Graphene and Beyond-Graphene 2D Crystals for Next-Generation Green Electronics

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ABSTRACT

In this paper, we first review the impressive properties of two-dimensional (2D) nanocrystals, primarily graphene and beyond-graphene 2D crystals, such as transition-metal dichalcogenides (TMDs), and then highlight some applications uniquely enabled by these materials for designing next-generation low-power and low-loss "green electronics". Key challenges of 2D crystals relevant to such applications are discussed as well.

Keywords: Graphene, beyond-graphene 2D crystals, transition-metal dichalcogenides, green electronics

1. INTRODUCTION

Graphene – composed of a single layer of carbon atoms arranged in a hexagonal lattice with extraordinary physical properties was first experimentally demonstrated by Novoselov et al. [1] in 2004 and has drawn worldwide attention. Stimulated by the rise of graphene, various 2D crystals including layered hexagonal-boron nitride (h-BN) [2] and TMDs (such as MoS_2) [3]–[5] were subsequently demonstrated. These 2D crystals can be easily prepared by the micromechanical exfoliation technique used on the layered structures of their 3D bulk materials, where adjacent layers are held together by the relatively weak van der Waals (vdW) bonds, while the in-plane atoms are bonded by the strong valence bonds.

These emerging 2D materials have attracted tremendous attention due to their unique 2D nature that not only enriches the world of low-dimensional physics, but also provides unique platform for transformative technical innovations. Different from conventional materials, their unique properties include (1) pristine interfaces free of dangling bonds leading to low density of interface trap states and reduced scattering (**Fig. 1a, b**); (2) ultra-thin and uniform thickness leading to fluctuation-immune environment and excellent device electrostatics (**Fig. 1c, d**); and (3) wide range of choices from metals, insulators and semiconductors with controllable band gaps (**Fig. 1e**).

These properties enable the designing of next generation low-power, low-loss and ultra-energy-efficient active and passive devices targeted for next-generation "green electronics". In this paper, an overview of the essential physics

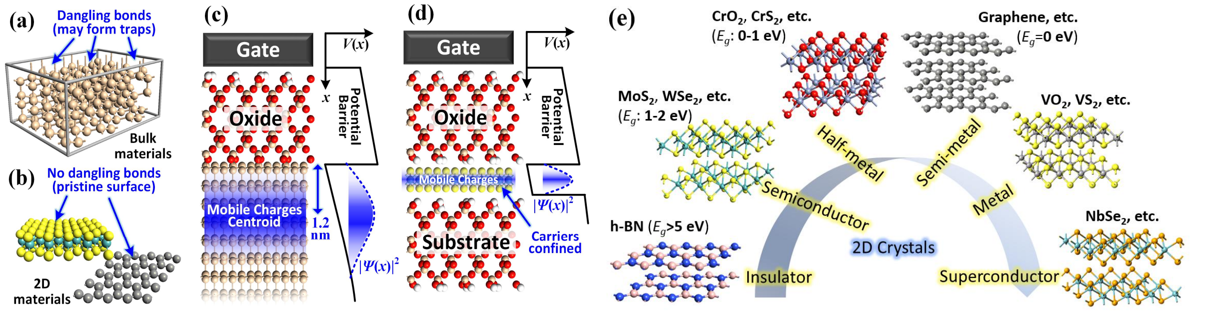

Figure 1. Schematic illustrating advantages of 2D materials: surfaces of **(a)** 3D and **(b)** 2D materials. The pristine interfaces (without out-of-plane dangling bonds) of 2D materials help reduce the interface traps. Mobile charge distribution in **(c)** 3D and **(d)** 2D crystals used as channel materials. The carrier confinement effect in 2D materials leads to excellent gate electrostatics. **(e)** Various types of 2D materials from insulator to superconductor. E_g denotes the band gap.

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and the key/unique electronic applications of graphene and beyond-graphene 2D materials are provided to highlight their role in emerging nanoelectronics.

