2D MATERIALS: SEMICONDUCTORS AND SEMIMETALS

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PREFACE

Historical: graphene as the "Father" of 2D materials

In 2004, a dozen years ago, a new chapter of Science opened with the experimental *rediscovery* of graphene when Andre Geim and Konstantin Novoselov, at the University of Manchester, isolated graphene flakes via mechanical exfoliation from a block of graphite. The two scientists have also pioneered the formalization of graphene as an atomically -thin and flat carbon material with electronic and mechanical properties unprecedented in the world of bulk, or even thin- film materials [1]. Graphene may in fact have already been observed long before, for instance in 1965, when Badami reported on the graphitization of hexagonal silicon carbide [2]. However, at that time Nanotechnology was still in its infancy, and a single-layer of atomically thin material, carbon included, was not expected to be stable. Times were mature only much later, roughly at the same time as Geim's and Novoselov's report in Science, when Walt De Heer's group at Georgia Tech also reported the synthetic achievement of an atomically -thin, purely two -dimensional carbon layer via thermal decomposition of silicon carbide at high temperature [3]. In fact, the early 21st century scientific community was so mature for the acceptance of 2D materials, that Geim and Novoselov were awarded a Nobel Prize just only a few years after their first publication on graphene. Meanwhile, the number of published papers on graphene started increasing exponentially to reach nearly 200,000 entries in a little over ten years (source: Web of Knowledge).

Graphene can be rightly considered the "Father" of all 2D materials. The scientific community has started considering the possibility of experimentally obtaining alternate 2D materials only since the rediscovery of graphene. Nevertheless, an enormous progress has been equally made within a few years in the area of alternative 2D materials, leading to the discovery of a plethora of nearly atomically -thin, atomically- flat materials.

Has graphene disappointed?

Great expectations were associated with graphene almost since its rediscovery, to the point that it has been dubbed a wonder -material, as well as, in some instances, accused of being a hype -material, associated too often with exaggerated claims. Not surprisingly, as the material properties deriving from a perfect covalent sp2 carbon bond matrix such as graphene are truly extraordinary under many different aspects, from an electrical and electronic perspective with ultrahigh carrier mobility (~200,000 cm2/V.s), micrometer-scale mean free path, electron-hole symmetry and quantum Hall effect, down to a mechanical viewpoint, with a reported elastic modulus around 1 TPa and an outstanding fracture strength [4-6]. Not to mention such other aspects as high thermal conductivity, extremely low surface -energy and permeability, the possibility for low -loss surface plasmons, and, last but not least its optical "transparency". It is hard to imagine any other single material characterized by so many outstanding and practically useful properties. So why has graphene not been considered yet for integration in any high -end application (ie excluding composites or simple protective coatings)?

There is a latent feeling of disappointment behind this question, and the large scale of scientific and technological interest from those early days of this "wonder" material is now starting to fade. However, this disappointment is only generated by a wrongly defined problem. The ground-breaking nature of this material, the scale and extreme pace of international attention and research effort and the exaggerated perceptions, are the reason why it's being so harshly judged:

- First of all, the extraordinary properties quoted for graphene can only be achieved for an ideal, almost defect -less graphene
- Ideal graphene may be obtained over rather limited areas in the lab, and scientific studies focus more on the best results rather than averaged results
- Any high -end application will require consistent high -quality and control over large areas over repeated runs, which at the moment is still far from established in most cases
- There is a terminology and standardization issue when talking about graphene. Graphene can be obtained by a large number of different methodologies, each of which can have vastly different properties (number of layers, surrounding environment and intercalation, amount of defects, etc.). Not all "graphene" is really graphene.
- The current theoretical models do not take into account all of the different flavours of graphene (disordered graphene), and as such, cannot be predictive. The latest developments in this area are presented in Chapter 2 of this book.
- additionally, graphene is a 2D material, and as such, its material properties have a different meaning than those of a thick 3D material. Graphene may have an outstanding electrical conductivity, but it is still only one -atom thick! Graphene is mechanically very strong or stiff, but as a consequence it is also very flexible. Also, graphene is only transparent because it is so thin. And so the list of misunderstandings goes on….

- Last but not least, graphene is a semimetal, and as such it cannot be fully considered as either a metal nor a semiconductor. Graphene has a long way to go to replace silicon, and more to the point, its properties may be ultimately best used as a complement rather than a replacement of silicon.

