the following Section.
4.6 Parallel factorization

Factorization of particular large numbers is a key aspect of modern cryptography. One of the most successful and implemented crypto-algorithm, the Rivest-Shamir-Adleman (RSA), relies on the fact that it is mathematically trivial to multiply large prime numbers while at the same time it is incredibly time and power consuming to do the opposite, find the prime factors of a given large number. The product of large prime numbers is what makes a security-key safe, the larger the prime numbers the safer the key. The sequential nature of von Neumann architecture, where each CPU can process only one operation at a time, makes retrieving a secret key a computationally demanding job for a computer. Here we present an alternative way of factoring numbers that can be executed in parallel, using natural bases (i.e. not binary) and at the same speeds of conventional PCM devices.

In Figure 4.12, for example, we show the process for parallel factorization of the number 6. In this first picture the number 2 is checked as to be prime factor of 6. Due to the limitation of our CAFM set up we are bound to test one number at a time. Having a real PCM device would allow all the numbers to be checked as prime factor in parallel. In order to find if 2, 3 and 5 are prime factors of 6, Cell A (Figure 4.12) was set-up so that it switched after two pulses were inputted, i.e. it operated as a base-2 accumulator, Cell B (Figure 4.13) was set-up as a base-3 accumulator and Cell C (Figure 4.14) was set as base-5 accumulator.
Next we inputted to each cell pulses equal in number to the number to be factored (6 in this case), re-setting a cell (or in our case, since, as previously shown, re-amorphization in the CAFM environment is difficult,[123, 128], we moved to a new cell) should it cross the decision threshold. Once this process has been completed, any cell whose end point is below the decision level has its base as a factor.
Figure 4.14 - Parallel factorization implementation example. Here the number 5 is checked as prime factor of 6, Cell C. The last (second) cell doesn’t switch to SET state on the sixth pulse thus 5 is a prime factor of 6.

After the inputting of 6 pulses to all three cells the end-point of Cell A and Cell B were below the decision level, so 2 and 3 are factors of 6, whereas the end-point of Cell C was above the decision level, so 5 is not a factor of 6. Note that in our CAFM system it was not possible to apply pulses in parallel to multiple cells (since we only have one tip), however, fast parallel operation would obviously be eminently feasible with real PCM type devices.
4.7 Implementing Serial Logic gates

Accumulation might also be used to provide a form of serial non-volatile logic, since accumulator responses, such as those shown in Figure 3, also perform a serial AND (or NAND) function. For example a base-2 accumulator provides a 2-input serial AND ‘gate’, a base-4 accumulator a 4-input AND etc.

Figure 4.15 - Serial 13 input logic AND implementation.

In Figure 4.15 we show a 13-input AND logic operation; interestingly, conventional CMOS 13-input AND gates are available from several manufacturers (see [129] as an example).
4.8 Re-amorphization experiments on patterned GST medium

So far we explored the nucleation-driven crystallization properties of GeSbTe phase-change materials, using electrical pulses to provide an alternative way of performing non von Neumann arithmetic computation. We utilized pseudo-devices made of a continuous phase-change medium patterned with platinum electrodes for reliable contact purposes. This approach has the advantage of being fast, easy and indeed suitable for a proof-of-concept study. The main disadvantage however is the uneasy re-amorphization of a written bit which has proven to be extremely difficult using a CAFM approach [123, 128]. Here we have initially tried to re-amorphize a written bit similar to the one in Figure 4.2 with our standard high frequency set up, unfortunately with no success.

![Figure 4.16 - Partial or incomplete re-amorphization of a phase-change pseudo cell.](image)

After each single pulse (up to 10V, 10 ns width), the written region tends to increase both in diameter and value of conductivity. This is in contrast with the expected behaviour of phase-change materials that should return to high resistivity, RESET, state when heated with short electrical pulses when quenched. We then
tried the same pulse patterns on one of the patterned electrode (similar to the one in Figure 3.31). Figure 4.16 shows the data collected from a series of DC I-V followed by high frequency pulses on a single phase-change pseudo-cell. Two states of conductivity are emerging from our data, applying a (0 to 5V) I-V on the cell lowered the resistance value in all cases, while pulsing it with 10ns, 10 V pulses brought it slightly higher. It would appear that, under these circumstances some form of partial re-amorphization is occurring. Unfortunately, due to time constraints we couldn’t explore further this apparently partial re-amorphization of our pseudo-devices.
4.9 Capping layer role in memory switching

The phase-change continuous medium used in all the experiments of Chapter 4 has a thin protective capping layer made of sputtered amorphous carbon material. This carbon protective layer acts as a barrier that avoids oxidation of the GST [130], protects it from physical damage while, contrary to conventional SiO$_2$ based capping layers, being conductive enough to allow bit writing with a CAFM system.

We discussed in §2.6 the possibility of using amorphous carbon as a new materials for future ReRam memories (see §1.3). Understanding the role of the amorphous carbon layer in the observed memory switching is therefore important, not only to assess its possible implication in phase-change devices but also as an entirely new material candidate for both data storage and arithmetic computation applications.

Thus, the following Chapters will focus on the production, characterization and testing of amorphous carbon thin films and devices.
4.10 Discussion: Phase-change materials for beyond Von Neumann Computing

In Chapter 4 we showed how the so called "accumulation regime" of nanoscale phase-change memory devices can be used to perform not only a full range of arithmetic operations (addition, subtraction and multiplication in §4.4, subtraction and division in §4.5) but also carry out complex processing such as parallel factorization (§4.6) in any base. Arithmetic computation is executed using a novel, beyond Von-Neumann, method where processing and storage are executed simultaneously by the same nanoscale phase-change cell. Interestingly, arithmetic processing has been shown capable of direct base-10, human-like, operation paving the way to future simpler human-machine integration systems. Phase-change accumulator-based arithmetic computing also has the potential to be extremely power efficient compared to conventional CMOS-based arithmetic processors. As already mentioned, this ability to work directly in high-order bases with a single phase-change cell is exceedingly efficient; by comparison a conventional binary 3-bit full adder requires five AND, five XOR and two OR gates, i.e. around 100 CMOS transistors, to perform the equivalent of the addition of two base-8 numbers. We should also mention that phase-change devices have the potential for excellent scalability, down to the single-nanometre scale[26, 131], so that a phase-change based approach to computing could potentially offer very significant savings in terms of chip area as compared to conventional CMOS implementations.
The same accumulation regime that endows arithmetic operation can also be used to provide a simple form of non-volatile serial logic gate. Such phase-change logic has the advantage of being non-volatile, but the requirement to enter data serially, to reset the cell after each logic operation and to have a separate read cycle means that such devices would not be logic ‘gates’ in the classical sense. Nonetheless, their simplicity and efficiency of implementation may be attractive for certain specialized applications. Interestingly we note that 13-input AND/NAND gates are commonly available from many semiconductor manufacturers (Philips 74F133, St M74HC133) and typically need over 50 CMOS transistors to implement. A 13-input serial phase-change AND/NAND could however be realized with a single nanoscale phase-change cell, using the base-13 accumulator response shown in Figure 4.15.

This thesis, in particular in Chapter 4, shows how phase-change devices potentially offer a range of functionalities that goes far beyond the traditional simple binary memory concept and encompass new efficient and powerful forms of computing based on their intrinsic material properties. It is of fundamental importance to stress that this new form of computation doesn't require the use of any particular software to control or synchronize the various cells. This special characteristic brings the possibility to process as many inputs as wanted in a fully parallel fashion without having to create specific data buses for memory / CPU / memory data transfer. More importantly a continuous source of energy (i.e. DC supply) is not required thanks to the inherent non-volatile character of phase-change materials.

To protect the phase-change layers in our samples, an sp-2 rich amorphous carbon (a-C) was used as a capping layer to avoid oxidation of the GST layer, and
to prevent mechanical damage during CAFM studies. It was found that this a-C layer also underwent a form of resistive switching when subject to voltage pulses. There are relatively few reported works in the literature on voltage-induced resistive switching in sp2-rich amorphous carbon films [30, 89, 132], and so the rest of this thesis contributed to this field.
5 Deposition and structural characterization of amorphous carbon thin films
5.1 Scope

In §4.9 we discussed the possibility for the amorphous carbon capping layer protecting the phase-change medium to be implicated in the observed voltage induced switch in conductivity. In this chapter the focus is on the deposition process of carbon thin films using the magnetron sputtering system described in §3.2. Subsequent characterization of the deposited thin films is carried out using four point probe electrical measurements and Raman spectroscopy (see §3.5) under various annealing conditions.

