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Graphene against Other Two-Dimensional Materials: A Comparative Study on the Basis of Electronic Applications

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Abstract

The evolution of the electronics industry since almost 75 years ago has depended on the novel materials and devices that continuously are introduced. In first decades of this century, 2D materials are impelling this development through materials such as graphene, graphane, graphone, graphyne, graphdiyne, silicene, silicane, germanene, germanane, stanene, phosphorene, arsenene, antimonene, borophene, hexagonal boron nitride (*h*BN), transition metal dichalcogenides (TMDs), and MXenes. In this work, the main strategies to modify electrical properties of 2D materials are studied for obtaining dielectric, semiconducting, or semimetallic properties. The effects of doping, chemical modification, electrical field, or compressive and/or tensile strains are considered. In addition, the light-matter interaction to develop optoelectronic applications is analyzed. In next three decades, a lot of scientific research will be realized to completely exploit the use of 2D materials either as single monolayers or as stacked multilayers in several fields of knowledge with a special emphasis on the benefit to the electronic industry and ultimately our society.

Keywords: Graphene, 2D materials, electronic devices, electrical properties, nanoelectronics, flexible electronics

1. Introduction

The more novel electronic devices that will be produced in the current century will be made a reality, thanks to the emerging two-dimensional (2D) nanomaterials based on carbon (C), silicon (Si), germanium (Ge), tin (Sn), phosphorus (P), arsenic (As), antimony (Sb), boron (B), and their

combinations. Until now, many papers presenting reviews related to 2D materials have been presented [1–5]; however, a direct comparison of these materials for electronic applications is necessary. This study will allow us to know the advantages and disadvantages of 2D materials for electronic applications. A clear trend related to the choice of these materials for determined applications must be established. In this context, a comparison of the physical properties of these materials is used to exploit them from several technical points of view. Moreover, the possible synergy between 2D materials is presented as a strategic way to exploit these materials completely in more complex applications such as the development of hybrid or multifunctional materials.

Several 2D materials, such as carbon-based 2D materials, silicate clays, transition metal dichalcogenides (TMDs), and transition metal oxides (TMOs), have been used in electronic devices. Particularly, materials such as graphene, molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), molybdenum trioxide (MoO_3), and silicon carbide (SiC) provide enhanced physical and chemical functionality making use of uniform shapes, high surface-to-volume ratios, and surface charge [1–5]. While dichalcogenides and buckled nanomaterials have sizeable band gaps, graphene has zero band gap and they also become semiconducting or metallic materials. These materials are very sensitive to the number of layers, ranging from indirect band-gap semiconductor in the bulk phase to direct band-gap semiconductor in monolayers. 2D materials are leading to ubiquitous flexible and transparent electronic systems for applications in integrated circuits, solar cells, and storage energy [2, 4]. Comparison of the performance in electrical and optical properties of 2D materials is presented here.

A few decades ago, the potential of the electronics industry depended entirely on silicon. New materials such as carbon allotropes of the groups III, IV and V are being introduced to increase efficiency, specific capacity, and speed of information processing. Actually, in electronics, 2D materials are used in the manufacture of supercapacitors, batteries, field-effect transistors (FETs), solar cells, light-emitting diodes, transparent electrodes, coatings for electrostatic dissipation, and/or electromagnetic interference shielding, etc. The potential of the 2D materials has not been fully discovered yet; however, new potential applications are being invented and others are emerging from the laboratory, which are beneficial for the development of materials science and engineering. The use of 2D materials in the electronic industry will be extended in the design of new electronic devices being applied either individually or as a component within a composite, hybrid, or functional material. This chapter has been divided as follows: Section 2 introduces basic concepts about 2D materials. Graphene and its derivatives are studied in Section 3. Section 4 analyses different allotropes based on chemical elements with the exception of carbon. 2D materials such as hexagonal boron nitride (*h*BN), TMDs, and MXenes are discussed in Section 5. In Section 6, optoelectronic applications are presented. Finally, conclusions about the work are given in Section 7.

