

Review on 2D Materials

S. Sugumaran

Department of Electronics and Communication Engineering,
Galgotias University, Yamuna Expressway,
Greater Noida, Uttar Pradesh.

Email ID: s.sugumaran@Galgotiasuniversity.edu.in

ABSTRACT: Together with recent advances in exfoliation techniques, the discovery of graphene and other two-dimensional (2D) materials has laid the foundations for the manufacture of single layered sheets from any 3D layer. The 2D materials family includes a wide selection of compositions covering almost all of the periodic table elements. This result in a wide range of electronic properties including metals, semimetals, insulators and semiconductors with direct and indirect band gaps varying across the visible range from ultraviolet to infrared. Therefore, they have the potential to play a crucial role in the future of nanoelectronics, optoelectronics and the assembly of modern ultra-flexible devices. We classify the 2D materials by their structure, composition and electronic properties. In this review we distinguish atomically thin materials (graphene, silicene, germanene, and its saturated forms; hexagonal boron nitride; silicon carbide), rare earth, Semimetals, metal transition chalcogenides and halides, and finally organic 2D synthetic materials, exemplified by 2D covalent organic frameworks. Our exhaustive data collection provided in this Atlas reveals the wide range of electronic properties, including band gaps and mobilities of electron. To cover their range of applications, peculiarities and drawbacks, the key points of the current analytical methods applied to 2D materials are discussed with special emphasis.

KEYWORDS: Flexible Electronics, Graphene, Graphite, 2D Materials.

INTRODUCTION

The existence of two-dimensional (2D) materials[1] was a highly debated issue in the physics community during the early decades of the 20th century. 2D materials are thermodynamically unstable at any finite temperature, due to variations in thermal lattice, according to classical physics. This was in line with the rising melting temperature seen when thin film thickness was decreased. Modern spectroscopy[2] technology revealed the existence of layered-structured 3D materials, such as graphite or molybdenum di-sulphide. While their exfoliation down to their two-dimensional monolayers was assumed to be possible only in the theoretical domain because Mermin showed that only one- and two-dimensional materials can only exist hypothetically – i.e. when the crystal is represented within the harmonic approximation. Materials science had a major scientific breakthrough in 2004, when Novoselov and Geim isolated graphene, the first single layer of 2D content, via the Scotch graphite exfoliation tape (Fig. 1). The importance of this accomplishment was sealed in 2010, when both researchers received the Nobel Prize.

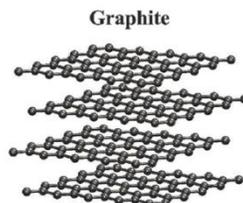


Fig.1: Graphite Structure (5×5×2 Unit Cells)

Graphene[3] is a carbon-layered substance of atomically thin sp² with a honeycomb lattice that has almost the same crystal strength as diamond. Since each graphene carbon has only three bonds for diamond instead of four, the graphene C–C bonds are about 25 % stronger. Consequently, this is the most durable substance known to date. Graphene has a very distinctive electronic structure. It's a semi-metal, defined by not having a band gap, but at the Fermi stage, the density-of-states is zero. Electronic bands cross the Fermi stage near the six corners of the hexagonal two-dimensional Brillouin region (Fig. 2a).

At these scales, the dispersion relationship (the shift of a band's electron energy within the Brillouin zone) is linear, a unique feature that leads to zero effective mass for electrons and holes, and thus to very high currents. Electrons and holes near these six points function like relativistic particles defined by the Dirac equation[4] because of this linear or conical dispersion relation. The electrons and holes are therefore called Dirac fermions, and the six corners of the Brillouin field are called the Dirac dots. The cones at Dirac points are positioned at the high-symmetry K points in the honeycomb lattice's Brillouin region and have been recently investigated for valleytronic applications (Fig. 2a and b). The massless Fermi-level Dirac electrons also derive in the highest known mobility of finite-temperature electrons. Additionally, the extremely low graphene spin-orbit (SO) interaction makes it an ideal spin carrier for spintronics. Work on graphene electronic structure engineering quickly emerged to create semiconducting modifications that exhibit a (very) small band gap, a significant step towards electronic and optoelectronic applications. Such devices however require larger band gap semiconductors as well as dielectric materials as insulators. Nature, luckily, offers a variety of layered materials beyond graphene, including metals, semimetals, insulators and semiconductors with direct and indirect band gaps varying from ultraviolet to infrared via the visible range.