A complete discussion of this chapter’s results can be found in §5.13.
5.2 Film resistivity with increasing deposition power

After calibrating the deposition rate of the sputtering system described in §3.2, a series of amorphous carbon thin films on silicon substrates were systematically prepared. The deposition time was calibrated in relation to the increasing deposition power in order to obtain films with identical thickness. The remaining deposition parameters: working pressure (1.5x10^{-3} Torr), Ar gas flow rate (30 sccm), high vacuum pump throttle (85%) remained fixed for the whole series. Once deposited, the resistivity of the films was measured using a standard in-line four point probe technique. Figure 5.1 shows how increasing the DC deposition power decreases the initial resistivity of the material over three orders of magnitude.
5.3 Film resistivity with increasing annealing temperatures

The series of thin films prepared in §5.2 were later used for annealing experiments in vacuum at various temperatures. Studying the effect of thermal heating is essential to later quantify the effects of local Joule heating experiments on the structure of a-C thin films.

![Figure 5.2 - Resistivity vs. annealing temperature at different deposition powers.](image)

The annealing experiments were carried in a vacuum of 2.5x10^{-2} Torr using a tube furnace connected to a rotary pump system. The temperature was increased at a constant 3.8 °C/min and the final temperature kept at a specific point for 30 min by use of a PID controller. The furnace was then left to cool down to room temperature before breaking the vacuum and unloading the samples. The resistivity of each film was measured using an in-line four-point probe connected to a Keithley 2400 source meter. To ensure that the a-C thin films were not evaporating during heating, due to residual oxygen gas promoting CO formation, before and after thickness measurements were performed on a piezo tuning fork.
system (LNA Tencor). No difference in thickness was found in the sensitivity range of the system (±1 nm), even for samples annealed at 800˚C. Figure 5.2 shows the resistivity of the a-C films deposited at different DC powers and for various annealing temperatures. An approximate linear relationship (in the semi-logarithmic scale) between annealing temperature and film resistivity is revealed.
5.4 Film opacity with increasing annealing temperature

In Figure 5.3 a picture of the complete 50 W DC deposited series after annealing 30 min in vacuum at 150°, 300°, 500° and 800° C is shown.

![Figure 5.3 - Annealing experiment on 50W DC deposited sample.](image)

The 800° C film is visibly darker than the "as-deposited" one. A significant confirmation of this comes from the Raman profile of the films, as shown in Figure 5.4. The sharp peak at 520 cm\(^{-1}\) is the common Raman peak of the Si (100) substrate, as the temperature increases the peak becomes less intense, this is due to the a-C layer becoming less and less transparent to the incoming laser. All the Raman measurements were made at low laser power to avoid any modification (i.e. graphitization) of the probed area by optical heating. A second peak around 920 cm\(^{-1}\), which originates from the SiO\(_2\) thermally oxidized layer between the Si substrate and the carbon layer, also decreases because of the increasing opacity of the a-C film. The 800°C treated sample has almost no sign of such a Raman peak.
Figure 5.4 - Raman profiles of 50W DC deposited series with increasing annealing temperature.
5.5 $I_D/I_G$ peak ratio with increasing deposition power

To better understand the evolution of the structure of a-C with increasing deposition power, we used Raman microscopy to obtain the $I_D/I_G$ ratio of the same thin film series deposited for the resistivity measurements in §5.2. An theoretical introduction to Raman microscopy can be found in §3.5. Figure 5.5 shows the relation between $I_D/I_G$ ratio and DC sputtering power for these thin films.

![Figure 5.5 - $I_D/I_G$ ratio with increasing DC deposition power.](image)

Increasing the deposition power resulted in carbon films with a higher $I_D/I_G$ ratio, approaching an ultimate value of 0.6 for the 1100 W DC deposited sample. Comparing to the resistivity measurements of Figure 5.1, it can be seen that as the $I_D/I_G$ ratio increases, the resistivity decreases in a monotonic fashion.
5.6 $I_D/I_G$ peak ratio with increasing annealing temperatures

Samples deposited with increasing deposition powers were vacuum annealed at various temperatures and their $I_D$ and $I_G$ peaks measured using visible Raman (532 nm) as described in §3.5.

Figure 5.6 shows an increase in $I_D/I_G$ ratio with increased annealing temperature following an approximately linear trend. The ratio increases for all the samples even if the starting point (i.e. the $I_D/I_G$ ratio for an as-deposited sample) is higher for high power deposited samples.
5.7 G Peak position with increasing deposition power

Here we used Raman spectroscopy (532 nm) to extract the position of the G peak with increasing deposition DC power.

![Graph](image)

**Figure 5.7 - G peak position (cm\(^{-1}\)) with increasing deposition power.**

Figure 5.7 shows how higher power DC sputtering up-shifts the position of the G peak with respect to the low power deposited samples, the up-shift is linear in respect to the power.
5.8 G peak position with increasing annealing temperature

Samples deposited at various powers were vacuum annealed at various temperatures and their G peak position acquired with visible Raman (532 nm) microscopy as described in §3.5.

Figure 5.8 - G peak position vs. annealing temperature at different deposition powers.

Figure 5.8 shows the G peak position with respect to the increasing annealing temperature; an up-shift is shown for all the deposition powers, with the G peak position increasing linearly (to higher values) with increasing temperature. At 800°C, all the G peak positions are very close together.
5.9 G peak FWHM with increasing deposition power

The Raman microscope was here employed to probe the value of the G peak Full-Width-Half-Maximum (FWHM).

![Graph showing G peak FWHM with increasing DC power deposition.](image)

In Figure 5.9 the FWHM of the G peak with increasing deposition powers is reported; a broadening of the peak with increasing power emerges. The monotonic trend resembles that of the $I_D/I_G$ peak of Figure 5.5.
5.10 G peak FWHM with increasing annealing temperatures

The Raman microscope was here employed to probe the value of the G peak FWHM with increasing annealing temperature. Experiments were once again carried in vacuum with same procedures previously described (§3.5).

Figure 5.10 - G Peak FWHM (cm$^{-1}$) vs. annealing temperature (°C) at different deposition powers (W).

Figure 5.10 reports the value of G peak FWHM for all the samples prepared at different powers and annealed with increasing temperatures. The FWHM value decreases monotonically in all the series as the annealing temperatures increases.
5.11 Film roughness evolution with increasing deposition time

Figure 5.11 shows the evolution of a-C film roughness with increasing deposition time. The roughness of the films was measured using standard tapping-mode AFM. In this series the substrate is a SiO$_2$ over Si wafer covered with 35 nm of sputtered TiN. The carbon sputtering power is 400 W DC, with a fixed deposition rate of 8.2 nm/min.

The roughness of the film at zero time refers to the bare TiN over Si/SiO$_2$ substrate. Depositing amorphous carbon on top of titanium nitride gradually reduces the roughness of the film with a minimum roughness observed at around 8 min, which corresponds to an a-C film thickness of 65 nm. After passing the minimum at 8 min the roughness begins to increase, reaching the initial film roughness again at 32 min, with a film thickness of 265 nm.
5.12 Film roughness with increasing deposition power

The roughness of thin films with increasing deposition power was measured using a tapping-mode AFM and the results reported in Figure 5.12. Each film has a fixed thickness of 50 nanometres with the initial roughness of the bare TiN over Si/SiO$_2$ substrate being 0.537 nm RMS.

![Graph showing film roughness with increasing deposition power](image)

**Figure 5.12 - Amorphous carbon thin film roughness vs. deposition power. The green line represents the initial roughness of the SiO$_2$ / TiN substrate.**

Increasing the deposition power (while keeping the thickness of the film constant) results in a-C layer with decreasing roughness.
5.13 Discussion: Structural characterization of sputtered a-C thin films

In Chapter 5 we described how to deposit and characterize amorphous carbon thin films using a magnetron sputtering system. First, we found a linear dependency between film resistivity and deposition power (Figure 5.1), with values ranging over 3 orders of magnitude. This is typical of all types of amorphous carbon materials and it has been reported many times with different deposition techniques [68, 111, 133-135]. Other studies of a-C deposition by sputtering [136] attribute the increase in conductivity to a higher deposition temperature at elevated sputtering powers. This picture is somehow not supported by our experiments, we found the temperature of the substrate to remain below 50°C, at any given time, even with extremely high 1100W DC deposition power. Moseler et al. [137] demonstrated by MD simulations the high mobility of carbon ions during any kind of physical deposition process. We therefore propose a picture where ions sputtered with higher DC power reconfigure into stable graphite-like structures before "freezing" into their final position on the substrate. This picture is supported by our data on film roughness shown in Figure 5.11 and Figure 5.12. Films prepared at higher power have a lower final roughness compared to films prepared at lower powers (see Figure 5.12). The evolution of the roughness also demonstrates that high power generated a-C ions are highly mobile and can lower the initial roughness of the metallic substrates with increasing deposition time (Figure 5.11). With 400W DC deposition power, the initial roughness of the film (dictated by the TiN substrate) gradually becomes smaller for a-C thicknesses up to 65 nm, before eventually starting to increase for thicker films. These films sputtered at high powers have a more graphite-like structure and show a hundred times increase in conductivity.
compared to low power deposited samples. The 50 W DC deposited films were found to be highly amorphous films with small, well dispersed \( sp^2 \) like clusters. It is also important to point out that, even at high powers, the kinetic energies of the ions is still quite low, around a few eV \([138]\), which is 2 or 3 orders of magnitude less energetic than ion plating techniques used to create high \( sp^3 \) fraction diamond-like-carbon materials \([139]\).