2. Basic concept about 2D materials

2D materials, also known as 2D topological materials or single-layer materials, can be defined as crystalline materials with a single layer of atoms or chemical compounds. These materials

are substances with a thickness of a few nanometres or less (one or two atoms thick). The extraordinary properties of these 2D materials have opened new opportunities for scientists and engineers to increase the research activities in this novel engineering materials field [4]. Electronic transport is realized in the 2D plane of the material, where electrons move freely [2]. In addition, electrons have restricted motion in the third direction, due to which this phenomenon is governed by quantum mechanics. They can be constituted by 2D allotropes of diverse chemical elements or compounds. Actually, graphene is the most researched 2D material till now. In addition, they can be classified as elemental, compounds, or van der Waals heterostructures. The elemental 2D materials use the -*ene* suffix in their names, for example, graphene, germanene, borophene, silicene, stanene, and phosphorene. Compounds consist of two or more covalently bonded elements and carry the -*ane* or -*ide* suffixes in their names, for example, graphane, hexagonal boron nitride (*h*BN), germanane, chalcogenide, Molybdenum disulfide (MoS_2), and tungsten diselenide (WSe_2). Van der Waals heterostructures are constituted of layered combinations of different 2D materials and as examples they are presented as MXenes (few atoms thick layers of transition metal carbide or carbonitrides) or organic compounds, such as $Ni_3(HITP)_2$, where HITP is 2, 3, 6, 7, 10, 11-hexaaminotriphenylene.

The first 2D material discovered was graphene in 2004, which was isolated from graphite. Since 2010, graphene is not alone. Since this success a large amount of research has been realized to isolate other 2D materials due to their remarkable chemical, electronic, optical, and mechanical properties. 2D materials possess exceptional properties, since they are strong, lightweight, flexible, and good conductors of heat and electricity. 2D materials exhibit diverse electronic properties, ranging from insulating, semiconducting to semimetallic properties [3]. Some 2D materials are nearly optically transparent. Such properties proceed from the variations in structure (tunable architectures) as a consequence of changing metal centres [6]. Despite great advances achieved until now, none of these materials has been used for large-scale commercial applications with the possible exception of graphene. Their main areas of applications are electronics and optoelectronics, sensors, biological engineering, filtration (water purification), lightweight/strong composite materials, photovoltaic systems (electrodes), medicine, quantum dots, thermal management, ethanol distillation, and energy storage [3, 7].

Optical and electronic properties of the 2D materials are completely different from those of the bulk materials due to confinement of electrons and absence of interlayer interactions, which play an important role in the band structure presented in these materials [6]. On the other hand, mechanical and chemical properties are obtained thanks to geometric effects (chirality, dilution, defects, etc.) and to the high surface-volume ratio (it trends to infinity in the thinnest materials) [8]. Graphene and TMDs are building blocks for optoelectronic applications in areas such as ultrafast and ultrasensitive detection of light in the ultraviolet, visible, infrared and terahertz frequency ranges [3, 7].

Three different strategies have been developed to achieve a finite band gap in 2D materials: (1) chemical modification, (2) deposition on substrates, and (3) application of 2D chemical compounds [1–5]. Each of the above strategies has a direct influence on the properties and applications of each of the different types of 2D materials that have been discovered. Section 3 studies graphene-based materials; the 2D allotropes of groups III, IV, and V, with the

exception of the carbon (C), are analyzed in Section 4; the *h*BN, 2D TMDs, and MXenes are discussed in Section 5, and finally, the optoelectronic applications are analyzed in Section 6.

3. Graphene and its derivatives

Graphene is a stable 2D material based on carbon (C). It has been very successful, since it is composed of van der Waals type layers which are one or few atoms thick [1]. It has attracted designers due to its exceptional electronic properties. In addition, graphene is one million times thinner than paper, transparent, and the strongest material in the world. Gapless graphene strongly interacts with light from terahertz to ultraviolet (mainly, photodetectors) range [3]. Graphene has a very high carrier mobility (15,000 cm^2/Vs for graphene on SiO$_2$ substrate and 200,000 cm^2/Vs for suspended graphene) and low losses through the Joule effect. Unfortunately, graphene has zero band gap, which disqualifies it due to its low on/off ratio required by FETs for applications in digital circuits.