2. GRAPHENE PHYSICS AND APPLICATIONS

2.1. Graphene Physics

The carbon allotropes (**Fig. 2a**), from zero-dimensional (0D) fullerenes, one-dimensional (1D) carbon nanotubes (CNT), to three dimensional (3D) graphite and diamond are all bonded by various combinations of the four $2s^2 2p^2$ orbital valence electrons of each carbon atom. In 2D graphene, a carbon atom shares electrons with three nearest neighbors (**Fig. 2b**), in the form of three sp^2 bonds, leaving out-of-plane p_z orbitals with one electron per atom (**Fig. 2c**). The three electrons forming the sp^2 bonds are responsible for the outstanding mechanical and thermal properties of graphene. On the other hand, the electrons in the p_z orbitals can easily hop between the neighboring atoms, since the hopping energy is high (~3.0eV), and thus form the π bands in the conduction bands (E_c) and π* bands in the valence bands (E_v). These electrons contribute to the outstanding electrical properties of graphene. As shown in **Fig. 2d**, E_c and E_v meet at the six corners of the first Brillouin zone (named as Dirac points) resulting in a zero bandgap. At the Dirac points, linear E-k dispersions and zero density of states (DOS) are found. Hence, graphene behaves like a semi-metal [1] with ultra-low and equal electron/hole effective masses, a constant group velocity $v_F = 10^6$ m/s and ultra-high electron/hole mobility. In addition, graphene patterned into narrow strips (width $w < 10$ nm) known as graphene nano-ribbons (GNR) has a spatial confinement along the width (w), and thereby has a band gap ($E_g \sim 1.4/w$ eV), as shown in **Fig. 2f**.

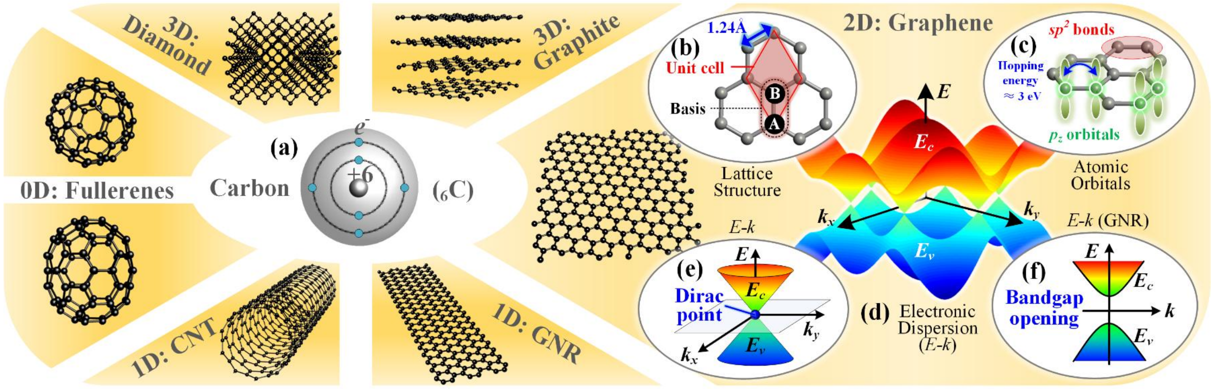


Figure 2. **(a)** Schematic of carbon atom and carbon allotropes, from 0D to 3D; **(b)** unit cell, basis and bond length of graphene; **(c)** atomic orbitals of graphene; **(d, e)** energy dispersion of graphene, where the energy dispersion is linear for low energies near the six corners (Dirac points) of the two-dimensional hexagonal Brillouin zone. **(f)** Energy dispersion of a semiconducting GNR, where a bandgap can be engineered by varying the width.