Annealing the a-C samples in vacuum also increases the conductivity by several orders of magnitude (Figure 5.6). To identify the origin of such a remarkable change, a proper understanding of a-C structure and its evolution are required. Takai et al. \([111]\) analyzed tetrahedral amorphous carbon thin films with different spectroscopic techniques (Synchrotron XRD, Thermoelectric power, low temperature transport measurements) and found that with increasing annealing temperature, no significant transformation from \( sp^3 \) to \( sp^2 \) hybridized sites was evident for temperatures up to 1100°C. Rather, a reorganization of \( sp^2 \) bonds due to the migration of \( sp^3 \) sites was identified as responsible for the increase in conductivity. Ferrari et al. used UV Raman and EELS to study the rearrangement of hybridized bonds in FCVA deposited ta-C \([140]\). They found the \( sp^3/sp^2 \) ratio to remain constant up 700°C, decrease slightly up to 1100° and drop dramatically above 1200°C. It's important to note that although different groups have used visible Raman spectroscopy to probe the ratio between \( sp^2 \) and \( sp^3 \) sites, Ferrari et al. \([140]\) has shown that visible Raman spectroscopy is not a reliable technique for such measurements in low \( sp^3 \) content films, as in the case of sputtered amorphous carbon. UV Raman, EELS or NMR are the best way to quantify the correct fraction of \( sp^3 \) sites \([140]\). Unfortunately none of the above techniques were
available for the work of this thesis, so we can only approximate the ratio from the available literature. Work reported in [141, 142] estimates the fraction of 15-20% \( \text{sp}^3 \) content for DC magnetron sputtered carbon films. We consider our as deposited samples to have a similar crystalline fraction (15-20%), with different degrees of \( \text{sp}^2 \) clustering ultimately dictating the optical and electronic properties of the films [81].

The degree of \( \text{sp}^2 \)-clustering, for different deposition and annealing conditions, was investigated using a visible Raman microscope (532 nm laser). As explained previously, the Raman \( I_D/I_G \) ratio reflects the degree of clustering of a carbon sputtered film. In \( \text{sp}^3 \)-rich films, or a-C:H (hydrogenated amorphous carbon) films, the \( I_D/I_G \) ratio can also be used to directly quantify the \( \text{sp}^2/\text{sp}^3 \) ratio of the material; however, for our \( \text{sp}^2 \)-rich samples this is not the case. The complete collection of \( I_D/I_G \) ratios with varying annealing temperature and deposition DC powers can be found in Figure 5.6, which is also consistent with resistivity measurements reported in Figure 5.2. Starting from a low \( I_D/I_G \) value of roughly 0.35, it increases to almost 1 for 800°C thermally treated samples. The increase of \( I_D/I_G \) with increasing annealing temperatures represents a picture of \( \text{sp}^2 \) sites reorganizing and clustering with increasing temperature.

Ferrari et al. [112] describes a three stage model which includes most common forms of amorphous carbon including magnetron sputtered a-C. In this model the fingerprint of \( \text{sp}^2 \) clustering is, together with the already discussed \( I_D/I_G \) ratio increase, an up-shift in the G peak position from 1510 cm\(^{-1}\) to 1600 cm\(^{-1}\) and a reduced dispersion of the same peak (i.e. the G peak FWHM becomes smaller). These effects are indeed all shown in our results. Figure 5.10 reports how the
FWHM value of the G peak decreases with increasing temperature. A narrow G peak reflects a less disordered sp² system; heating is clearly slowly reordering the amorphous film into graphite crystals. It’s again important to remember that, even at 800˚C, the small percentage of sp³ sites is still likely to be fixed at the same initial value as in the initial starting film [111]. Clustering of sp² sites is thus thought to be the sole responsible factor for the changes found on our Raman spectra, with temperatures above 1100˚C needed for any significant sp³ to sp² conversion.

We can now use Eq. 2 (p. 92) to quantify the average dimension of the sp² clusters in our samples. The 50W DC sputtered sample is used as a significant case to test the equation, since the difference in I_D/I_G between pre and post annealing samples is the largest.

\[
\frac{I_D}{I_G} = C' \cdot L_a^2
\]

\[
L_a = \sqrt{\frac{I_D}{I_G}} \left( \frac{1}{C'} \right)^{-1} \text{ [Å]}
\]

- \(L_a\) : sp² average cluster size in Å.
- \(C' (514nm)\) : fitting factor of 0.0055. From [140].
- \(I_D/I_G\) : from Raman data of Figure 5.6.

Thus for 50W samples, the room temperature value of \(L_a\) is 0.8 nm and for an 800˚C annealed sample \(L_a\) is 1.2 nm. Samples with an \(L_a\) value of around 1.2 nm in size are commonly referred to as nano-crystalline graphite films, where a sp² island of graphitic nature are embedded in a highly distorted amorphous matrix [112].
Figure 5.13 and Figure 5.14 show a cartoon model of a pre and a post annealing clusters in the a-C film.

![Figure 5.13](image1.png)

**Figure 5.13** - Cartoon showing the a-C structure of as deposited 50W sample. Sp2 clusters are here shown as congruent series of hexagonal blocks dispersed in an amorphous "sea" of carbon material.

![Figure 5.14](image2.png)

**Figure 5.14** - Cartoon showing the a-C structure of a 800˚C thermally annealed sample. Sp2 site cluster have increased in diameter according to Raman spectroscopy leaving an increasingly smaller amorphous "sea" between them.

The cartoon is simplified and shows only sp$^2$ clustering sites here drawn as congruent blocks of hexagonal shape. The model doesn’t distinguish between even an odd ordered rings of carbon usually present in a-C [81]. Chains are also not taken into account. Note that the 800˚C thermally treated sample shows a 50% increase in cluster dimension and roughly 5 orders of magnitude increase in
conductivity. These results help to understand and interpret the electrical switching behaviour of a-C films, as reported in Chapters 6 & 7 (and discussed further below).

To sum up, sputtered amorphous carbon films were deposited and characterized under various conditions and subject to post-deposition thermal annealing. DC deposition power was found to be a fundamental driver in terms of resulting a-C optical and electrical characteristics. Low power deposition produces highly amorphous samples with well dispersed sp² hybridization sites, high electrical resistivity and transparent to visible light. High power deposition gives more graphitic-like films with much higher conductivity, larger clusters of sp² sites and more opaque towards visible light. Annealing a sample in vacuum lowers its resistivity several orders of magnitude, lowers its degree of amorphization and increases the size of sp² sites.
6 Electrical characterization of continuous amorphous carbon thin films
6.1 Scope

In this Chapter amorphous carbon thin films with different characteristics (thickness, deposition conditions and bottom electrode material) are electrically characterized (with CAFM techniques) in an effort to identify possible relationships between film structure and electrical switching behaviour.

Film stacks of different thickness, different initial conductivity and different back electrode materials were tested and compared.

I-V measurements reveal basic switching properties, and voltage pulses down to 300 ns in duration are also shown to be enough to switch locally the conductivity of an amorphous carbon thin film.

Finally 800°C annealed amorphous carbon layers are shown to be an interesting possible replacement for the metallic underlayer (bottom electrode), opening the path for an all-carbon memory system.
6.2 I-V measurements on a-C films with increasing thickness

To understand the thickness dependence on the I-V induced conductivity switch of a-C samples, a series of increasingly thicker carbon films were deposited over 40 nm Pt / 10 nm Ti electrodes. All the deposition parameters were set to fixed values for the entire series. A CAFM system equipped with a diamond conductive tip (DDESP-10, Bruker) was utilized as the top electrode for near-DC I-V measurements.