For example, graphene has been chemically modified into different versions such as graphane [9], graphone [10], graphyne [10], graphdiyne [10], fluorographene [11], or graphXene [12]. Graphyne is better than graphene in directional electronic properties and charge carriers. Graphone (partially hydrogenated) and graphane (100% hydrogenation of graphene with stoichiometry CH) have applications in nanoelectronics and spintronics due to the presence of band gap and magnetic properties [1]. Graphone with hydrogen coverage of 8% reaches a band gap of ~1.0 eV due to the rehybridization from sp^2 to sp^3, and other authors have reported a band gap of 1.25 eV for different coverage [13]. Therefore, the size of the band gap depends exclusively on the H/C ratio, where band gaps of up to 1 eV are obtainable. Graphane achieves a band gap of 3.5 eV (insulating behaviour), although theoretically it achieves a value of 4.5 eV [13–14]. The presence of configuration changes from sp^2 to sp^3 configuration, should lead to a band gap of 3.12 eV. Unfortunately, graphane has an optical band gap different from the electronic band gap, which is not expected for direct band gap materials. FETs based on graphane and/or graphone present large I_{on} and I_{on}/I_{off} ratios [2], reduced band-to-band tunnelling, without disadvantages such as lithography and patterning requirements for conventional circuit integration [9]. Graphyne (allotrope of graphene with one atom thick planar sheet of sp and sp^2 bonded carbon atoms arranged in a crystal lattice) and graphdiyne (allotrope of graphene containing two acetylenic linkages in each unit cell rather the one linkage as in graphyne), thanks to their crystalline structures, present tunable band gap giving place to semiconducting materials [10]. The band gap is increased with the reduction in the ribbon width and the number of sheets involved. Graphyne ribbons have band gaps in the semiconducting range from 0.59 to 1.25 eV. A tensile strain of 0.15 increases the band gap in 1 eV, while a compressive strain of 0.1 reduces the band gap in 0.3 eV. For strain-free graphdiyne, its band gap is 0.47 eV, while with strain it varies from 0.28 to 0.71 eV. Graphdiyne with low doping levels of boron nitride (BN) increases its band gap by 1 eV, and the trend is linear with the increasing dopant concentration [15]. When BN replaces all carbon atoms, a new material is formed, which is called BNdiyne with band gap of 4.39 eV (achieving an insulating behaviour) [10]. Fluorographene (FG), which results due to the exposure of graphene to atomic F,

has an excellent behaviour as an insulator and possesses a high thermal and chemical stability [11]. It presents an optical band gap of 3.0 eV and an electrical band gap of ~3.5 eV (electrical insulator). Graphene can be made to interact with Group IA and Group VIIA elements to form materials called graphXenes [12]. These materials present a range of band gap between 0 and 6.4 eV. Therefore, metallic, semiconducting, and insulating behaviours are presented, and it is obtained through a mixture of sp^2/sp^3 systems. Combinations, such as $C_2HCl_{0.5}F_{0.5}$ and C_2HCl, show semiconducting behaviour, while combinations C_2HF and C_2F_2 show insulating behaviour [12].

4. 2D allotropes of Si, Ge, Sn, P, As, Sb, and B

Elemental monolayers of the Group III (B), IV (Si, Ge), and V (P, As, Sb) are emerging as promising 2D materials with electronic applications. These materials are denominated as borenene, silicene, silicane, germanene, germanane, phosphorene, arsenene, and antimonene. A brief summary of the applications in the electronics area of the different 2D allotropes of groups III, IV and V, excluding carbon, is presented below.

Silicene is a crystalline 2D allotrope of silicon, with a hexagonal honeycomb structure similar to that of graphene [16]. Silicene has a buckled honeycomb atomic arrangement of sp^3/sp^2-like hybridized Si atoms, which produces a non-trivial electronic structure and a spin-orbit coupling of 1.55 meV (under pressure it is increased to 2.9 meV), whose value is much larger than that of graphene (10^{-2} meV). In addition, silicene is more easily integrated into current Si-based electronics compared to graphene. The use of inert substrates such as hBN monolayer and SiC (0001) has silicene-substrate interaction energies range in 0.067–0.089 eV per Si atom, belonging to typical van der Waals interaction [17]. The characteristic Dirac cone is preserved for silicene deposited on substrates as hBN monolayer or hydrogenated Si-terminated SiC (0001) surface. On the other hand, silicene presents a metallic behaviour, when it is deposited on a hydrogenated C-terminated SiC (0001) surface. Therefore, silicene presents different electronic properties in accordance with the substrate where it is deposited, which allow to tune a different band gap via the substrate [17]. The presence of Stone-Wales (SW) defects in silicene can be effectively recovered by thermal annealing. The existence of single and double vacancies (SVs and DVs) in silicene induces small band gaps, and SV defects may transform semimetallic silicene into metallic silicene. Dramatic changes in the electronic properties of the silicene are produced by the presence of Si adatoms, for example, a semimetal behaviour is changed into magnetic semiconductor behaviour [18]. Its thin films provide novel electronic properties suitable for semiconductor device applications at room temperature. It has no band gap, but it can be used in the channel of high-performance FETs when a vertical electric field is applied [19]. Moreover, it has been predicted that silicene will exhibit a quantum spin Hall effect (QSHE) under an accessible temperature regime [20]. This effect is adequate to applications where it is desired that electrical conductance cannot be destroyed by magnetic fields applied to the sample. The physicochemical properties of the silicene will allow the design of novel devices in future electronic industry. Its applications are completely similar to those of graphene. Silicene presents excitonic resonance ($\pi \rightarrow \pi^*$ excitation) at 1.23 eV due to its quasiparticle excitation and optical absorption spectrum [21]. It is thermodynamically more stable

than graphane. It can be used for digital electronic applications, photonic and spintronic (magnetic semiconductor) devices, and lithium ion battery electrodes [22].

