Van der Waals Solids: Properties and Device Applications

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ABSTRACT

Recently, layered 2D crystals of other materials similar to graphene have been realized which include insulating hexagonal-BN (band gap ~5.5 eV) and transition metal di-chalcogenides which display properties ranging from semiconducting, superconducting, metallic to insulating. The device applications of such van der Waals solids also show promising characteristics where MoS_2 transistors have been formed on flexible and transparent substrates, and transistors derived from 2D monolayers of MoS_2 show ON/OFF ratios many orders of magnitude larger than the best graphene transistors. In this paper, an overview of the novel properties of these layered 2D nanomaterials is provided that can enable their device applications in electronics, photonics, sensors and other related applications.

1. INTRODUCTION

Similar to its nanocarbon derivatives such as carbon nanotubes and fullerenes, it is now widely recognized that graphene, the thinnest material physically in existence, has shown exceptional electronic, thermal, mechanical and optical properties [1]. Graphene consists of a single sheet of carbon atoms arranged in a 2D-honeycomb crystal lattice and has often been coined the "miracle material". 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) [2], the band gaps nonetheless are small (< few hundred meV), and it is challenging to maintain pristine edge chirality due to defects that are induced during the nanofabrication of the ribbons. Other techniques to induce band gaps utilize chemical functionalization [3], and the application of an electric field in bilayer graphene [4]. 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. Owing to the great success of graphene research, the question of whether 2D atomic layers from other materials can be isolated and exploited for fundamental study and applications has become very relevant.

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

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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 [5,6] over the coming years.

2. PROPERTIES AND DEVICE APPLICATIONS

Two-dimensional (2D) layered materials beyond graphene exhibit interesting and exciting properties. There are already reports suggesting that materials such as hexagonal boron nitride (h-BN), di-chalcogenides, tertiary compounds of carbo-nitrides, and complex oxides such as clays and zeolites can be exfoliated and isolated as stable single atomic layers [7,8]. Given the wide range of compositions of 2D-layered materials beyond graphene, it is not surprising that they offer a rich spectrum of properties. For example, h-BN, a layered material closest in structure to graphene, is an insulator, while monolayers of some transition metal di-chalcogenides such as MoS_2 and WS_2 are direct band-gap semiconductors. The rich variety of properties that 2D layered material systems offer, can potentially be engineered on-demand, and they create exciting prospects for device and technological applications such as in electronics, sensing, photonics, flexible electronics, energy harvesting and storage, thermal management, mechanical structures, catalysis, bio-engineering, and gas adsorption, in the future.

In one family of 2D layered materials, the transition metal dichalcogenides, 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.

Quantum confinement effects turn some of these 2D layered materials such as MoS_2, WS_2, WSe_2, $MoSe_2$ and $MoTe_2$ from indirect-band gap semiconductors to direct band gap semiconductors in going from the bulk to monolayers [9,10]. For example, MoS_2 has an indirect band gap in the bulk of ~1.2 eV which transforms gradually to a direct band gap of ~1.8 eV in single-layer samples. This is in contrast to pristine graphene with a band gap of ~0 eV and few-layered h-BN with a band gap of ~5.5 eV. The existence of an intrinsic band gap in these layered materials implies possible applications in electronics and photonics, as promising compliments to graphene and h-BN. This inherent band gap, coupled with the potential for atomically-smooth, pristine interfaces, can also potentially enable low-power and low-dissipation devices that have the potential to one day replace conventional semiconductors for ultra-scaled, thin-body transistors as one example. Other layered structures such as hexagonal boron nitride (h-BN) are attractive candidates for atomically-thin dielectrics, allowing for the design of various device architectures with metal/dielectric/semiconductor interfaces. Heterostructure field-effect-transistors (FETs) or tunneling-FET devices formed by stacking 2D semiconductors as the channel, 2D insulator layers as the dielectric, and 2D metallic layers (graphene, $TaSe_2$, etc.) as gates and interconnects can enable energy-efficient transistor devices for digital and analog circuit applications.