Figure 6.1 - I-V response for a-C films with increasing thickness.

Figure 6.1 shows I-V curves for such films. What appears to be a threshold voltage similar to that observed in phase-change memory devices (see §2.2) is present in all films and gradually increases with the thickness of the film. All the switching events occur at currents of around 10-20 µA.
6.3 I-V measurements on a-C films with different resistivity

Sputtered amorphous carbon can be deposited with a wide range of as-deposited resistivity values (see §5.2). By switching similar films deposited at different powers one can study how the initial resistivity of the carbon layer affects the apparent threshold voltage.

Figure 6.2 - Threshold dependence over a-C resistivity.

Figure 6.2 shows two I-V curves made on films with identical bottom electrodes (40 nm Pt over 10 nm Ti) and carbon layers of 45 nm deposited at both 50W and 400W DC powers. As for the previous experiment, all the switching events occur at around 10-20 µA, with the threshold voltage for the 50W (higher resistivity) deposited sample being higher.
6.4 I-V measurements on a-C films with different back electrode materials

In order to understand the role played by the bottom electrode, a series of identical a-C films were deposited on various electrodes and an I-V response was measured using a CAFM system. For each metallic electrode the deposition rate of a-C had to be recalibrated to ensure a relevant comparison between a-C films with identical thickness. For completeness, the deposition rates are here reported in the case of Ar plasma with $1.5 \times 10^{-3}$ Torr working pressure, 400W DC power and static (no rotation) substrate table:

- a-C on Ta: 11.18 nm/min.
- a-C on Pt: 7.66 nm/min and 0.81 nm/min @ 50W DC.
- a-C on Ag: 7.86 nm/min.
- a-C on Au: 8.28 nm/min.
- a-C on TiN: 8.3 nm/min.

Figure 6.3 collects a series of standard, near DC, I-V sweeps on a-C films with various metal electrodes. Each metal underlayer has been deposited using same the deposition conditions: $1.5 \times 10^{-3}$ Torr working pressure, 30 sccm Ar, 200 W DC, 9 rpm substrate rotation speed. The a-C thickness is 40 nm on a 50 nm metal underlayer for all samples. The I-V measurements were carried using the same CAFM system previously discussed. Before and after each sweep a 'calibration' I-V was systematically carried on a gold test sample, to ensure perfect linearity of the tip. An example of such test is reported in Figure 6.3 with the "Tip on bare Au" series.
Figure 6.3 - I-V sweeps for a-C films with different metal electrodes.

All the films switched between 3.8 and 5 V. After each I-V measurement, a CAFM conductivity map was used to read the post-switching current, the increase in conductivity is reported in Table 6 for all the tested samples.

Table 6 - Effect of bottom electrode material composition on the conductivity switch of a-C films.

<table>
<thead>
<tr>
<th>Conductive Under layer</th>
<th>Voltage Threshold [V]</th>
<th>Change in conductivity [x times]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>5.0</td>
<td>7.92</td>
</tr>
<tr>
<td>Tantalum</td>
<td>4.8</td>
<td>9.2</td>
</tr>
<tr>
<td>Gold</td>
<td>4.7</td>
<td>4</td>
</tr>
<tr>
<td>Silver</td>
<td>3.9</td>
<td>8.75</td>
</tr>
</tbody>
</table>
6.5 I-V measurements on a-C films with different bottom electrode thicknesses

Understanding the effect of the back electrode thickness is another important aspect in non-volatile memory research. Here we selected a standard stack composition [300 nm SiO$_2$ / TiN / 50 nm a-C] and varied the TiN layer thickness leaving everything else (deposition parameters, cleaning procedures, etc.) fixed for the whole series. The thickness of the carbon layer was set to 125 nm.

![Figure 6.4 - Bottom electrode thickness role in memory switching.](image)

Figure 6.4 shows the I-V curves for two samples: the green curve represents a sample with 40 nm TiN electrode and purple curve a sample with 10 times smaller electrode. The only appreciable difference is a steeper change in current, post-switching, for the thinner TiN film.
6.6 I-V measurements on annealed a-C films

Here I-V curves were measured of annealed a-C samples on TiN electrodes to understand the effect of thermal heating on a sample with a metallic bottom electrode. The as-deposited a-C films were cut into several pieces and divided into groups. Each group was annealed in vacuum at different temperatures. The annealing was carried out in vacuum (2.5x10^{-2} Torr), the temperature was increased at a constant 3.8 °C/min and the final temperature kept stable at the set point for 30 min. The annealing chamber was then left to cool down to room temperature before breaking the vacuum and retrieving the samples. Each annealing group contains several samples with a-C layers of different thicknesses.

![Figure 6.5 - I-V curves for 250 nm a-C on TiN electrode at different annealing temperatures.](image-url)

Figure 6.5 - I-V curves for 250 nm a-C on TiN electrode at different annealing temperatures.
Amorphous carbon layers ranging from 250 nm to 75 nm were tested and the results reported in Figure 6.5, Figure 6.6 and Figure 6.7 respectively. All the samples exhibit a decrease in the threshold voltage, together with a decrease in
resistance, with increasing annealing temperature (up to 500°C). The initial resistance of a-C goes up monotonically with the annealing temperature and, at some specific point between 500°C and 800°C, no more conduction switching can be induced using an I-V curve.
6.7 Pulse-induced resistance switching in a-C vertical pseudo-devices

After performing the previous low frequency I-V experiments of §6.2 to §6.6 we switched to high frequency pulsed I-V measurements in an effort to quantify the speed at which a future carbon memory might operate. The experimental set up required for high frequency operation is reported §3.3. The sample used in these experiments had a 40 nm TiN bottom electrode with a 70 nm amorphous carbon layer sputtered on top. The a-C layer was sputtered at 400 W DC with an expected resistivity of 1 Ω·cm (from Figure 5.1) and has a low frequency voltage threshold of 3.5V. Electrical pulses with decreasing duration were applied to pristine areas of the film and their real time response recorded and displayed in Figure 6.8, Figure 6.9 and Figure 6.10, for pulse widths of 10 µs, 1µs and 300ns respectively. Before and after each 4V "writing" pulses, two small 1 V "reading" pulses were used to check the resistivity of the pseudo-device. Using pulses of just 1 V in amplitude ensures that no change in conductivity is likely to be caused by the reading process itself.
Figure 6.8 - Pulsed switching of a vertical a-C pseudo-device using a 4 V pulse with 10 µs width.

Figure 6.9 - Pulsed switching of a vertical a-C pseudo-device using a 4 V pulse with 1 µs width.
Conductivity switching is evident in all three samples with no real difference discerned from the two longer pulses of 10 µs and 1µs. The 300 ns (250 ns FWHM) shows the change in conductivity appearing in real time after 30 ns from the moment the applied voltage reaches its maximum at 4V. The current reaches its maximum value in roughly 20 ns. A more detailed view of the switching event is shown in Figure 6.11. This reveals a delay of roughly 25 ns between the application of the voltage and the start of the current increase. Also small ripples appear on voltage signal. Such effects are most likely due to minor parasitic capacitance and impedance mismatch in the electrical test system (which could be overcome with a more sophisticated test system).
In order to better understand the relation between input voltage amplitude and time required before a switching event appears (specified as the time from the moment the applied voltage reaches its maximum to the time the switching event occurs), a series of real time pulses similar to Figure 6.11 were applied. For this series a sample with 5 V threshold was chosen, and a pulse width of 600 ns. Increasing the voltage amplitude reduces the 'time-to-switch' linearly as shown in Figure 6.12.
Figure 6.12 - 'Time-to-switch' versus amplitude of the input voltage,
6.8 Relation between pulse amplitude and resistivity change

To better understand the relation between changes in resistivity and maximum amplitude of the writing pulse, a series of pulses with different amplitudes were applied to the same film configuration of §6.7 and the 'before and after' electrical resistivity recorded. Figure 6.13 shows the difference in resistivity $R_{\text{SET}} / R_0$ with $R_{\text{SET}}$ being the resistivity of a pseudo-device after a single pulse and $R_0$ the initial resistivity of the material. The applied pulses were trapezoidal in shape, 600 ns in width and with 50 ns rise and fall times. The a-C/TiN sample a voltage threshold of 5.0 V, found initially using a standard DC I-V sweep.