Germanene is a material made up of a single layer of germanium atoms, which is deposited under high vacuum and high temperature on a substrate such as gold (111) [23]. Its high-quality thin films provide novel electronic properties suitable for semiconductor device applications. It has no band gap, but it can be used in the channel of high-performance FETs when a vertical electric field is applied [19]. Germanene presents excitonic resonance ($\pi \rightarrow \pi^*$ excitation) at 1.10 eV due to its quasi-particle excitation and optical absorption spectrum [21]. The first bright exciton in germanane is located at 1.45 eV with a binding energy of 0.92 V. It is thermodynamically more stable than graphane. It has no band gap, but attaching a hydrogen atom to each germanium atom creates one band gap that can be exploited in diverse electronic applications [24].

Silicane is the hydride of silicene, that is, it is a crystalline single layer composed of silicene with one hydrogen atom bonded in each atom of Silicon. It is a semiconductor with indirect band gap [25]. Hydrogenation produces an indirect band gap in silicene called silicane, in the range of 2 to 4 eV, due to the rehybridization from sp^2 to sp^3. Its applications may include polariton lasers and optical switches for the observation of excitonic effects at high temperature and in the visible optical range [26]. The first bright exciton in silicane is located at 3.00 eV with a binding energy of 1.07 V. It presents strongly bound excitons with considerable binding energies [21].

Germanane is a crystalline single layer composed of germanium with one hydrogen atom bonded in the z-direction for each atom, that is, with a similar structure to graphane. It is a semiconductor with indirect band gap [25]. Hydrogenation opens a direct band gap in germanene called germanane, in the range of 1.5–3 eV, due to the rehybridization from sp^2 to sp^3. This material is potentially interesting for optoelectronic applications in the blue/violet spectral range such as light-emitting diodes due to the value of its direct band gap [24]. Its optical band gap is smaller than that of graphane to detect lower photon energies [26]. It presents strongly bound excitons with considerable binding energies [21].

Stanene is a crystalline allotrope of tin arranged in a single layer of atoms as graphene, whose behaviour is of a topological insulator with the capacity of displaying dissipationless currents at its edges near room temperature. It has an inverted band gap which can be tuned by compressive strain [27]. When magnetic doping and electrical gating are applied in stanene deposited on InSb substrate, then properties such as quantum anomalous Hall effect, Chern half metallicity, and topological superconductivity can be implemented. The spin-orbit interaction opens a 70 meV energy band gap in the k point of first Brillouin zone, but by applying strain the energy band gap in the band structure is closed [28]. It has a behaviour of topological insulator and phonon-mediated superconductor (doping with calcium and/or lithium) at a very low transition temperature ($T_c \sim 1.3$ K) [29]. 2D stanene with hydrogenation (Stanane) has a band gap that can be modulated by electric field and strain, and also, it has room-temperature ferromagnetic behaviour. These qualities are dependent on the arrangement of hydrogen atoms in the stanene [30].

Phosphorene is the 2D crystalline allotrope of phosphorus consisting of a single layer of atoms as graphene, which possesses a non-zero band gap (~0.1 eV) while displaying high electron mobility. These qualities make it a better electronic material than graphene [31]. Zigzag phosphorene nanoribbons have metallic behaviour regardless of the ribbon width, whereas armchair phosphorene has semiconducting behaviour with indirect band gap which decreases with increasing ribbon width [32]. A compressive (or tensile) strain can reduce (or enlarge) the band gap of phosphorene, while in-plane electric field can reduce the band gap of phosphorene. Phosphorene is a p-type semiconducting material with a band gap value of 0.31–0.36 eV, carrier mobility of 286 cm²/Vs, and presents photoluminescence in the visible optical range [33]. Besides, phosphorene has a high specific capacity, superb stability, and high electrical conductivity [34]. These capacities allow its use in FETs, batteries, radio receivers, and gas sensors.