2.2. Graphene Applications

Graphene, in addition to its planar structure and outstanding electrical properties (such as high current density [6]), also has fascinating mechanical and thermal properties, which make them very attractive for next-generation interconnects and passives [7]. Graphene based global interconnects (**Fig. 3a**) can consume significantly less power than their Cu counterparts [8], [9]. On the other hand, the lossy conductor problem of Cu, which leads to low-Q inductors, can be overcome by using graphene inductors (**Fig. 3b**) [10], [11].

As the cost of the commonly used transparent electrode material Indium Tin Oxide (ITO) increases, high transmittance, high conductivity, high mechanical flexibility as well as impermeability to moisture (leading to improved reliability) make graphene a promising electrode material (**Fig. 3c**) for a variety of photovoltaic applications [12], such as touch panels, displays, light emitting devices, light sensors and solar cells.

Graphene Field-Effect Transistors (GFETs) (**Fig. 3d**) is highly attractive for RF applications due to the high transconductance, high mobility, atomically thin structure and high mechanical flexibility [13]. Band gap opening caused by etching of graphene into GNR can be employed to build GNR Tunnel-FETs (GNRTFET) for low-power and energy-efficient logic applications. The GNRTFET's performance is highly dependent on the length and width scaling [14]. Hence, in order to exploit the low E_g of wide-GNR to achieve high I_{ON} and the high E_g of narrow-GNR to attain low I_{OFF}, a hetero-GNRTFET has been proposed [15]. I_{ON} up to 1.3 mA/μm, I_{ON} /I_{OFF} up to 10^9, and subthreshold swing down to 10 mV/dec were obtained via simulations, which represent 2X and 10^4X improvement in I_{ON} and I_{ON}/I_{OFF}, respectively, compared to 25-nm CMOS technology.

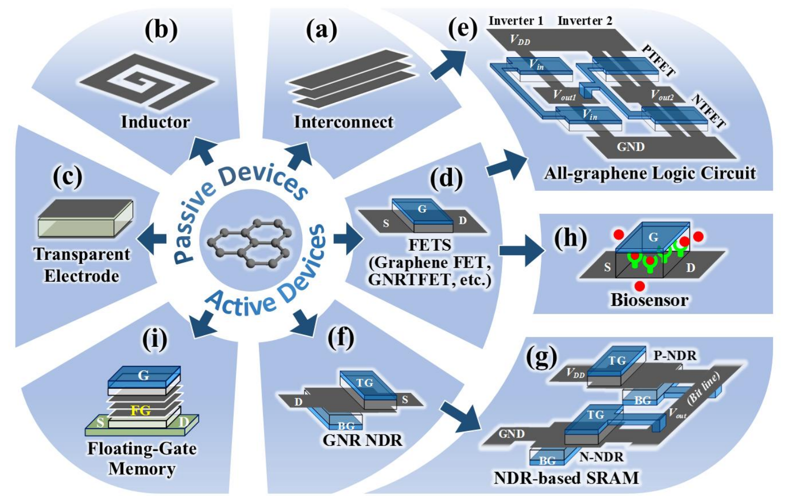


Figure 3. Schematic of **(a)** graphene interconnect; **(b)** graphene inductor; **(c)** graphene transparent electrode; **(d)** GNRTFET; **(e)** all-graphene circuit (2-stage inverter chain); **(f)** GNR NDR device; **(g)** GNR-NDR-based SRAM cell; **(h)** GNRTFET biosensor and **(i)** floating-gate memory with graphene floating-gate.

While separate analysis of GNR-based devices and graphene interconnects have been researched, the real benefits can be harvested through an integrated device-interconnect co-design scheme. Hence, a unique all-graphene circuit scheme (**Fig. 3e**) [16] has been proposed and theoretically explored, in which graphene was employed to fabricate both active (GNRTFETs) and passive (interconnects) devices in a seamless manner. Simulation results indicate that the all-graphene logic circuit exhibits better performances including 1.7X higher static noise margin, 2X higher inverter gain and 1–2 decades lower power consumption, compared to state-of-the-art CMOS technology.