![Figure 6.13 - Resistivity change for a-C/TiN film after application of a 600ns voltage pulse of different amplitudes. The voltage threshold of this particular 'device' is 5.0 V.](image)

A higher amplitude turns devices to a progressively lower final resistivity. This conductivity increase reaches a maximum value of roughly 10 times the as-deposited value, similar to the DC I-V cases shown previously in §6.2 to §6.6.
6.9 a-C devices as a candidate for accumulation type arithmetic processing

The possibility of using a-C devices for accumulation type processing, discussed in Chapter 4 (using phase-change pseudo-cells), was also investigated. Figure 6.14 shows an example of an amorphous carbon based accumulator. In this particular case pulses of 4.9 V (the threshold voltage is 5.0 V for this device), 1 µs width and rectangular shape were used. After setting an arbitrary 'decision level' at 80 µA identical pulses were applied while checking the device current in real time. The pseudo-device switches abruptly (crosses the decision level) after 14 pulses, making it suitable for a base-14 accumulator.

![Figure 6.14 - a-C vertical pseudo-cell for accumulation type processing. The device switches after 14 pulses making it a base-14 accumulator.](image)

This demonstrates the feasibility of performing accumulation-type arithmetic with a-C devices. Further test of these arithmetic functionalities were not carried out,
instead we concentrated on understanding the underlying physics of a-C switching; this was accomplished using a series of different techniques which will be discussed in the following chapters of this thesis.
6.10 I-V measurements on an all-carbon pseudo-device

In §6.6 we showed that for a-C films annealed above 800°C in vacuum for at least 30 minutes, no I-V induced switching was observable. Such an annealed amorphous carbon layer may be useful as conductive bottom electrode for a future all-carbon memory device. Thus, a 50 nm a-C layer was deposited on a standard SiO₂ substrate, and annealed or 30 min at 800°C in vacuum, before finally depositing a fresh 50 nm a-C layer of top. Since our CAFM tip is made of conductive diamond we now have an all carbon memory stack ready to be tested.

![I-V measurement](image)

Figure 6.15 - I-V measurement on a all-carbon memory stack. The conductive under layer is made of vacuum annealed a-C layer.

Figure 6.15 shows an I-V curve made on such a structure. The switching appears around 8.2 V at roughly 15 μA, similar to previous cases. This result is compared to those achieved with other electrodes in Figure 6.16.
Figure 6.16 - Current density related switching.

All samples show what appears to be a threshold voltage, as seen in the switching of phase-change memory devices (see §2.2). Table 7 reports the threshold voltages and the increase in conductivities for all the different bottom electrodes.

Table 7 - Threshold voltage for different bottom electrode compositions.

<table>
<thead>
<tr>
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<td>4</td>
</tr>
<tr>
<td>Silver</td>
<td>3.9</td>
<td>8.75</td>
</tr>
<tr>
<td>800° C a-C</td>
<td>8.2</td>
<td>11.25</td>
</tr>
</tbody>
</table>
6.11 Discussion: Electrical characterization of continuous a-C thin films

In Chapter 5.13 we applied various electrical stimuli to a-C thin films on metal (bottom) electrodes, and recorded a localized increase in conductivity in all the cases. Before concentrating on the reason behind such electrically induced change, a deeper understanding of the role played by the different layers was necessary. As shown in §4.2, all the films exhibit a change in conductivity in an area directly proportional to the radius of the CAFM tip used as the top electrode (few tens of nanometres). The voltage at which is switching occurs is directly related to the thickness of the a-C film; this is re-iterated in Figure 6.17 where the threshold switching voltages from Figure 6.1 are plotted as a function of a-C film thickness.

\[ V_{th} = 0.0333t + 3.6 \, \text{V} \]

![Figure 6.17 - Switching voltage related to a-C film thickness.](image)

Such linear relation excludes the possibility of an interfacially-confined type of switching, where one would expect a more constant \( V_{th} \) over all the thicknesses, instead pointing toward a switching mechanism proportional to the intensity of the electrical field in the a-C film. It is also interesting to note that, for all electrode types, including carbon electrodes, all films showed a switching event when the current reached a current of around 15(±5) µA. Considering the CAFM tip as a
fixed cylindrical, 40 nm in diameter, electrode this implies a switching current
density of around:

\[
J_{\text{switch}} = \frac{I}{dA} = \frac{15 \, \mu A}{(\frac{40 \, nm}{2})^2} = 1.2 \cdot 10^{10} \frac{A}{m^2} = 1.2 \cdot 10^6 \frac{A}{cm^2}
\]

Figure 6.3 collected the I-V curves of similar a-C films deposited on various metal electrodes. Here, switching occurred at slightly different voltage amplitudes, but always between 4 and 5 volt (again, the switching current was around 15µA).

The thickness of the metallic underlayer (i.e. the back electrode) does not seem to play a fundamental role in switching, the differences in the I-V curves between a thick electrode sample and a thin electrode sample being minimal (see Figure 6.4) with the pre-switching conduction in both thick and thin electrode films, together with the final value of the resistivity reached after switching, being similar.

It's important to underline that the threshold voltage (and current) remains much the same (~3 V, 20 µA) for both electrode thicknesses in Figure 6.4, due no doubt to the fact that the a-C layers have the same thickness and composition. Also, since the initial and final value of the resistance are much the same for both thick and thin electrodes, at least with near-DC I-V curves, it can be assumed the heat transferred in both cases is enough to produce similar switching results. Thus, it is clear that amorphous carbon thin films deposited via magnetron sputtering undergo a switching from a higher resistivity state to a lower resistivity state when a certain threshold voltage is reached and when the current density is above a certain value (~ 1.2 x 10^6 A/cm²).
In addition to the above ‘static’ I-V induced switching, the pulsed-switching behaviour of a-C films, using vertical pseudo-devices, was also investigated in Chapter 6. Figure 6.10 shows the voltage and current signals recorded during a voltage pulse of 4 V and 300 ns width. The conductivity change appears around 30 ns from the moment the applied voltage reaches its maximum value. The whole switching event is completed in a time window of roughly 20 ns. Interestingly, the time passed before a switching event is inversely proportional to the applied voltage pulse, as seen in Figure 6.12. We propose a model where the heating generated electrically by the voltage pulse is transferred from the tip / sample interface to the a-C film in a finite amount of time. The heat is partially dissipated by the CAFM tip, very efficiently since is made of diamond-like carbon (having high thermal conductivity), while the rest is transferred to the a-C sample heating up at a localized spot. Once the temperature of the sample reaches adequate values the switching event occurs and a new, permanent, state with increased conductivity appears. Applying a higher voltage pulse reduces the time required for the switching event to appear, following a linear relation as demonstrated in Figure 6.12.

From Figure 6.13 a relationship between pulse amplitude and relative change in resistivity emerges. Here a series of pulses with fixed width and variable amplitude were applied to a sample with a DC voltage threshold of 5 V. For amplitudes smaller than 5 V the resistivity of the sample is not affected, for values above 5 V an increase in conductivity emerges that is approximately proportional to the maximum value of the applied electrical pulse. This proportionality between applied voltage and increase in conductivity remains until an applied voltage of around 5.7
V, where the increase in conductivity eventually saturates to similar values obtained with standard DC I-V sweeps (roughly 10 times increase).

The threshold voltage switching behaviour reported here for a-C films is very similar to a threshold switching effect seen in phase-change systems [143] and shown in Figure 4.6.

As a final demonstration in Chapter 6 we showed how a-C films can, in a similar manner to phase-change materials, also provide accumulation type computation functionality (as in Figure 6.14).
7 Electrical study of amorphous carbon planar devices
7.1 Scope

In Chapter 7 we study the voltage induced conductivity switching of two-terminal amorphous carbon planar devices.

We analyzed devices of various sizes by meaning of I-V curve measurements and CAFM imaging. EBL fabricated devices were switched electrically in various conditions and the region of amorphous carbon switched by the electric field was later imaged with nanometre resolution using a CAFM system.

Environmental conditions are shown to have an effect on the increase in conductivity of a planar device with carbon evaporating in ambient atmosphere as an extreme case.

The -pre- and -post- switching transport mechanisms are also identified.
7.2 Electrical measurements of a-C devices in various atmosphere conditions

We started by fabricating various amorphous carbon planar devices as described in §3.7. Here we report the I-V curve measurements from devices switched in vacuum and in nitrogen atmosphere.

Figure 7.1 shows a collection of I-V switching curves for devices with different spacing between electrodes (here on a semi-logarithmic scale). x500 times change in resistivity is visible between the -pre- and -post- switching conduction. What appears to be a threshold voltage appears in all devices. This voltage threshold
increases monotonically with the size of the gap between the electrodes of various devices.