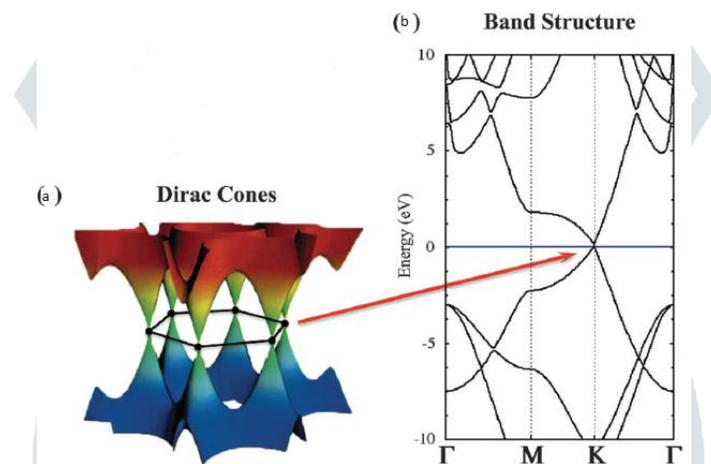


Fig.2: a) Dirac Cones in Graphene b) Graphene Band Structure (G–M–K–G). Fermi Level has been shifted to 0 eV and Depicted with a Blue Horizontal Line

The recent progress in exfoliation techniques such as micromechanical cleavage, ion intercalation, and surfactant-assisted ultra-sonication has laid the foundations in the monolayer limit for the manufacture of substantially any given layered bulk material. Layered materials cover an extremely wide range of compounds, including clays, layered oxides, chalcogenides, halides, carbides, nitrides, hydrides, hydroxides, phosphates, and phosphonates. Most of these materials are binary-layered compounds while ternary-layered compounds (i.e., CuSbS_2) are possible. Layered materials can be graded further, depending on the interaction between the layers. This interaction is controlled by interplay between the layers with hydrogen bonds, interstitial cations or London dispersion. Among the latter, the most prominent examples of these materials are transition metal chalcogenides (TMC), with MoS_2 as its flagship. Nonetheless, the development of MoS_2 -based transistors has sparked tremendous scientific interest in TMC monolayers for novel ultrathin and flexible applications, as well as other Nano electronic and optoelectronic applications.

In addition to the immense success of the science of 2D materials one should not neglect the underlying physics. 2D materials shouldn't exist above absolute zero according to all theoretical predictions. The analysis of free standing and graphene assisted revealed intrinsic ripples were formed. The experimental work on free-standing graphene sheets has corroborated these results. Therefore ripples deform the 2D lattice on a broad length scale, rendering it – strictly speaking – a 3D substance and thus addressing the debate over the presence of these materials beyond absolute zero. Analogously, in free-standing single-layer MoS_2 [5] sheets, spontaneous ripple formation was observed even though the material is not atomically thin and therefore not strictly two-dimensional.

In this review, in the theoretical description of their electronic structure, we will discuss the fundamental electronic properties of single-layer 2D materials with special emphasis on their scope of application, on their peculiarities and on pitfalls.

ATOMICALLY THIN TWO-DIMENSIONAL MATERIALS

They address graphene and materials directly related to this 2D prototype device in this section. These include isoelectronic hexagonal boron nitride (h-BN), 2D materials of Si and Ge (silicene and germanene) main group IV elements Chalcogenides (TMCs), and atomically thin transition metal. The most interesting feature about these materials, compared to their bulk counterparts, is the significant change in properties. Although some of these structures have not yet been free-standingly isolated, they are highly debated within the Nano electronics[6] community.

1. Graphene, Silicene and Germanene:

While Boehm had already coined the word graphene in 1962, the electronic structure of a monolayer of graphite has been studied since 1947. Surprisingly; Geim's group was not able to isolate a sheet of monolayer graphene until 2004. Graphene was then the focal point of comprehensive theoretical and experimental studies. Graphene is regarded as a very promising material for nanoelectronics due to its remarkable physical properties, such as its high carrier mobility and high electrical and thermal conductivity, even being a candidate for replacement of silicon in future electronic equipment. Nonetheless, graphene is a band-free semimetal, which renders it unacceptable to use as an electronic switch. It includes band gap engineering to open a band gap in graphene without losing any of its other properties. Doping[7], functionalization, defective or hybrid structures, substrate-induced band gap opening, and quantum containment are the most common techniques and methods reported so far. A wide range of potential graphene applications are under development to date, and many more have been suggested. These include flexible display screens, electrical circuits, and solar cells, as well as medical, chemical, and industrial processes which could be enhanced by using new graphene materials.

