REVIEW ARTICLE

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Van der Waals Heterostructures for Device Applications

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ABSTRACT

Advent of two-dimensional (2D) materials owing to their extraordinary properties can revolutionize the field of nano-electronics. Experimental advancements have now made it possible to stack different 2D layers on top of each other to form a single system. Due to van der Waals bonding between the layers, the properties of each layer are not perturbed much. It helps in generating new functionalities for nano-electronics applications. The present paper focuses on the application of van der Waals heterostructure.

Keywords: Two-dimensional materials, van der Waals heterostructure, synthesis, applications

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INTRODUCTION

Mermin-Wagner theorem states that due to thermal fluctuation, the existence of purely two-dimensional materials is questionable.[1] Despite the belief established in mid 19th century, in the University of Manchester, UK, in 2004 using the mechanical exfoliation method Konstantin Novoselov and Andre Geim isolated one atom thick layer of graphite,[2] known as 'graphene'. They were awarded the prestigious Nobel prize in Physics for their breakthrough discovery in 2010. Soon after discovering graphene and its alluring properties, many other 2D materials, e.g., hexagonal boron nitride (h-BN), was invented in labs.[3] Indeed, in the past 16 years, many 2D materials with metallic (MXene[4]), semiconducting ($MoS_{2,}$[5] phosphorene[6]), insulating band-gap (h-BN[7]), are added to the family of two-dimensional materials.[8] Ferromagnetic, e.g. $CrI_{3,}$[9] superconducting, e.g., $RbSe_2$,[10] semi-metallic e.g. Si, Ge[11] are also discovered.

Mostly, the properties of these 2D layers are quite different from their bulk counterparts. For example, MoS_2 is a direct band-gap semiconductor,[12] whereas bulk Mo is an indirect band-gap semiconductor. Graphite is an insulator, whereas graphene is semimetal. Fascinated by the intriguing properties of these 2D layers, in 2013, Andre Geim et al. made the first van der Waals heterostructure by stacking the different types of 2D layers on top of each other.[13] The successful synthesis of such graphite-type structure with weak van der Waals bonding and atomically sharp interface further opened the possibility to create heterostructure similar to the ordinary three-dimensional materials for nano-electronics purposes.

Strong in-plane and weak out-of-plane bonding between different layers guarantee that the properties of individual layers will not be perturbed much and sometimes helps in bypassing the weakness of individual layers. For example, a small band-gap can be opened when two layers of graphene are stacked together.[14] A small semiconducting gap can be created in an otherwise insulating h-BN when placed over graphene. A huge number of possible heterostructures can be formed with very few numbers of 2D layers. For example, with 10 different 2D materials, we can form $10^{\mathbf{10}}$ different 10 layer heterostructures.[15] Indeed amazing!!

The stacking order of layers is important, and these heterostructures' properties may depend critically on the order in which layers are placed on top of each other.[16] It provides a playground to exploit the properties of these layers to create specific functionality for device applications. Many applications of vdWh are demonstrated at the lab level, and a variety of applications are also suggested theoretically. In fact, due to fabrication process complexity, the vdWh applications were found with much theoretical attention.

In this review, we briefly discuss the synthesis and electronic, optical, and mechanical properties of the vdWh, many good quality reviews on the synthesis methods are available.[17-19] Our main focus is on applying vdWh, in particular, theoretically predicted, for nano-electronics, optoelectronics and thermoelectrics.

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SYNTHESIS OF 2D HETEROSTRUCTURES

The synthesis of heterostructure also uses the two approaches to synthesize two-dimensional materials: top-down mechanical transfer and bottom-up *in situ* growth methods.