To infer the effect of moisture and/or absorbed oxygen in the carbon layer on the switching properties of a planar device a series of planar devices were switched in vacuum using the experimental apparatus of §3.8. A heating wire was installed around the vacuum chamber to help drying the sample from possible absorbed moisture. The tape was left operating at 75˚C for two days while pumping in order to extract as much moisture as possible from the sample before applying an I-V curve to study its switching behaviour.

![Figure 7.2 - Resistivity of a planar cell left drying in vacuum for two days.](image)

Figure 7.2 plots the evolution of the cell resistance (always measured at room temperature) after hours of drying in vacuum using a heating wire at 75˚C. Once dried the device was cooled down and an I-V curve used to switch its conductivity to the high state and compared to a device that had not been subject to the drying process (see Figure 7.3). A 50 times change in resistivity is visible for both devices with no particular differences evident.
Figure 7.3 - I-V curves from two vacuum switched devices. The green plot represent a device switched in vacuum with no particular extra precaution. The red line represents an I-V plot of a similar device switched in vacuum after 2 days of drying.
7.3 Optical images of a-C planar devices switched in various atmosphere conditions

Inspection of devices by optical microscope after electrical switching reveals a darker region between the two platinum electrodes.

![Optical images of a-C planar devices](image)

Figure 7.4 - Switching location photographed using an optical microscope. This particular device is the 700 nm spacing of Figure 7.1 and was switched in nitrogen atmosphere.

Figure 7.4 shows a before and after comparison of an amorphous carbon planar device switched in nitrogen atmosphere. This particular device has a 700 nm spacing between the electrodes with a width of 320 nm.

A different situation is shown in Figure 7.5 where an I-V curve was used in vacuum to switch a device after two days of drying (as described in §7.2). At this stage the
device is considered mostly dry. The darker region, once again, appears, but now with considerably smaller size.

Figure 7.5 - Optical microscope pictures of the same a-C planar device before and after a switching event in vacuum (after two days drying). The corresponding I-V curve can be found in Figure 7.3.
7.4 CAFM study of a-C planar devices switched in different ambient conditions

We employed a conductive atomic force microscope to look at an electrically switched region of carbon between the two platinum electrodes. A constant 1 V DC voltage is kept between a scanning conductive tip and the sample. The AFM records both topography and conductivity at the same time revealing the actual regions responsible for the increase in conductivity.

Figure 7.6 shows the topography and conductivity map of a carbon planar device switched in nitrogen atmosphere. The region between the two electrodes has undergone a permanent change in conductivity with the biggest transformation near the positive electrode. More interestingly, outside the electrode gap area, two 'rings' of what seems to be melted and / or evaporated fragments of carbon material have appeared.

Zooming on the left 'ring' reveals a conductive path of 200/300 nm in thickness (Figure 7.7) with a complex structure extending almost 1000 nm from the switched spot.
Figure 7.6 - Topography (up) and conductivity (down) images of an electrically switched a-C planar device in nitrogen atmosphere. The region between the two electrodes shows a permanent increase in conductivity with the biggest increase near the positive electrode. Two symmetric 'rings' have also appeared parallel to the switched area.
Figure 7.7 - Zoom images of the left "evaporated ring" of carbon material created after electrically switching a carbon planar device (topography is the upper one, conductivity is the down one).
Switching a planar device in vacuum however results in a different situation. Figure 7.8 reports a device switched in ultra high vacuum using the experimental set up of §3.8. As for the previous case (samples switched in nitrogen) a ring structure parallel to the two electrodes has appeared once the device has shown an increase in conductivity. The evaporated region is now smaller, but contrary to the previous case some carbon is now missing from between the two electrodes (as indicated in Figure 7.8). The distance separating the electrodes is about 5 times bigger than the previous case of Figure 7.6 and Figure 7.7.
Figure 7.8 - a-C planar device electrically switched in UHV. As for the previous devices switched in nitrogen atmosphere a ring structure appears parallel to the two electrodes.
Switching in vacuum after drying for two days results in topography and conductivity changes as seen in Figure 7.9. No evaporation of carbon material is now visible from both topography and conductivity images. The area of increased conductivity has also physically changed in shape with the formation of a ‘terrace-like’ structure between the two electrodes, starting from the a-C layer and growing perpendicularly toward the observer (as indicated in Figure 7.9). This structural changes might be caused by a thermal expansion mismatch and void formation between the amorphous carbon layer and the SiO$_2$ substrate during the Joule heating event. The same terrace-like structure is shown by the corresponding conductivity map. Around the region that suffered physical changes a small, 100 nm in diameter, aura of apparently pristine carbon material with increased conductivity is also evident from the CAFM image. A 3D image with local conductivity values overlapped on topographic information is presented in Figure 7.10 for better data visualization.
Figure 7.9 - a-C planar device switched in vacuum after two days of drying.
Figure 7.10 - 3D reconstructed image of a vacuum switched region of an amorphous carbon planar device shown in Figure 7.9. Topographic information is overlapped with the corresponding conductivity map texture. Brighter spots are more conductive spots.

Using the same scanning conductive tip used for imaging, a small voltage I-V curve was used to characterize the electrical transport behaviour of the regions with enhanced conductivity and those with standard (low) conductivity in various switched devices.
Figure 7.11 - Using the conductive tip to assess the local electrical conductivity of a switched vs. pristine area of an amorphous carbon planar device. The switched region shows a x50 increase in conductivity.

Figure 7.11 shows two I-V curves made respectively on a pristine area (light blue curve) and a switched area (green curve) of amorphous carbon.
7.5 Electrical transport in a-C planar devices

After obtaining an experimental I-V curve of an a-C planar device as shown in §7.2 theoretical models are employed in an effort to identify the electrical transport characteristics of a pristine (before switching) device. We found electron transport to be well described by a modified Poole-Frenkel conduction defined in [144] using Equation 4. Figure 7.12 reports three experimental I-V curves at 26°C, 32°C and 40°C, together with their respective analytical models.

Figure 7.12 - Comparison between simulated and experimental electron transport mechanism of a-C planar devices with increasing temperature.
\[ l = K' e^{\left( -\frac{\Phi_B}{K_b T} \right)} \sinh \left( \frac{q}{K_b T \cdot 2t} \cdot \frac{V dz}{2t} \right) \]  

Eq.4

with \( K' \) : fitting parameter. **Chosen as 0.114.**

\( \Phi_B \) : energy barrier at zero electric field. **Fitted as 0.3 eV.**

\( k_B \) : Boltzmann constant.

\( T \) : temperature in K.

\( q \) : elementary charge.

\( V \) : voltage applied in V.

\( dZ \) : average trap distance. **Fitted 5 nm for this case.**

\( t \) : distance between electrodes. **300 nm in this case.**

In this analytical model a high trap density, such that the average distance between two traps is a few nanometres. The main difference from the standard Poole-Frenkel conduction model [144]. In Figure 7.12 both experimental and simulated data are reported and found to be in excellent agreement. The same modified Poole-Frenkel transport mechanism has been identified in vertical a-C planar devices by Sebastian et al. [88].
7.6 Comparison between pre- and post-switching electrical transport in a-C planar devices

In this section we studied the electronic transport mechanism of a-C planar devices before and after a switching event to identify potential differences between the two cases.

For a planar device switched in nitrogen, both cases obey to the same transport mechanism previously identified as modified Poole-Frenkel conduction (Figure 7.13). The only differences, besides the 1000 times increase in conductivity, are a decrease of the activation energy at zero electrical field, \( \Phi_B \), that was found (by fitting) to shift from a pre-switching value of 0.30 eV to an post-switching value of...
0.15 eV and an increase of the average distance between traps from 5 nm to 10 nm.

In Figure 7.14 we report the case of an a-C planar device dried and switched in vacuum. Once again, both pre- and post-switching transport obeys the modified Poole-Frenkel conduction mechanism. Here a more modest 50 times increase in conductivity is followed by a reduction of the activation energy $\Phi_B$ from an initial 0.29 eV to a final 0.21 eV and an increase of the average trap distance from 2.5 nm to 5.0 nm.
7.7 Rewriteability of a-C planar devices

In an effort to demonstrate the rewriteability of our carbon planar devices we applied various electrical pulses to previously DC switched devices. The electrical set up used for this last series of experiment is presented in §3.8. Amplitudes ranging from -10 V to 10 V were applied at frequencies straddling from DC to 100 MHz, the ultimate values available from our experimental systems. Unfortunately in all the cases tested no change in resistance was recorded after the initial increase in conductivity from the SET operation.
7.8 Discussion: Electrical characterization of a-C planar devices

In Chapter 7 we conducted, for the first time, a series of experiments on amorphous carbon planar devices. In this particular study the lateral size of the device is of a few hundreds of nanometres.