In summary, graphene will certainly be a key material in future technologies, but the road is still long, significant work is still needed in terms of controlled synthesis and full understanding of the graphene system and its interaction with the environing materials and ambient. Also, graphene will not replace the device materials we use now, though it will augment a plethora of future devices which will be entirely engineered ex-novo for 2D materials. As graphene science and technology is much further ahead than the rest of the 2D materials, and counts already on a large number of books and reviews, in this book we decided only to feature a chapter on the advances of the graphene theory. The bridging of the theory developed around an ideal graphene lattice with the experimental often disordered graphene is nowadays a strong necessity for practical progress.

Interest and specificity of 2D materials

Two -dimensional materials are a class of recently -discovered crystalline substances which can exist as atomic -thin sheets over large in-plane areas. Some of the 2D materials can exist in nature as a macroscopically stacked form such as graphene in graphite, from which single sheets can be exfoliated. Some others do not exist in nature as layered materials, can only be produced by synthetic routes, and are generally not stable in the environment. All of them though are characterized by the fact that they possess (almost) only in-plane bonds, and only but very weak bonds in the z -direction, typically Van der Waals type, hence 2D materials.

The interest in 2D materials is from both a scientific and technological aspect. From a scientific point of view, the study of graphene and other 2D crystals has opened a completely novel chapter of the study of condensed matter. Their discover has allowed science to refine the basic theory and models of Van der Waals interactions, and the detailed understanding of the profound consequences of 2D confinement on all of the physical and chemical properties of materials. 2D confinement strongly modifies the band structure of the materials, making for example conductive materials out of substances that otherwise would have been semiconducting or insulating, and strongly affecting charge transport phenomena in general. Novel extraordinary properties in such materials are discovered almost on a daily basis, attracting growing attention from the global scientific community.

From a technological point of view, the interest clearly lies in harnessing such novel properties in devices with added functionalities for scopes as broad as electronics, photonics, energy, sensing and more. 2D materials offer a combination of properties not obtainable from conventional thin -film materials. Yet, though nanomaterials, they have strong similarities to thin films (the thinnest!), simplifying significantly device design. Although in reality this is only just an

apparent advantage. A 2D monolayer is essentially a thin -film made almost exclusively of surfaces, and we all know too well how the control (passivation) of surfaces has been one of the nightmares for the fabrication for example of electronic devices. How about when, additionally, controlling film doping means controlling the doping of a surface that anything in the surroundings can influence? Moreover, if the film/surface itself is not stable? These are just some of the big challenges ahead from a technological standpoint.

Semiconductors, semimetals….. and insulators

Essentially, all material types are represented in the 2D family, which is a fast -growing group of materials all characterized by their monolayer nature. Quite a few different classes of 2D materials have been identified experimentally or are at least theoretically predicted, as discussed in detail in Chapter 1. At the moment, some materials are more mature than others, so we have decided to have extended chapters only for the materials or classes of materials which have been extensively studied by at least a number of groups world- wide. Here we'll go briefly through the different materials, with no pretension of being exhaustive.

The first obvious class is that of the so -called Dirac 2D materials. These are materials presenting a Dirac cone band structure typology, semimetals with their valence and conduction bands around their Brillouin points shaped as inversed cones touching at their vertex, with "massless" fermions around that point. This class includes graphene, which is also the most stable Dirac material, thanks to the favorable energetic state of its sp2 hybridization. Following down from carbon the column of Group IV elements, we find the 2 next monoelement Dirac 2D materials: silicene and germanene (Chapter 4). These allotropes of Si and Ge are unstable and exclusively synthetic. They are reported to physically buckle because of their instability, introducing as a consequence a bandgap in their band structure, and hence are of large potential interest for electronics.

A well- studied, and quite long known 2D insulator is hexagonal boron nitride (h-BN), sometimes referred to as the insulating counterpart of graphene, given their matching hexagonal structures (Chapter 3). hBN is another stable material in its monolayer form and can be obtained by exfoliation, though its bulk form is usually a powder substance.

A large class of 2D semiconductors are the Transition Metal Dichalcogenides (TMDs, Chapter 5). Though of recent discovery, already an extensive body of literature has been produced on these layered materials which are often obtained by mechanical or chemical exfoliation.

There are a few more monoelement 2D materials, of which only phosphorene, a semiconducting material obtained by exfoliation of black phosphorous, is somewhat more mature (Chapter 7). Some other predicted but not yet fully demonstrated monoelement materials are stanene or tinene (from Sn), borophene (from B) and antimonene (from Sb).