Besides the observed band gap transition from indirect-to-direct gap, it is also interesting to note that the band gaps in some bilayer MX_2 materials, where M is a transition metal and X is a group VI element (S, Se, Te) can be tuned through the application of an external electric field. For example, density functional theory calculations conducted on bilayer MoS_2, WS_2, $MoSe_2$, and $MoTe_2$ show that that their band gaps undergo a gradual semiconducting-to-metallic transition through the application of an external electric field oriented orthogonal to the plane of the layers. Other quantum scale effects, such as superconductivity and charge density wave effects, are also manifested at low temperatures in some 2D layered materials such as $NbSe_2$, TaS_2 and Cu-intercalated $TiSe_2$.

In addition, the mechanical properties of some of these 2D layered materials, in particular MoS_2, also appear to be very attractive. It has been found that MoS2 is 30 times as strong as steel and has the ability to accommodate strains well in excess of 11% without showing signs of mechanical degradation [11]. Such mechanical properties makes MoS_2 one of the strongest 2D semiconducting materials known. Other interesting properties include the strong influence mechanical strain has on the band gap of some 2D layered semiconducting materials [12,13,14,15]. In general, strain in semiconductors modifies the lattice constant and crystal symmetry, causing the energy bands to shift which in turn induces changes in the relative effective masses. The optical band gap is found to decrease at a rate of ~ 45 meV/% and ~ 120 meV/% of strain for monolayer and bilayer MoS_2, respectively. These early reports clearly suggest the potential for strain engineering to modify band gaps, carrier effective masses and mobilities, in order to yield a number of interesting tunable devices [16].

Two-dimensional layered semiconductor materials are also very attractive for optical applications since they can lead to strong light emission, as demonstrated in recent photoluminescence experiments. In depth photoluminescence measurements in these 2D layered materials will allow for the optimization of quantum yield, which can have a pay-off for photo-sensing applications. The direct band-gaps of monolayers of some of the 2D layered materials and the ability for band-gap engineering through compositional variations will allow ultra-wide wavelength tunability from the THz, through the IR to the UV. Depending on the choice of material, compositional variations, and layer thickness, the optical absorbance in such materials can be engineered, making them particularly attractive for photo-detectors and photo-voltaic applications.

Due to the unique combination of high strength, excellent out-of-plane flexibility, low-broadband absorption and outstanding and diverse electronic properties, some of the 2D-layered materials can be envisioned as promising candidates for conformal conductors, semiconductors and dielectrics in flexible and transparent electronics applications. Two-dimensional layered materials can thus enable potential applications in flexible and transparent electronics, such as paper-like displays and wearable electronics that need to sustain large deformation while maintaining their intended functionalities.

While isolating single layers of 2D layered crystals through mechanical exfoliation has proven to be the natural choice for quickly unveiling their intriguing properties and exploring their device possibilities, there is an urgent need to explore novel synthesis techniques that can provide a path for scalable manufacturing. The challenges of synthesizing 2D layered materials with atomically smooth interfaces, particularly using scalable techniques, is thus an important area of research for fully exploiting the promise of these materials. For the large scale synthesis

of such nanomaterials, solvent based exfoliation methods have been demonstrated recently which yield mono and few layer nanosheets. Such materials have proven valuable in forming hybrid and composite materials, potentially in a scalable manner. Another technique for forming thin layers of transition metal dichalcogenides is ion intercalation. The intercalation of transition metal dichalcogenides by ionic species such as Li allows the layers to be exfoliated in liquid [17]. It is not surprising that such solution-based techniques result in material that contains more structural imperfections compared to other approaches such as vapor-based techniques.

Non-solution based approaches such as chemical or physical vapor deposition, as well as atomic layer deposition, offer more control on the physical properties, which is important when considering such materials for electronics, photonics or magnetic device applications where defect-free materials are highly desirable. Unlike the vapor-based growth techniques for graphene and carbon nanotubes which require catalysts for growth, the synthesis of 2D chalcogenide materials is not a catalytic process. One way for synthesizing MoS_2 is to expose deposited Mo metal to a sulphur vapor by heating a solid sulphur source to temperatures in excess of 700ºC [18]. The thickness of the MoS_2 grown appears to be dictated by the thickness of the pre-deposited Mo metal. Another interesting report that has emerged recently presents a synthetic technique that can enable the growth of centimeter-scale, uniform, high-quality MoS_2 films with controlled layer number [19]. These reports of some 2D layered materials are still relatively early in development but hold promise for the production of uniform, large-area sheets of transition metal dichalcogenides and other 2D layered materials.

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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