We were not able to reset the a-C planar devices to their initial low conductivity state (as-deposited state) with our current electrical characterization equipment. A possible reason might be the high sp$^2$ content of sputtered a-C films. In §2.6 we summarized the current state of research in amorphous carbon resistive memories. [29, 87, 91] show rewriteability on amorphous carbon samples with a high degree of sp$^3$ clustering, generally prepared by Filtered Arc Cathodic Deposition (FACD). The switching mechanism proposed, the formation and rupture of conducting sp$^2$ filaments within a insulating sp$^3$ matrix by electrical pulses, would require prohibitively high voltage pulses if to be applied to a highly clustered sp$^2$ sample. An alternative, possibly complementary, approach could be reducing the active region (i.e. the region interested by switching) to a few nanometres using, for example, nanometre sized electrodes. Unfortunately due to time constraint we couldn't spend the fabrication time needed to obtain such a small lithographic features. We decided to concentrate on imaging a switched region at different ambient conditions.

After switching similar planar devices in both air and vacuum a clear contribution of the ambient atmosphere becomes evident. A 50 times increase in conductivity is the typical characteristic of devices switched in vacuum (with or without heat drying) as seen from I-V curves of Figure 7.3. For devices switched in nitrogen
atmosphere or air a 1000 times increase in conductivity is generated by a similar I-V curve (Figure 7.1). A difference is also visible both optically and using a scanning probe system. Samples switched in air show a region, between the two electrodes, as seen in Figure 7.6 and Figure 7.7 where carbon appears to have evaporated. Interestingly the region closer to the electrodes, has not evaporated while the region a few hundred nanometres further along has. Carbon is well known for its high stability upon heating, however, an oxygen atmosphere is known to have a catalytic effect on the graphitization of amorphous carbon materials [145]. The graphitization which starts at 1100° C in vacuum [111] begins at temperatures as low as 200° C in air, accompanied by physical evaporation and material softening starting at around 300 °C [145].

In §6.11 we correlated the properties of an electrically switched film as comparable to a 450° C vacuum annealed one. The increase in temperature following an applied I-V curve in planar devices is likely to reach values comparable to the vertical pseudo-devices of our study, forcing the carbon not sufficiently cooled by (i.e. further from) the metal electrodes to quickly graphitize and eventually to evaporate. Carbon material regions sufficiently cooled do not evaporate and reach a structure more similar to graphite than the vacuum switched samples, this involves a final higher (1000 times compared to 50 times) increase in conductivity. Overall the planar devices show a switching behaviour very similar to the previous vertical pseudo-devices and we speculate formation of nanocrystalline graphite (sp² clustering) as the mechanism responsible for the increased conductivity. In Figure 7.10 we show a CAFM image of the switched region of an amorphous carbon planar device. This image confirms that the switching mechanism involves
the whole a-C area between the two electrodes, thus excluding a limited, interfacial effect at any of the two a-C / electrode (Pt in this case) boundaries.
8 Resistive switching mechanism in a-C devices
8.1 Scope

In Chapter 8 we study the switching mechanism of sputtered amorphous carbon thin films.

Using a CAFM with a high frequency pulsing mode (see §3.3) we electrically switch micrometre sized regions of an amorphous carbon continuous medium. We then probe the same area using optical microscopy, scanning Raman microscopy, CAFM and finally SIMS depth profiling.
8.2 Optical Image of pulsed switched array

Using the CAFM pulsing technique shown in §3.3, a large (micrometre sized) area of a-C was electrically switched in order to use optical microscopy, Raman Microscopy and CAFM scanning as imaging tools. The film structure is as follows: starting from a 300 nm SiO$_2$ layer thermally grown on a Si (100) wafer, 40 nm of sputtered TiN was deposited as a bottom electrode, immediately followed by 50 nm of amorphous carbon deposited at 50 W DC. 10x15 µm electrically switched area was created scanning many times the same region while continuously applying pulses to the CAFM tip (making sure that the whole a-C area is effectively switched). An optical picture was taken using an optical microscope equipped with a 100X lens. The results are shown in Figure 8.1.

![Optical image of a switched array.](image)

Figure 8.1 - Optical image of a switched array.
The area with increased conductivity has a slightly different optical reflectivity compared to the pristine area around it. This was very helpful in finding the region once again when the sample was being moved between different systems for further analysis.
8.3 CAFM imaging of a pulse switched array

The same square photographed in Figure 8.1 was later imaged using a CAFM system with a 1 V constant voltage applied to the scanning sample.

Where the pulsing sequence was applied a region of enhanced conductivity appeared as expected.

Figure 8.2 - Conductivity profile and CAFM image of a switched array. Brighter colors means more conductive.
8.4 Raman map of a pulsed switched array

After scanning the sample with the CAFM system, a Raman map was constructed by placing the sample on a computer controlled XY scanning stage and probing the sample on different points using the same 532nm laser Raman system described previously (§3.5).

The Raman microscope allows the user to take pictures with the built in optical microscope before deciding which area of the sample is needed to be analyzed. Figure 8.3 shows a picture of the pulsed array sample from the aforementioned microscope. The red square in the middle defines the area we chose to examine.

Figure 8.3 - Optical microscope picture taken from the Raman system.

Figure 8.4 shows a reconstructed image of the $I_D/I_G$ ratio (refer to §3.5) of the entire red square. Higher values of the ratio are characterizing the middle of the square.
Figure 8.4 - $I_D / I_G$ ratio of an electrically switched region.

Figure 8.5 presents a reconstructed picture of the G peak frequency shifts around its central value (set to 1547 cm$^{-1}$), the pulsed switched region shows an up-shift of the peak frequency.

Figure 8.5 - G peak position an electrically switched region (cm$^{-1}$).
8.5 SIMS depth profiling of a pulsed switched array

A switched array similar to Figure 8.1 was studied by a SIMS depth profiling system (see §3.6) to see if metallic filament formation within the amorphous carbon layer might be a possible cause of the increased conductivity. The principle of electrochemical memories, where metallic filament formation has been observed, has already been illustrated in §1.3.2. It is beneficial, in respect to the understanding of the switching mechanism of future amorphous carbon ReRam memories, to examine whether the formation of metallic filament is occurring in electrically switched a-C films. A [50nm a-C/45nm TiN/SiO$_2$] sample with various electrically switched arrays was sent to CERAM (Stoke on Trent, UK) for SIMS analysis. Both written and unwritten (pristine) regions of the sample were probed and the results compared to look for evidence of filament formation.

In Figure 8.6 results from depth profiling of an unwritten (pristine) region are reported. A minor diffusion of titanium inside the amorphous carbon layer is present. Titanium oxide is also present in the TiN region possibly due to thermodynamic instability at the boundaries between the SiO$_2$ substrate and the TiN layer. Traces of oxygen are detected in all the layers.

Figure 8.7 shows a depth profile measurement on an electrically switched area of amorphous carbon film. The concentration profiles of the various atoms and molecules appear virtually identical for both written and pristine areas of the film. The increase in conductivity is therefore not due to migration of any of the constituent of the film.
Figure 8.6 - SIMS depth profile of a pristine area of a carbon thin film. A minor diffusion of Ti into the C layer is present for sample.

Figure 8.7 - SIMS depth profile of an electrically switched area of a-C film. There is no discernible difference between a pristine and electrically switched area.
8.6 Discussion: Resistive switching mechanism in a-C devices

Understanding the switching mechanism responsible for the increased conductivity in a-C devices is imperative for the possible future development of a-C based memories. In this thesis we concentrated on understanding the writing (SET) voltage induced switching.

A most informative experiment to investigate the switching mechanism is reported in Figure 8.4. Here, a region of an a-C film switched using a continuous array of electrically switched bits shows a higher $I_D/I_G$ ratio; this is the first hint that the sp² bond sites in the film have locally increased their cluster size. This clustering effect is likely to be caused by Joule heating produced by a switching event occurring as shown in Chapter 6.11. Ferrari et al. [112] demonstrates that to ensure clustering of sp² hybrid sites, together with an $I_D/I_G$ ratio increase, an upshift in the G peak is also required. Figure 8.5 shows that this is indeed the case, where electrical pulses were applied an upshift of the G peak position becomes visible. Although the increasing $I_D/I_G$ ratio and G peak upshift are relatively small, they are both in agreement with results from bulk annealing experiments discussed in §9.2.