Arsenene is a 2D crystalline allotrope of arsenic consisting of a single layer of atoms as the graphene, which can absorb light atoms to develop an effective method to functionalize it with B, C, N, and/or F to induce magnetism or N and/or F to induce n-type doping [35]. Its electronic band structure is dependent on edge shapes; armchair nanoribbons have large indirect band gap (due to stronger quantum confinement), while zigzag nanoribbons have small direct band gap [36]. In addition, arsenene has small carrier mobilities in the orders of magnitude of 0.5–1.2×10^3 cm²/Vs for potential applications in nanoelectronics and nanodevices. A tensile strain (6%) applied to the monolayers provides an indirect-direct band gap transition (whose value is reduced with the strain), which allows these materials to be applied in light-emitting diodes and solar cells [37]. Under compressive strains, the band gap of monolayer and bilayer arsenenes initially increases and then rapidly decreases [38].

Antimonene is a 2D crystalline of antimony consisting of a single layer of atoms as the graphene, which has two stable and semiconducting allotropes (α and β), and with indirect band gap. α-Sb has a puckered structure with two atomic sub-layers, and β-Sb has a buckled hexagonal lattice. A moderate tensile strain applied to the monolayers provides an indirect-direct band gap transition, which allows these materials to be applied in optoelectronics [39]. In addition, antimonene can be tuned as a topological insulator to achieve QSHE at high temperatures using large tensile strain up to 18% and a band gap of 270 meV and whose characteristics meet the requirements of future electronic devices with low power consumption [40]. It has the same behaviour as that of arsenene with respect to the electronic band structure.

Borophene is a crystalline allotrope of boron consisting of icosahedral B_{12} units fused as supericosahedra arranged in a 2D sheet with a hexagonal hole in the middle on silver surfaces under ultrahigh vacuum conditions [41]. Boron is non-metallic by nature as a bulk material, but it shows metallic and semiconducting behaviour at the nanoscale and has atomic thickness. Thanks to the hexagonal holes, various chemical modifications are possible to tune the electronic, optical, and chemical properties of borophenes [42]. It has a higher tensile strength than any other known material. The stability of these sheets is enhanced by vacancies or out-of-plane distortions. Borophene has a highly anisotropic metallic behaviour, where electrical conductivity is confined along the chains [41]. It is maintained as a promising material for applications ranging from electronics (sensors and electronic devices), photovoltaics (electro-

des), and energy storage (batteries); however, a lot of work is still required to determine its practical applications.

5. Compounds: hBN, TMDs, and MXenes

hBN is an interesting 2D material with a band gap of around 6 eV, which makes it an excellent dielectric, and it can be incorporated into different heterostructures for the electrostatic gating (protective cover, substrate, gate dielectric, or tunnel barrier) of other 2D materials due to that it does not require a lattice matching to generate van der Waals structures (electronic bands near the Fermi level (E_f) have graphene-like linear dispersion) [3]. It forms a 2D-crystalline structure composed of alternating atoms of boron and nitrogen, with lattice spacing similar to that of graphene [43]. It is commonly used in FETs as ideal substrate and gate dielectric. The doping level can also be varied by applying an external electric field, and it decreases with increasing hBN layer thickness and approaches zero for thick layers. It can be partially oxidized (PO-hBN) to decrease its optical transmission (>60%) and band gap (from 3.97 to 5.46 eV) [44].

Transition metal chalcogenides (TMCs) are thin-layered semiconducting structures of the type MX_2, where M is a transition metal atom (Mo, W, etc.) and X is a chalcogen atom (S, Se, or Te) [45]. One layer of M atoms is sandwiched between two layers of X atoms. TMCs are commonly restricted to chemical elements of the groups IV (Ti, Zr, Hf and so on), group V (for example V, Nb or Ta), or group VI (Mo, W and so on), and X is a chalcogen (S, Se or Te) [46]. These materials have layered structures of the form chalcogen-metal-chalcogen (X-M-X), with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms. The overall symmetry of TMDs is hexagonal or rhombohedral, and the metal atoms have octahedral or trigonal prismatic coordination [46]. MoS_2 is one of the most typical TMDs; it has a direct band gap of 1.8 eV in monolayer, which can be tuned in different ways [47]. A MoS_2 monolayer has a thickness of 6.5 Å, and it has been used in chemical and gas sensors [48]. MoS_2-based sensors have been implemented to detect NH_3 down of 400 ppb [49]. Besides, MoS_2 has applications in fields such as flexible electronics, energy storage and harvesting as well as electrochemical catalysis [47].

