Two-dimensional atomic crystals beyond graphene

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ABSTRACT

Carbon-based nanostructures have been the center of intense research and development for more than two decades now. Of these materials, graphene, a two-dimensional (2D) layered material system, has had a significant impact on science and technology over the past decade after monolayers of this material were experimentally isolated in 2004. The recent emergence of other classes of 2D graphene-like layered materials has added yet more exciting dimensions for research in exploring the diverse properties and applications arising from these 2D material systems. For example, hexagonal-BN, a layered material closest in structure to graphene, is an insulator, while $NbSe_2$, a transition metal di-chalcogenide, is metallic and monolayers of other transition metal di-chalcogenides such as MoS_2 are direct band-gap semiconductors. The rich spectrum of properties that 2D layered material systems offer can potentially be engineered on-demand, and creates exciting prospects for using such materials in applications ranging from electronics, sensing, photonics, energy harvesting and flexible electronics over the coming years.

1. INTRODUCTION

Carbon is truly a remarkable material, for not only sustaining life on earth, but for the promising materials properties it encompasses that emerge from its diverse and rich physical structures. The exceptional physical properties of carbon-based nanostructures [1] has stirred interest in considering these materials for nanoelectronics [2,3,4], rf electronics [5,6], interconnects [7], ultra-capacitors [8], biosensors [9], stretchable electronics [10], thermo-electrics [11], photo-voltaics [12,13], optical applications and plasmonics [14,15], as well as nano-electro-mechanical-systems (NEMS) [16,17,18,19,20] given their remarkable mechanical properties [21,22,23].

Amongst the carbon-based systems, graphene, a 2D-layered material, has been widely explored over the past decade since it was isolated from parent graphite in 2004. While graphene has been shown to exhibit exceptional promise for a wide range of applications, its lack of a band-gap poses concerns for its attractiveness in some applications, particularly digital electronics where high ON/OFF ratios are desired. Although one approach for inducing a band-gap in graphene is through quantum confinement by creating graphene nanoribbons (GNRs) [24], the band gaps nonetheless are small (< few hundred meV), and it is challenging to maintain pristine edge

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chirality due to defects that are induced during the nanofabrication of the ribbons. Other techniques to induce band gaps utilize chemical functionalization [25], and the application of an electric field in bilayer graphene [26]. In the latter case, the gaps are still less than 400 meV and the voltages required are well in excess of 100 V which limits its use in low-power devices and circuits. In general, the methods used to induce a band-gap in graphene increase complexity and reduces the mobilities that pristine graphene has to offer.

Recently, layered 2D crystals of other materials similar to graphene have been realized. Such material systems display a diverse array of properties ranging from insulating hexagonal-BN, metallic NbS_2 to semiconducting MoS_2. The ability to engineer the materials properties in these 2D layered materials provides promising prospects for their use in a wide variety of applications. In this paper, an overview of 2D layered nanomaterials will be presented which are poised to play an important role for enabling innovative applications to emerge in electronics, photonics, sensing, energy harnessing, flexible electronics and other related areas [27] over the coming years.

2. Structure, Properties and Device Applications

The knowledge and infrastructure in developing characterization tools and techniques and manipulating monolayer thin graphene layers into novel device architectures has opened possibilities for the exploration of 2D crystals [28] beyond graphene. Such 2D atomic systems, particularly inorganic crystals, appear to have distinct and useful properties complementing those of graphene. These include the transition metal di-chalcogenides, transition metal oxides and other 2D compounds such as insulating hexagonal-BN, Bi_2Te_3 and Bi_2Se_3. These 2D crystals exhibit a diverse spectrum of properties; for example, NbS_2 is metallic while MoS_2 is semiconducting with an intrinsic band gap unlike graphene. The transition metal di-chalcogenides consist of hexagonal layers of metal M atoms sandwiched between two layers of chalcogen atoms X with stoichiometry MX_2 as shown in Fig. 1 for the case of MoS_2 (M = Mo, X = S). As with transition metal di-chalcogenides in general, the interatomic binding in MoS_2 is strong arising from the covalent in-plane bonding but the subsequent layers interact through the weaker van der Waals interlayer forces.