Another emerging class of 2D materials is the MXenes, which are transition metal carbides and carbonitrides. MXenes are obtained by etching away the A elements (usually metals) from a MAX compound [7]. As such, they are exclusively synthetic and a very special type of monolayer. Their characteristics vary from metallic to semiconducting with a small bandgap.

Many more 2D materials and maybe even classes may be discovered over the next few years. In the meantime, one area to consider will certainly be the organic route towards 2D materials. Conjugated polymers confined in two dimensions could become an alternate and cheaper route towards an "organic graphene" [8]. At the moment those materials still appear too disordered as compared to other 2D materials. However, if successful, this route could certainly open up a plethora of complementary technological applications, thanks to its versatility and bottom-up approach.

Challenges and opportunities, from hype to hope

There is no doubt that 2D materials over the next years will lead further to the discovery of more novel and exciting fundamental phenomena (Chapter 1). As such, this area will remain a great playground for many years to come for the scientific community. However, the larger community always rightly expects a societal impact accompanying such great discoveries. Opportunities are plenty, but there will certainly be many challenges ahead.

One group of technological challenges regards quite obviously the synthesis of 2D material in large volumes or over large areas with a consistent quality. Much of current 2D materials science is based on exfoliation of layered materials and flake transfer to the substrate of interest, which is useful to some of the bulk applications such as energy storage, but is not compatible with large scale nanodevice production. Also, some of the non-layered materials can be obtained in-situ by van der Waals epitaxy like silicene and germanene and others are not stable if exposed to ambient. Also, appropriate international standards for measurements, assessment and benchmarking of 2D materials will need to be developed before any step towards industrial applications can be made. To date, definite standards related to graphene are still lacking, including appropriate and widely accepted language defining all of the different types of graphene available.

Another critical aspect and intrinsic challenge of all 2D materials, is the fact that they are made up solely of surfaces. This needs to drive a substantial shift in mentality and approach, considering the fact that technologists have become familiar in dealing with thin films, while surfaces and interfaces were often considered like a headache, or an uncontrollable nuisance at the very least.

First of all, it is extremely difficult to keep a surface absolutely clean and well -controlled. Also, it is not trivial to do so when any dangling bonds or reactive molecules present in the environment around the 2D materials can potentially affect and change the materials response. Intercalation and hetero-stacking are the answers. The science related to molecular intercalation

as a way to control electrical and optical properties of layered materials has been extensively developed around graphene [9], and much more work in fundamental understanding and fine engineering will be needed to extend this knowledge to other 2D materials.

Also, the intimate understanding of how junctions between two or more vertically -stacked 2D materials can be achieved in a controlled fashion will be key to many of the applications (Chapter 6 by Dubey et al.). Surfaces, interfaces and 2D hetero-junctions will have to shift from being parasitic aspects to becoming central characteristics of the future components for nanodevices. This also inevitably means that rather than re-engineering older device concepts such as MOSFETs to adapt them to 2D materials, the future devices will have to be designed specifically for 2D materials, in order to extract maximum advantage from this new class of materials.

In summary, the road to a societal impact of 2D materials is still long, however there is reasonable hope that this will happen in due course, provided enough effort will be dedicated to the challenges mentioned above. Significant impact can be expected in a broad range of aspects, from efficient electronics allowing for ultimate miniaturization, to applications in sensing, energy, medical care, photovoltaics, and many others. In the meantime, 2D materials will continue to be for Condensed Matter Physics and Chemistry what the large particle accelerators are for High Energy Physics: a means to probe the frontiers of science and to develop a fundamental model of materials and their properties.

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[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306,** 666-669 (2004).
[2] D. Badami, Carbon **3,** 53-57 (1965).
[3] C. Berger et al., Journal of Physical Chemistry B **108** (52), 19912-19916 (2004).
[4] R. Nair, P. Blake, A. Grigorenko, K. Novoselov, T. Booth, T. Stauber, N. Peres, and A. Geim, Science **320,** 1308-1308 (2008).
[5] J.-H. Chen, C. Jang, S. Adam, M. Fuhrer, E. Williams, and M. Ishigami, Nat. Phys. 4, 377-381 (2008).

[6] A. A. Balandin, Nat. Mater. 10, 569-581 (2011).
[7] M. Naguib, O. Mashtalir, J. Carle, J.V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M.W. Barsoum, ACS Nano 6(2), 1322-1331 (2012)
[8] D.F. Perepichka, F. Rosei, Science 323, 216-217 (2009)
[9] C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, U. Starke, Physical Review Letters **103** (24) 246804 (2009)