Chemical formula	Chemical formula	Chemical formula	Chemical formula	Chemical formula	Chemical formula
C (graphene)	NbS_2	WTe_2	VBr_2	VS_2	CrS_2
FeSe	$NbSe_2$	$CoTe_2$	VI_2	VSe_2	$CrSe_2$
LiFeAs	$NbTe_2$	$RhTe_2$	PFeLi	VTe_2	$CrTe_2$
YSe_2	TaS_2-AB	$IrTe_2$	IYGa	Ni_2Te_2Sb	$ZnIn_2S_4$
$TiSe_2$	TaS_2-AA	$NiTe_2$	PTe_2Ti_2	Cu_2S	$Zn_2In_2S_5$
$TiTe_2$	$TaSe_2$-AB	$SiTe_2$	FeS	VCl_2	SbSiNi
$ZrTe_2$	$TaSe_2$-AA	$AlCl_2$	FeTe	$HfTe_2$	Ag_2ReCl_6
	$TaTe_2$				

Table 1. 2D materials with metallic behaviour, that is, band gap = 0.0 eV [50].

In order to compare the electrical properties of different 2D materials, three tables were created for ordering these materials in three groups, as follows: (a) 2D materials with metallic behaviour (**Table 1**), (b) 2D materials with semiconducting behaviour (**Table 2**), and (c) 2D materials with electrical insulator behaviour (**Table 3**).

Chemical formula	Band gap (eV)	Chemical formula	Band gap (eV)	Chemical formula	Band gap (eV)
Bi_2Se_3	0.9	MoS_2	1.6	PdS_2	1.1
Bi_2Te_3	0.9	$MoSe_2$	1.4	$PdSe_2$	1.3
TiS_2	0.02	$MoTe_2$	1.15	$PdTe_2$	0.2
ZrS_2	1.1	WS_2	1.8	PtS_2	1.8
$ZrSe_2$	0.4	WSe_2	1.5	$PtSe_2$	1.4
HfS_2	1.3	TcS_2	1.2	$PtTe_2$	0.8
$HfSe_2$	0.6	ReS_2	1.4	SnS_2	1.6
PbIF	2.3	$ReSe_2$	1.3	$SnSe_2$	0.8
HgI_2	1.8	P_2AgSe_6Bi	1.4	GaS	2.4
ZrClN	1.9	P_2CuSe_6Bi	0.8	GaSe	1.8
$Bi_{14}Te_{13}S_8$	0.9	CdI_2	2.5	BiIO	1.5
PbO	2.5	$PbBi_2Te_4$	1.0	$FeBr_3$	0.5
$Sb_2Ge_2Te_5$	0.2	$PbSb_2Te_4$	0.8	ScP_2AgSe_6	1.8
$MgPSe_3$	2.1	$CrSiTe_3$	0.6	$FePSe_3$	0.05

Table 2. 2D materials with semiconducting behaviour ($0 < E_g < 3$ eV) [50].

Chemical formula	Band gap (eV)	Chemical formula	Band gap (eV)	Chemical formula	Band gap (eV)
BN	4.7	BaIF	4.3	$KC_6FeO_3N_3$	4.5
YI_3	3.1	SrIF	4.5	$MgBr_2$	4.8
				MgI_2	3.6

Table 3. 2D materials with insulating dielectric behaviour ($E_g > 3.0$ eV) [50].

TMCs can be formed with multiple layers bound to each other by van der Waals forces. 2D TMDs are exciting materials for future applications in nanoelectronics, nanophotonics, and sensing [49]. TMDs monolayers such as MoS_2, $MoSe_2$, $MoTe_2$, WS_2, and WSe_2 have a direct band gap and can be used in electronics as FETs and in optoelectronics as emitters (light-emitting diodes) and optical detectors (photodetectors) [3]. Molybdenum and tungsten dichalcogenides are a family of compounds that is structurally and chemically well defined. WS_2 is a layered material consisting of stacked S-W-S slabs with a binding energy in c-direction of 0.14 eV.

WS_2 has optical band gap energy of 1.46 eV; its electrical conductivity is in the order of 10^{-3} S/cm and has *n*-type conductivity [51]. Also, this material can be used in heterogeneous catalysis and electrochemical hydrogen storage. MoS_2, $MoSe_2$, WS_2, and WSe_2 are promising semiconducting materials for solar energy conversion, since they work as absorber materials due to the weak connection by intermolecular van der Waals forces among monolayers.