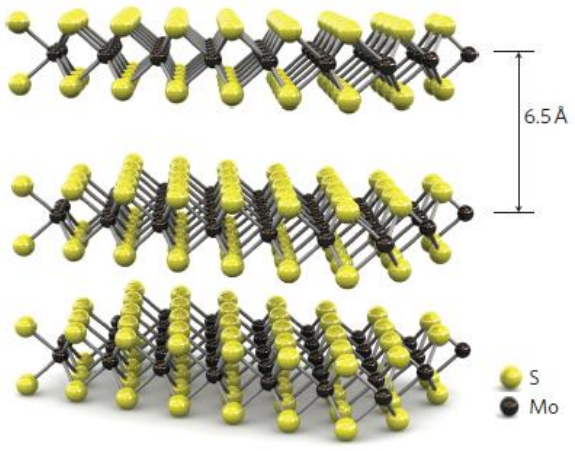

Figure 1. Crystalline structure of layered MoS_2 where the Mo atom is sandwiched between the S atoms. The interlayer bonding occurs via the weak van der Waals interaction. Unlike graphene, monolayers of MoS_2 exhibit a large band-gap ~ 1.8eV and it is also a direct-band gap semiconductor.

Depending on the combination of the transition metal atom and the chalcogen (S, Se or Te), a wide variety of transition metal di-chalcogenides are possible, as illustrated in Fig. 2, each offering a unique set of properties. The coordination and oxidation state of the metal atoms determines whether the transition metal di-chalcogenide will be metallic, semi metallic or semiconducting. Superconductivity and charge density wave effects have also been observed in some transition metal di-chalcogenides. Besides the transition metal di-chalcogenides, the chalcogenides of group III (GaSe, GaTe, InSe), group IV (GeS, GeSe, SnS, SnSe, etc.) and group V (Bi_2Se_3, Bi_2Te_3) also show a graphite like layered structure and offer promise in electronics, photonics and energy harvesting.

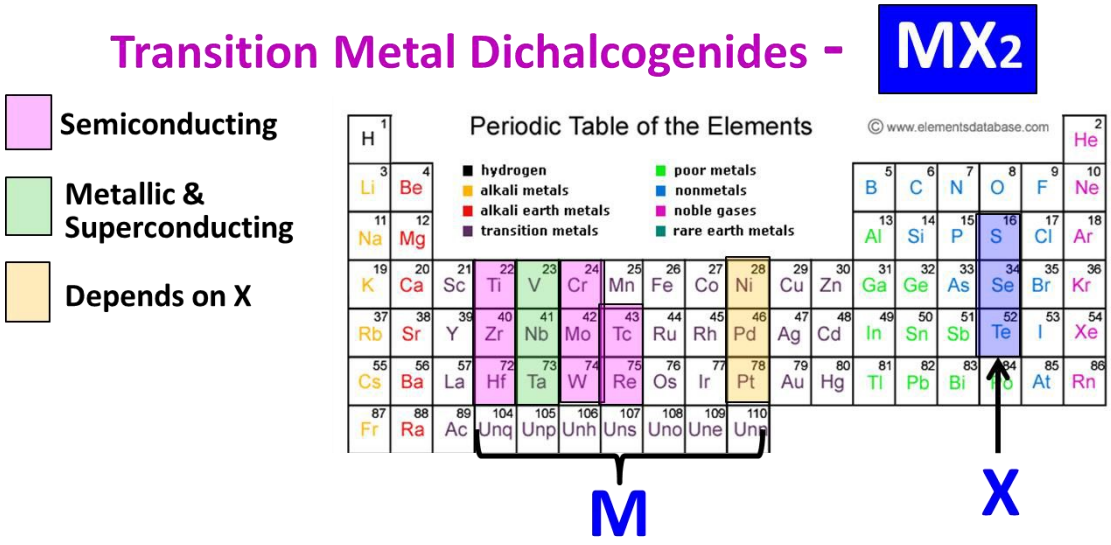

Figure 2. The transition metal di-chalcogenides are an example of 2D layered materials. Depending on the combination of the transition metal M, and the chalcogen atom X (S, Se, Te), a wide range of properties can arise.