Because of the fascinating properties and comprehensive graphene applications, scientists have begun asking whether the other elements in main group IV, i.e. Si, Ge, Sn, and Pb have the ability to form stable layered structures. Wen et al. discussed main group IV structures theoretically in 2010, ranging from 1D to 2D to 3D. We found that Si, Ge, Sn, and Pb graphene layers effectively collapse to five-coordinated structures with interlayer bonds. This is because of the p-bonding in main group IV. It is only possible for carbon, but not for Si, Ge, Sn, or Pb, to be central in all graphene structures. Due to the poor p-type overlap between neighboring p orbitals at the distance imposed by normal s bonding, carbon easily forms sp² hybrid orbitals, the same is not possible for the other elements. Hence, Si, Ge, Sn and Pb graphene-like sheets are highly unlikely to have an independent existence. To be compatible with the nomenclature widely used, silicene is the term used to describe the graphene silicon analog. In the last few years, the theoretical prediction of the electronic and structural properties of silicene has been made. Among those studies, Cahangirov et al. stated that silicon and germanium may have robust, 2D, slightly corrugated (b-type), honeycomb structures that are more stable than their counterparts of the corresponding planar layer form. Notwithstanding this buckling, the free-standing structures of silicene and germanene have adequate symmetry to maintain the characteristic of linearly crossing bands around Fermi. That makes silicene electrons behave as massless Dirac Fermions as in graphene.

2. Silicon Carbide:

Naturally, silicon carbide (SiC)[8] occurs in the form of cubic, hexagonal and rhombohedral structures, where Si and C support sp³ hybridization. Theoretically, however, SiC's planar structure with sp²-hybridized bonds, thus resembling graphene, was expected to be highly structural stability. The graphene-like SiC consists of alternating Si and C atoms where each Si atom has three C atoms as its closest neighbors and vice versa, with a length of 1.79 Å for Si – C bonds. The planar SiC device is a semiconductor with a direct K-K band gap of about 2.55 eV, which increases to 3.63 eV when tested with GLLB-SC, due to the Si – C ionicity. The p-orbital character of both valence and conduction bands is mainly Si and C. The upper valence band consists of

one p band consisting of the 2pz and 3pz orbitals, extending above and below the SiC layer axis, and two s bands containing the three C 2s, 2px, 2py and three Si 3s, 3px, 3py orbitals forming the Si – C s bonds.

ULTRATHIN 2D MATERIALS

In this section we speak about 2D materials that are thicker than one atom (ultrathin materials). They limit their study to three families of ultrathin 2D materials: hydrogenated and fluorinated graphene, silicene and germane derivatives; rare earth, semimetal, and transition metal chalcogenides; and rare earth and transition metal halides. Some of the presented structures in their bulk and/or free-standing form have not yet been isolated, but the theoretical prediction of their properties is the vanguard for the experimental growth and isolation of the most promising materials.

1. Graphane, Silicene and Germanene:

Chemical functionalization, especially hydrogenation and fluorination, is used to tailor graphene-like materials' electronic properties. Here we briefly describe the latest studies concerning these saturated structures. In 2013, Bianco et al. reported using topotactic deintercalation to synthesize stable, single-layered germanene. It requires a structural change to a crystalline solid and one or more crystallographically similar orientations equate the final lattice with the original material. When placed in aqueous HCl at 40 °C, a large β -CaGe₂ crystal was converted into a layered GeH. β -CaGe₂ has covalently bonded layers of germanium atoms separated by oddly bonded interstitial calcium alternating planes. The bonding form appears to have mixed hybridization of sp² and sp³ in Germanene. Ultrathin germanene has a remarkable oxidative degradation resistance and has been shown to be stable in air for five months. Germanene does not need a substrate to be stable, unlike silicene. Germanene's atomic structure is strongly corrugated, rather than smooth like graphane or graphene. Calculations do not indicate the presence of a Dirac cone but Germanene still has surprisingly high mobility of electrons, which is much higher than that of its bulk material. A theoretical analysis showed that Germanene has a 1.53 eV direct band gap, making it a possible solar cell source. Unlike graphene, hydrogenation is not a reversible process in germanene. It becomes above 75 °C an amorphous material.