The TMD monolayer crystalline structure has no inversion centre, which allows a new degree of freedom of charge carriers called the *k*-valley index giving place to the new field of physics called valleytronics (technology that controls the valley degree of freedom of certain semiconductors, that is, a local maximum/minimum on the valence/conduction band, that present multiple valleys inside the first Brillouin zone) [48]. WSe_2-$MoSe_2$ heterostructures can be optically polarized to produce valley-specific interlayer excitons with lifetimes of 40 ns, which can be exploited in optoelectronic applications [52]. In addition, spin-orbit coupling among TMDC monolayers allows control of the electron spin through of the tuning the applied photonic energy, due to that a spin splitting in the meV range is presented in conduction and valence bands. TMDs can be combined with other 2D materials such as graphene and *h*BN to generate a new class of van der Waals heterostructure devices. TMDs can behave as electrical conductor, semimetal, semiconductor, and dielectric material, [50, 53–54], as well as, superconductor [55–56]. In the case of semiconductors, they have direct and indirect band gaps with values ranging from ultraviolet range to infrared range through the visible range. TMD monolayers are structurally stable; these have band gaps and show electron mobilities with comparable values to those of silicon. Therefore, they can be used to fabricate FETs [46].

Stacking of 2D materials on top of each other in a controlled fashion can create heterostructures with tailored physical properties that offers another promising approach to design and fabricate novel electronic devices [5]. In addition, either the in-plane heterojunction or the vertical stacking heterostructures can be realized by delicately tuning the composition and stacking sequences among 2D materials [5]. The development of FETs based on MoS_2 increased the scientific interest in the research of TMCs monolayers for novel ultrathin and flexible devices applied in electronics and optoelectronics [54]. Tunnel field-effect transistors (TFETs) based on vertical stacking of 2D materials can be used to build *p*-*n* junctions of TMC monolayers to design low-power logic devices [57]—VIB-MeX_2 (Me = W, Mo; X= Te, Se) monolayers as the *n*-type source and IVB-MeX_2 (Me = Zr, Hf; X= S, Se) as the *p*-type drain [57]. The two groups of semiconductors have distinct band edge characters, which will generate intervalley scattering during the electron tunnelling process. Strain is highlighted as an effective way to modify the band edge properties of these 2D TMDs [57]. Graphene (contact electrodes and circuit interconnections)/MoS_2 (transistor channel) heterostructures offer a technological alternative to design FETs with metallic drains and sources for practical flexible transparent electronics [58]. Graphene/MoS_2 heterostructure opens a 1 meV band gap in MoS_2-supported graphene, and the band gap is tunable under different interlayer distances [59]. Moreover, this heterostructure displays an enhanced light response, which allows even photocatalytic applications. 2D heterostructures play a pivotal role in electrochemical energy storage, sensing, hydrogen generation by photochemical water splitting, and electronic device applications such as FETs [60]. Particularly, in the field of energy conversion and storage, these hybrids will be

useful as anodes in lithium ion batteries and supercapacitors [60]. MoS_2 and WSe_2 have potential applications in electronics because they present high I_{on}/I_{off} current ratios and unique electro-optical properties [61]. Lateral WSe_2-MoS_2 heterojunction is a key component for building monolayer p-n rectifying diodes, light-emitting diodes, photovoltaic devices, and bipolar junction transistors [61].

2D TMDs under out-of-plane pressure decrease their band gap with increasing pressure and it can be closed too, which implies a semiconductor-metal transition [62]. The critical pressure for the semiconductor-metal transition is larger for the thinner nanoribbons, and the band gap closes faster for the Mo-containing nanoribbons than the W-containing ones. In addition, the physical mechanism of the band gap variation relates to the charge accumulation and delocalization in the interlayer region [62].

Layered TMDs are susceptible to electronic instability because its charge density wave (CDW) phases are diverse and commensurate, which leads to a strong electron-phonon and electron-electron interactions due to the Mott insulating phase presented [55]. Therefore, it is necessary find an adequate ordering of atoms to produce star-of-David clusters that allow boost superconductivity in a layered chalcogenide such as $1T$-$TaS_{2-x}Se_x$ to achieve different electronic degrees of freedom leading to tunable band gaps. Because the Ta $5d$ orbital allows superconductivity and Se $4p$ orbital leads to metallic phase, an unusual Se/S ordering creates superconductivity stable states [55]. Superconductivity can be induced through electrostatic gating using ionic liquid in materials such as $MoSe_2$, while electrochemical gating can be induced using $KClO_4$/polyethylene glycol (PEG) using a crossover from surface doping to bulk doping in materials such as $MoTe_2$ and WS_2 [56]. Moreover, the discovery of superconductors based on Mo and W allow to affirm that superconductivity is a common property for semiconducting TMDs. In bulk materials, the Zeeman effect is detrimental to superconductivity, however, in nanomaterials such as MoS_2 monolayers, it allows the development of ionic-gated transistors capable of realizing magnetotransport at coupling the spin-orbit with the spins of Cooper pairs in a direction orthogonal to the magnetic field [63]. This discovery leads to the Ising superconductor with a critical magnetic field B_{C2} far beyond the Pauli paramagnetic limit, consistent with Zeeman-protected superconductivity [63].