Figure 6.1 shows an I-V on the same sample used for the Raman map experiment of Figure 8.4, the difference in resistance between the pre and post switching conductivity is roughly a 27 times. From Figure 5.2 we can extract a 27 times increase in conductivity which reflects with an annealing temperature of 450°C in vacuum. Looking at Figure 5.6, 450°C temperature gives an $I_D/I_G$ ratio of 0.4. The a-C region switched using electrical pulses in Figure 8.4 has an average $I_D/I_G$ ratio between 0.38 and 0.45, showing very good agreement. A similar level of
agreement is found between Figure 5.8 and Figure 8.5; the Raman G peak for 450°C annealing temperature is at 1550 cm\(^{-1}\), the same position found at the center of the pulsed rectangle on Figure 8.5. This brings us to the conclusion that electrical switching has the same effect of annealing the sample in vacuum at roughly 450°C.

Thus, it is likely that the increase in conductivity seen in electrically switched devices is directly connected to the clustering of sp\(^2\) sites in the area directly affected by Joule heating. This view is consistent with experiments carried out by Sebastian et al. [88], where Raman measurements on electrically pulsed micrometre-sized areas of a-C were almost identical to measurements on samples thermally annealed at 400-500°C.

Another suggestion for thermally driven switching comes from the real time RF pulsing experiment of Chapter 6.7. Figure 6.11 shows a time frame of 30 ns from the moment the applied voltage reaches its maximum at 4V and the appearance of the switching event. The switching event is completed in less than 20 ns enough to be recorded by the GHz - enabled oscilloscope used for the experiments. Even more importantly the time delay for switching decreases linearly as the pulse amplitude is increased. The appearance of a time delay once again points to an electrically induced thermal effect that requires a finite amount of time to heat the carbon material to the significant temperature required to increase its conductivity. This is once again in agreement with Sebastian et al. [88].

In §1.3.2 we introduced a novel class of ReRam identified as Nano-Ionic memory systems. In this class of memories a reversible switching memory effect is caused
by a solid metallic filament formed between the cathode and the anode via a solid electro-chemical process caused by an applied voltage. To ensure that filament formation wasn’t responsible (even partially) for the resulting increase in conductivity in the a-C films use in this thesis, a SIMS comparison analysis between a pristine region and a continuous pulsed switched array was made. Figure 8.6 and Figure 8.7 report the analysis; the absence of any discernible difference rules out the filament related switching hypothesis for the a-C films investigated here, pointing further toward a genuine, thermally driven switching mechanism.

Finally, the transport mechanisms of pre- and post-switched amorphous carbon lateral devices were investigated using standard I-V curve techniques. Figure 7.13 and Figure 7.14 show a comparison between I-V curves of (experimental) raw data points and an analytical Poole-Frenkel conduction model from [144], with excellent agreement. PF transport is accountable for both pre- and post-switching conduction mechanism the only differences, besides the increase in conductivity, are a decrease of the activation energy at zero electrical field, $\Phi_B$, and an increase of the average distance between charge traps. These results support the picture of conducting sp$^2$ clusters embedded into an amorphous sp$^2$ / sp$^3$ mix of hybridized sites discussed in §5.13. Once a switching event occurs, an increase of the average distance between traps together with a decrease of the activation energy are expected and indeed shown.
9 Conclusions and further work
9.1 Conclusions

The ITRS Roadmap highlights as one its 'Grand Challenges' the pressing need for entirely new device concepts, and in particular asks for 'A new “beyond-CMOS” information processing technology’ and also recognizes that ‘A non-binary data representation may be required’ [9]. Phase-change based systems are potentially one way of achieving this incredibly relevant technological "dream".

During the realization of this thesis we demonstrated that phase-change memory devices represent an attractive opportunity for new ways to perform of arithmetic and biologically inspired processing on a single, nanometre sized, memory cell. Our arithmetic and bio-inspired computing mechanism exploits the nucleation kinetics of GST materials and the sudden increase in conductivity at the percolation threshold as a reliable way of assessing the state of a cell. Arithmetic computing in arbitrary bases, parallel factorization of prime numbers were all successfully implemented using standard, generic, phase-change memory pseudo-devices.

Unlike in multi-level phase-change memory applications, arithmetic computing via accumulation should not require special methods to combat resistance drift and does not require the use of multiple analog-to-digital converters during the readout of a stored bit (unlike the multilevel regime) which could truly exploit the ultrafast (< 1 ns) operation of phase-change materials [39].

While studying the electrical rewrite-ability of phase-change pseudo-devices, the amorphous carbon capping layer on top of continuous phase-change media was found to be partially responsible for the observed electrically-driven conductivity
switching. In this thesis, therefore, a study was made of the effect of temperature, electrical field and current density on the structure and properties of sputtered amorphous carbon thin films, in particular in the context of their use for resistive memory applications.

Experimentally, we started by fully characterizing the structure and the electrical properties of a-C under various deposition conditions. The electrical conductivity of the as-deposited samples was found to depend strongly on the deposition conditions and, more significantly, the conductivity was increased dramatically as a result of post-deposition thermal annealing. A similar increase in conductivity was achieved in electrically switched a-C films and devices. SIMS analysis allowed us to exclude metal migration as a possible origin of this electrically-induced resistance switching mechanism. Rather, Raman measurements and a comparison between electrically switched and thermally annealed samples pointed to an electrical mechanism in devices governed by Joule heating induced clustering of sp² carbon bonds. We also imaged a post-switched a-C planar device with nanometre resolution using AFM and CAFM techniques, finding that the entire region between the two platinum electrodes was at a higher conductivity after the switching event, excludes an interface-mediated phenomenon as the cause of switching.

Importantly, an all-carbon memory device using an annealed a-C under layer was also demonstrated for the first time, potentially paving the way for the first truly sustainable all-carbon based solid state memory device.
9.2 Further Work

There are many interesting possibilities that could follow this work in both phase-change and carbon based memory devices. Following the single phase-change memory device demonstration of arithmetic processing from Chapter 4, the use of multiple devices, in parallel, to perform advance forms of computing would represents an important milestone in the development of a future phase-change microprocessor (PCµP). A PCµP would work performing complex, low power, ultra high speed operations on a beyond Von Neumann computational scheme. PCM devices have also demonstrated the possibility to be used as both synapses and neurons (see Chapter 2.3), so that building a complex, low power, brain-inspired computer is now theoretically possible. A brain-inspired computer would solve the type of problems that are easy to for humans and computationally intense for general purpose computers, such as pattern recognition, speech recognition, image processing etc.. This might allow a new generation of robotics, self driving cars, surveillance systems, etc. to be possibly implemented.

Amorphous carbon is an interesting candidate for future ReRAM devices, but much more is needed to explore its capabilities for real commercial applications. In this thesis we concentrated on the SET switching mechanism, showing that sp$^2$ clustering is responsible for the increase in conductivity in sp$^2$ rich a-C films. However, a subsequent in-depth study of methods and/or film compositions/device structures to enable a reliable RESET mechanism is now required. Amorphous carbon could also potentially be easily integrated with graphene and carbon nanotubes allowing higher storage densities in future memory devices.
In this thesis we employed an EBL system to fabricate amorphous carbon planar devices. Compared to vertical devices, planar devices have the advantage of leaving the switching active region of a-C exposed for further study. On the other side vertical devices with a-C layer of a few nanometre size are simple to make, since the thickness of the carbon layer is easily controlled during the deposition step. Planar devices with small electrodes and small gap are considerably more complicated, the minimum size feature depending on the resolution of the EBL system, the organic resist employed, the deposition technique utilized, the initial nature of the substrate. Unfortunately due to time constraint, in this thesis we did not make devices at the resolution limit of the EBL system, so did not explore the ultimate scalability of a-C memory devices. This could certainly be done in future work.

Another interesting route to follow that would encompass the advantages of vertical devices (simplicity) and planar devices (a-C active region exposed for further studies) could be obtained by employing a transparent conductor as top electrode of a standard vertical device. Indium tin oxide (ITO) is a highly conductive, highly transparent, stable up to 1400° C, material commonly used in touch screen and solar panel technologies. A vertical device with a SiO$_2$/metal/a-C/ITO structure would allow the active carbon region to be easily controllable down to a few nanometres while leaving the top surface optically accessible to further study such as Raman or infrared spectroscopy.

If such devices are successfully demonstrated to reliably switch between low and high conductivity state one could then move even further and study Glass/ITO/a-C/ITO structures. In §5.4 we showed that a-C transparency varies when annealed
or switched electrically. An ITO/a-C/ITO system might even therefore represent a novel “E-Ink” technology, where the opacity of a cell is controlled electrically without the need of a constant DC supply, possible refreshing speed in the MHz range and, finally, be extremely cheap.
References


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