A recently proposed GNR based negative differential resistance (NDR) device (**Fig. 3f**) [17], in the form of an Esaki tunnel diode, exhibits a peak-to-valley current ratio of 10^5, and operation voltage of 200 mV, which significantly exceeds the performance of conventional Esaki tunnel diodes. The GNR based NDR device can be used in the design of ultra-compact bi-stable static random access memory (SRAM) cell (**Fig. 3g**). Due to the compactness and high drive current, the proposed SRAM can outperform conventional SRAM cells in terms of switching speed and power consumption.

TFET biosensors have been shown to surpass the performance of conventional FET biosensors by several orders [18]. Due to the tunability of band gap and thereby the SS, GNRs can also be attractive for making low-power biosensors based on TFETs (**Fig. 3h**).

3. BEYOND-GRAPHENE 2D CRYSTALS AND APPLICATIONS

2.1. Physics of Beyond-Graphene 2D Crystals

The demonstration of graphene has truly opened up a new era for a wide range of 2D materials (**Fig. 1e**). For example, h-BN has similar lattice structure as graphene (**Fig.1e**), but has a large bandgap (E_g >5 eV) and can be used as an ultra-thin dielectric.

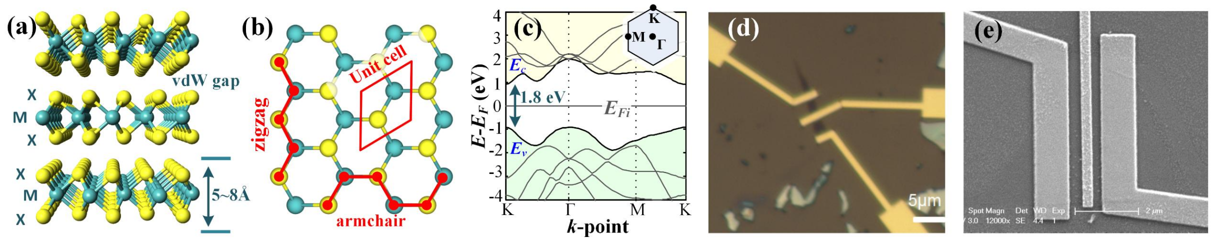


Figure 4. (a) Schematic of a typical layered TMD. **(b)** top view of the lattice structure. **(c)** Energy dispersions of monolayer MoS_2. Inset figure shows the 1st BZ of monolayer MoS_2. **(d)** Optical image of a fabricated WSe_2 monolayer FET. **(e)** SEM image of a top-gated MoS_2 FET with Ti contact.

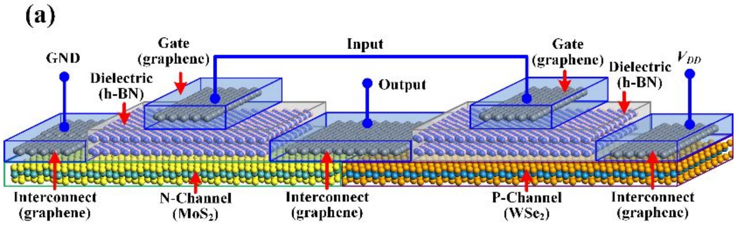
Similarly, TMDs such as MoS_2, WSe_2, WS_2, etc. (**Fig.1e**) have attracted tremendous attention. As shown in **Fig. 4a,b**, the in-plane lattice of TMD has two types of atoms, M and X, which are arranged in a 2D honeycomb array within the TMD plane, and in an X-M-X sandwich formed by covalent bonds. M stands for transition metal, such as Mo, W etc. X stands for chalcogen, including O, S, Se and Te. As in graphite, TMD layers are linked by weak van der Waals bonds. The thickness of monolayer TMDs is typically ~0.5-0.8 nm.