In 2D TMDs with 1T-MX_2 structure, where M = (W or Mo) and X = (Te, Se, or S), it is possible that a structural distortion causes an intrinsic band inversion between chalcogenide-p and metal-d bands [64]. Moreover, spin-orbit coupling opens a band gap that is tunable by vertical electrical fields and/or strains. It is feasible to develop a topological FET made of van der Waals heterostructures of 1T-MX_2 and 2D dielectric layers that can be switched off by electric field through a topological phase transition instead of carrier depletion [64].

MXenes can be defined as layered transition metal carbides and carbonitrides with general formula of $M_{n+1}AX_n$ (e.g., Ti_2AlC, Ti_3AlC_2, Ta_4AlC_3), where M stands for early transition metal, A is mainly a group IIA or IVA (i.e., groups 13 or 14) element, X stands for carbon and/or nitrogen with n = 1, 2 or 3 [65]. MXenes have high electric conductivity (1500 S/cm, due to the metallic conductivity of transition metal carbides) combined with hydrophilic surfaces (due to their hydroxyl or oxygen terminated surfaces) [66], that is, they behave as conductive clays.

These materials show to be promising in energy storage applications such as Li-ion batteries and supercapacitors [65–66].

6. Optoelectronic applications

2D materials have interesting properties for photonics and optoelectronics compared with other materials. 2D materials enables charge carrier generation by light absorption over a very wide energy spectrum including the ultraviolet, visible, short-wave infrared (SWIR), near-infrared (NIR), mid-infrared (MIR), far-infrared (FIR), and terahertz (THz) spectral regimes [7]. Moreover, 2D materials have ultrafast carrier dynamics, wavelength-independent absorption, tunable optical properties via electrostatic doping, low dissipation rates and high mobility, and ability to confine electromagnetic energy in small volumes [3]. Electrons in 2D crystals possess a valley degree of freedom (DOF) in addition to charge and spin [67]. 2D materials exhibit an anomalous Hall effect whose sign depends on the valley index effect (VHE). It implies that circularly polarized light excites electrons into a specific valley in the structure band, causing a finite anomalous Hall voltage whose sign is controlled by the helicity of the light [67]. The electronic structure changes at the edges of the 2D crystalline structure of MoS_2 resulting in strong resonant nonlinear optical susceptibilities due to the translational symmetry breaking [68]. Graphene layers are used as electrodes with tunable work function, while TMDs are applied as photoactive material due to the strong light-matter interaction and photon absorption. TMDs exhibit transparency, mechanical flexibility, and easy processing [7]. Also, they have the ability to tune the optical band gap by varying the number of monolayers to allow the detection and emission of light (electroluminescence) at different wavelengths. 2D materials present the photovoltaic effect, the photo-thermoelectric effect, the bolometric effect, the photogating effect and the plasma-wave-assisted mechanism [3, 69]. Applications such as transparent electrodes in displays, photovoltaic modules, photodetectors, optical modulators, plasmonic devices, and ultrafast lasers have been developed [7]. 2D TMDs exploit their primary figure of merit and low room-temperature photoluminescence quantum yield (QY) for applications such as light-emitting diodes, lasers, and solar cells based on MoS_2 [70].

7. Conclusions

2D materials represent the set of materials more prominent that will be exploited for electronic industry in the following three decades. The most representative 2D materials are graphene, graphane, graphone, graphyne, graphdiyne, silicene, silicane, germanene, germanane, stanene, phosphorene, arsenene, antimonene, borophene, hBN, TMDs, and MXenes. The main strategy to change electrical properties of 2D materials containing single- and multilayer nanoribons consists in modifying its structure band leading to dielectric, semiconducting, or semimetallic behaviours. Their electrical properties can be modified either by doping (addition of chemical elements), chemical modification (for example, hydrogenation for changing the sp^2 orbitals into a sp or sp^3 type), electrical field, or by means of strains (compressive and/or

tensile type). The emerging fields called valleytronics and spintronics will be possible thanks to 2D materials. They are an exceptional family of materials that will enhance the light-matter interaction to develop light emission, detection, modulation, and manipulation applications. The prospects for commercializing of 2D materials will be dependent not only on their performance, distinct advantages and capabilities but also on the ability of the researchers to achieve a production to large scale at low cost and their integration to the existing photonic and electronic platforms.

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