2. Fluorographene, Fluorosilicene and Fluorogermanene:

Fluorographene [9] is the fluorinated graphene equivalent, namely, it is a 2D carbon monolayer of sp³ hybridized carbons, each of which is bound to one fluorine atom. Fluorographene is highly insulating, and has a high thermal and chemical stability, comparable to other fluorocarbons. Nonetheless, a reaction with potassium iodide at high temperature will turn it back into graphene.

Fluorographenes are supposed to exhibit similar structural and electronic features as graphene. Since fluorine has a much greater electronegativity than hydrogen, the transfer of charges in fluorographene between graphene and F atoms is distinct from that in graphene. The single layer fluorographene has a wide band gap [10] semiconducting activity with an optical distance of approximately 3eV, which is in good agreement with one of about 3.8 eV of the latest experimental scale. Nevertheless, first principle calculations again show that band gap estimation can be a challenging task, because GGA offers a band gap of 3.29 eV, hybrid (HSE06) 4.9 eV, whereas multi-electron approaches based on GW approximation provide a band gap of 8.1 eV (twice as large). Therefore, the excitation binding energy must be included in order to obtain the right band gap value.

Fluorinated silicene has been theoretically studied by Ding et al. who stated that there is a direct band gap in the lattice whose values can be adjusted by strain. For these structures the values of the formation energies are negative; suggesting that silicene hydrogenation / fluorination is an exothermic reaction and that the resulting H-/F-silicene is stable.

CONCLUSION

2D materials research has started a new era in materials science. New materials are available, atomically thin and mechanically, thermally and electronically stable, with a wide range of electronic properties and can be assembled in compact ultrathin packages. Fabrication of new devices requires a detailed understanding of the properties of 2D materials, which is supported by the electronic properties presented in the work. Band gaps and effective electron and hole masses allow the estimation of load and spin mobilities for the simulation of basic devices. The band structures allow the parameterization of tight-binding models which are useful for more detailed calculations of electron transport and simulations of devices. Our results show that all classes of 3D world known materials have 2D counterpart. We consider metals and insulators, semiconductors with a great variety of band gaps and different band characteristics. Alternatively, 2D materials show unknown properties from the bulk, for instance massless Dirac electrons.

REFERENCES

- [1] R. Mas-Ballesté, C. Gómez-Navarro, J. Gómez-Herrero, and F. Zamora, "2D materials: To graphene and beyond," *Nanoscale*, 2011, doi: 10.1039/c0nr00323a.
- [2] Z. Zhang, Y. Yue, and J. He, "Spectroscopy," in *Springer Tracts in Modern Physics*, 2018.
- [3] H. Ago, "Graphene," *Kobunshi*, 2012, doi: 10.1201/b15545-2.
- [4] R. Gerritsma, G. Kirchmair, F. Zähringer, E. Solano, R. Blatt, and C. F. Roos, "Quantum simulation of the Dirac equation," *Nature*, 2010, doi: 10.1038/nature08688.
- [5] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer MoS₂ transistors," *Nat. Nanotechnol.*, 2011, doi: 10.1038/nnano.2010.279.
- [6] S. Wang, P. K. Ang, Z. Wang, A. L. L. Tang, J. T. L. Thong, and K. P. Loh, "High mobility, printable, and solution-processed graphene electronics," *Nano Lett.*, 2010, doi: 10.1021/nl9028736.
- [7] O. Panchuk and P. Fochuk, "Doping," in *CdTe and Related Compounds; Physics, Defects, Hetero- and Nano-structures, Crystal Growth, Surfaces and Applications*, 2010.
- [8] S. Carbide and S. Material, "Silicon Carbide, SiC Ceramic Properties," *Accuratus*, 2013.
- [9] R. R. Nair *et al.*, "Fluorographene: A two-dimensional counterpart of Teflon," *Small*, 2010, doi: 10.1002/smll.201001555.
- [10] J. Millan and P. Godignon, "Wide Band Gap power semiconductor devices," in *Proceedings of the 2013 Spanish Conference on Electron Devices, CDE 2013*, 2013, doi: 10.1109/CDE.2013.6481400.