The two-dimensional exfoliated versions of transition metal di-chalcogenides such as MoS_2, $MoSe_2$, WS_2 and WSe_2 indicates that they have an inherent and appreciable band gap that can extend the possibilities for such materials in electronics and photonics beyond that of graphene. As an example, one of the most important applications of semiconductors is for transistors in digital electronics which continue to be driven by miniaturization and Moore's Law. Recent reports have demonstrated non-graphene 2D atomic layers integrated into devices which exhibit exceptional performance; for example top-gated transistors derived from 2D monolayers of MoS_2 with high k HfO_2 dielectrics showed ON/OFF ratios many orders of magnitude larger than the best graphene transistors at room temperature, with comparable mobilities [29].

In general, 2D materials can potentially replace conventional semiconductors for ultra-scaled thin-body transistor applications given their pristine interfaces that are free of dangling bonds and where transport and scattering is confined to the plane of the material, to enable low-power and low-dissipation devices. Such semiconducting 2D layered materials can be combined with 2D dielectrics, such as hexagonal boron nitride (h-BN) which appears to be very promising and most similar in structure to graphene. This would allow for the design of

metal/dielectric/semiconductor interfaces and other device architectures, such as heterostructure-FETs or tunnel-FET devices [30] which are formed by stacking 2D semiconductors as the channel, 2D insulator layers as the dielectric, and 2D metallic layers (graphene, $TaSe_2$, TaS_2, etc.) as gates and interconnects to enable energy-efficient transistor devices for digital and analog circuit applications. In the past, FETs from 2D WSe_2 were also demonstrated which exhibited mobility up to 500 $cm^2\ V^{-1}\ s^{-1}$, comparable with single crystal Si FETS, with ON/OFF ratios of 10^4 at cryogenic temperatures[31].

By patterning electrodes on a single layer of MoS_2, multiple transistor devices have been integrated to enable digital circuits, such as inverters and NOR logic gates [32]. Recently complex integrated circuits built on bilayer MoS_2 were also demonstrated which included an inverter circuit and a logic NAND gate to achieve static random access memory (SRAM) operation, as well as a five-stage ring oscillator [33]. In future research, such principles can be extended to other classes of 2D materials for memory devices; for example, layers can be formed by charge trapping using heterostructured stacks or 2D-magnetic materials such as $FeSe_2$ and $CoSe_2$.

Given the tunable, direct band gaps of some of the 2D transition metal di-chalcogenides and their relative earth abundance, they appear to be a promising choice for solar cells or light-absorbing components, photo detectors, in addition to light-emitting devices. Also, given the thinness of these materials, the devices could be made transparent, light and flexible, and could provide an alternative choice to organic semiconductors, given that organic materials degrade at ambient conditions. For flexible and transparent optoelectronics applications such as displays and wearable electronics, materials such as conductors, semiconductors, optical absorbers, light emitters and dielectrics are desired. Semiconducting 2D transition metal di-chalcogenides, combined with other 2D materials such as conducting graphene and insulating BN, can enable 2D electronic circuits to be fabricated on flexible substrates.

In addition, the mechanical properties of MoS_2 also appear to be very attractive. It has been found to be 30 times as strong as steel and can tolerate deformations of up to 11% before breaking [34]. Such mechanical properties makes MoS_2 one of the strongest semiconducting materials and hence very attractive for flexible electronics applications.

3. Summary

The rich spectrum of properties that 2D layered material systems offer can potentially be engineered on-demand, and creates exciting prospects for using such systems in applications ranging from electronics, sensing, photonics, energy harvesting and flexible electronics in the coming years.

Although the idea of separating individual layers from 2D layered solids is straightforward, the challenges in obtaining large single crystal domains, chemical modification, characterization and modeling of such materials, transfer of these layers onto appropriate substrates, manipulating these and fabricating devices are significant. The importance of preparing mono- bi- and few-atomic layer materials with control and the ability to control chemical doping, carrier density and contact resistance, modification and lattice manipulation of atomic layers to tailor electronic, optical and magnetic properties will be of paramount importance for realistic applications to

emerge. The lessons learned from graphene research should thus greatly help accelerate research for successfully addressing the scientific and technological challenges in 2D layered materials research. The field of 2D-layered materials beyond graphene is poised to open up new avenues for research and exploration in the coming years in a number of scientifically-rich and technologically important areas in the future.

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