Fig. 4c shows the band structure of monolayer MoS_2 as an example, in which a direct bandgap of 1.8 eV can be found at K point, in contrast with bulk MoS_2, which has indirect bandgap (1.2 eV). Different from graphene, the energy dispersions of TMDs near the band edges exhibit classic parabolic shape, indicating that carrier transport in TMDs can be described by the effective mass based Schrodinger equation.

2.2. Applications of Beyond-Graphene 2D Crystals

First studies on the field-effect and carrier mobility of MoS_2 thin films were performed on back-gated FETs [3] in which extracted mobilities were in the range of 0.1-10 cm^2/Vs. Kis et al., [19] implemented the first top-gated monolayer-MoS_2 FET with high-k dielectric with ON/OFF current ratio of 10^8 and *SS* down to 74 mV/dec. Liu, et al. demonstrated the first n-type monolayer WSe_2 FET (**Fig. 4d**), which displays large ON/OFF ratios exceeding 10^6 with an electron mobility of 142 $cm^2/V.s$. Using In as contacts, the ON-current is around 210 μA/μm for V_{bg} = 30 V and V_{ds} = 3 V. This high ON current corresponds to a current density of $3.25\times10^7 A/cm^2$, which is about 50-60 times larger than that of nanoscale copper interconnects and only an order magnitude below that of graphene. Recently, biosensors based on MoS_2 FETs has been introduced and demonstrated [20], which provides extremely high sensitivity, easy fabrication and rapid, inexpensive, label-free detection.

Although dangling-bond-free 2D channels can potentially achieve superior interface properties and high mobilities, a gate dielectric material with pristine surfaces, such as h-BN, which is also dangling-bond-free, is one of the prerequisites. This also suggested that judicious combination of 2D crystals may lead to new device/circuit topologies with superior performance. An advanced 2D hybrid material based circuit scheme was first proposed by us in 2013 [21], which combined various 2D crystals such as MoS_2, WSe_2 and graphene (**Fig. 5a**). Moreover, by effectively combining various 2D material based components (both laterally and vertically) including 2D sensors, 2D photovoltaic devices, 2D memories (**Fig. 3i**, [22]), and 2D logic/analog circuits, a completely new generation of 3D ICs could be envisioned (**Fig. 5b**).



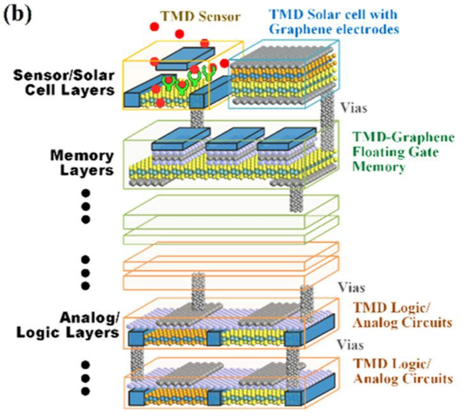


Figure 5. (a) An example of 2D hybrid material based circuits, where graphene electrodes, graphene interconnects, h-BN dielectrics, n-type MoS_2 FETs and p-type WSe_2 FETs are effectively integrated. **(b)** Schematic of an ultimate high-density monolithic 3D IC with sensor/solar cell layers, several memory layers, and logic/analog layers, all based on 2D materials, are interconnected by ultra-short vias.

4. CHALLENGES OF 2D CRYSTALS

Key challenges involved in employing 2D crystals for any application including active/passive devices and circuits include material synthesis, doping schemes and adequate understanding of contacts and interfaces.

4.1. Material Synthesis

The easy and economic method of preparation of monolayer, bilayer, or few-layer graphene/TMDs is the micromechanical exfoliation technique [1], which, however, is only suited for small-scale fabrication for prototyping purposes or for fundamental studies. Hence, beside micromechanical exfoliation, large-scale /wafer-scale synthesis is necessary for high-volume and cost-effective manufacturing of 2D cyrstals. Epitaxial growth of 2D crystals by chemical vapor deposition (CVD) is one of the research focuses. In case of graphene, we have advanced the synthesis of large-area/high-quality monolayer and bilayer graphene on metal substrate via CVD with record mobilities [23]. We have also demonstrated an ultra-fast and deterministic growth of high-quality and large-area bilayer graphene films with controlled stacking order (AB) required for low-power digital electronics [13]. Moreover, precise lithography (sub-10 nm) technologies need to be developed to provide feasibility for some of the above mentioned applications.

4.2. Doping

Doping is one of the essential technologies needed in various applications of 2D materials, such as complementary logic on 2D semiconductors as well as passive devices (such as interconnects and inductors) on graphene. Though various doping techniques have been developed for 2D materials, such as substitution doping [24], edge doping, surface doping and gate electrostatic doping, stable and highly-efficient doping techniques still remain a challenge.

Using Density Functional Theory (DFT), surface doping by noble metal nano-particles such as Ag and Au have been shown to be a reliable doping method for graphene, which can shift the Fermi level by up to ~0.6 eV [12]. While to effectively reduce the resistance of multilayer graphene interconnects, intercalation doping technique is needed, in order to outperform Cu [9]. Various doping schemes for 2D TMDs are currently under investigation.

4.3. Contacts and Interfaces

The parasitic contact resistance between metal electrodes and 2D crystals (including both top and edge contacts) is another key factor in device/circuit applications that demands careful attention to device/contact layout and layer-engineering [25], [26].

Because of the pristine surfaces of 2D materials, the properties of contacts strongly depend on the degree of atomic orbital overlapping at the interfaces as well as the contact geometry and cannot be intuitively predicted by solely considering work function values and Schottky theory. Hence, to evaluate the properties of metal-TMD contacts, Kang et al., developed a computational framework based on DFT [27], [28], which systematically studied the nature of such contacts accounting for the vdW bondings. Moreover, several successful experimental works on TMD transistors have been guided by that framework, including: (1) high-performance monolayer WSe_2 FET with In contacts with record FET mobility (142 $cm^2/V.s$) and record drive current (210 μA/μm) (**Fig. 4d**) [29]; (2) high-performance multilayer MoS_2 FETs with Ti contacts with record low contact resistance (~0.8 kΩ.μm on 15 layers) (**Fig. 4e**) [30]; (3) high-performance 1-5 layer MoS_2 FETs with Mo contacts with low contact resistance (~2 kΩ.μm on 4 layers) and high ON-currents (271 μA/μm) [31].

On the other hand, nature and quality of the interfaces to any 2D crystal can affect its electrical and thermal properties. In fact, interface traps in 2D FETs can arise from the dangling bonds at the gate dielectric side [32] as well as from other surface or substrate impurities. Such traps can greatly influence the electrical characteristics of the FETs including their threshold voltages. In order to understand the nature of such interface traps, we have recently carried out low-frequency (1/f) noise measurements and analysis on bilayer MoS_2 FETs [33]. Our analysis revealed that the 1/f noise peaks in 2D FETs originate from the fact that the decay time of the traps in a 2D layered material is governed by the vdW gaps between the different layers of the 2D material (in case of bilayer or multilayer 2D materials) as well as the surrounding dielectric or traps.

SUMMARY

In this paper, the essential properties of graphene and other beyond-graphene 2D crystals relevant to electronics are reviewed. Some of the interesting and unique applications in the nanoelectronics domain enabled by them, together with their challenges, are also highlighted. Due to the atomically-thin, flexible, bio-compatible, and transparent nature of these 2D materials, along with the wide range of electronic band gaps offered by them, a completely new generation of ultra-low power and ultra-dense green electronic devices and circuits can be envisioned. These properties can also be exploited for building various bio/chemical and gas sensors, energy harvesters, as well as "wearable", "implantable" and "invisible" electronics, which will usher unprecedented opportunities in electronics innovation during the next few decades.

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