1. Mechanical Transfer: Due to van der Waals bonding, except few, e.g., MXene, most 2D materials can be exfoliated mechanically from their bulk state. Different 2D layers are mechanically or chemically cleaved to fabricate the heterostructure and then, with the utmost care, stacked on top of each other after accurately aligning the two 2D layers under co-lamination. Using this method, high-quality heterostructures of various 2D materials can be prepared at a relatively low cost. Several vdWh are synthesized in labs, e.g. h-BN/Graphene,[20] $MoS_2/MoSe_2$,[21] WS_2/MoS_2,[22] $WS_2/MoSe_2$.[23] Although, the mechanical stacking method is the simplest way to construct 2D vertical heterostructures. However, the quality of the interface may not be good as the properties of these heterostructures can get affected by the trapping of solvents or chemicals present during the reaction.[24]
2. Chemical vapour deposition (CVD): Physical epitaxy or CVD method, a bottom-up approach, is another effective method to synthesize a large area of 2D materials and their heterostructure in a definite stacking ordering. In this method, a 2D layer is taken as a substrate which can be prepared by any top-down or bottom-up approach. Then, the layer of different 2D material is deposited over the existing 2D layer by CVD. Although this process is more complex and expensive than most top-down methods; however, it is highly scalable, and the quality of the films produced approaches is mostly free of the problem faced during the mechanical transfer method, e.g., wrinkles, bubbles, and trapping of foreign particles, etc. The graphene/h-BN,[25] MoS_2/WSe_2,[26] Sb_2Te_3/Bi_2Te,[27] etc vdWh are grown using this method. Using the CVD method, nanosized layers can be grown.

The 2D materials and their heterostructures are also grown using other methods like the solvothermal method,[28] magnetron sputtering,[29] molecular beam epitaxy,[30] pulsed laser deposition,[31] metalorganic chemical vapor deposition.[32] Although the lattice match limitation constrains the fabrication of these heterostructures. Significant lattice mismatch gives rise to various types of defects and can deteriorate the property of heterostructure.

PROPERTIES OF VAN DER WAALS HETEROSTRUCTURE

Ranging from insulator to superconductor, now the 2D materials with different electronic properties are available.

Depending upon the 2D materials used to fabricate the vdWh, the properties of these stacks can be the combination of properties of individual layers or can be very different from the properties of individual layers. Also, vdWh are very different from the 3D heterostructures of standard semiconductors. Here, each layer can perform as separate bulk material. Moreover, due to the structural relaxation, charge transfer and proximity effect at the interface given to the properties may be quite different from those of the individual layer. An electric field at the interface may get induced. A moiré pattern may form in the graphene/h-BN interface it results in the formation of secondary Dirac points.[33,34] Band-gap may open in electronic structure as observed at h-BN/Graphene vdWh.[35] Spin-orbit interaction can be evoked in graphene and transition metal dichalcogenides (TMDCs).[36] The optical properties of TMDC layers can be enhanced by heterostructure them.[37]

DEVICES WITH VAN DER WAALS HETEROSTRUCTURE

The two-dimensional family consists of material from an insulator to a conductor, which is extremely helpful for manufacturing new devices for various functionalities. Van der Waals heterostructure provides the following advantages over the 3D devices: small size, flexibility, high performance, and low power consumption. New devices based on heterostructure are developed in the past few years.

Heterostructure Based Transistor

A new generation of vertical field-effect transistors was designed and fabricated by vertical integration of heterostructure. In vertical field effect transistor, two-dimensional semiconductors, transition metal dichalcogenides, and graphene are used as channel and metal, forming Schottky-barrier of the heterostructure. In conventional planar graphene, the Schottky barrier height can not result in a large on/off ratio. However, in graphene/semiconductor, an applied gate voltage effectively modulates the work function of graphene and, therefore, the Schottky barrier height across the graphene/semiconductor interface results in large ON/OFF. Vertical field-effect transistor has ultra-short channel length, obtained by the thickness of semiconducting film rather than lithographic resolution. Because of inherently short channels, the vertical transistor has a high on-current density. On the flip side vertical field effect transistor has dozen times the off-current state than the planner field-effect transistor., which originates huge static power consumption.[38]

Photoelectric Device based on Van Der Waals heterostructure

Due to the direct semiconducting band gap and their strong optical absorbance, the two-dimensional semiconductor (especially transition metal diachalcogenides) finds it interesting to apply photoelectric devices. Due to the strong involvement of transition metal d-orbitals in transition metal dichalcogenides, the localized character of electronic bands leads to singularities in the density of states, which results in enhanced photoabsorption in the visible range.[39] A wellordered investigation and careful study were performed on WSe_2 and MoS_2 heterostructure, which form a 2D p-n junction. In single-layer WSe_2 and MoS_2 heterostructure, spatially direct absorption has been observed with string interlayer coupling of charge carriers.[40] Several combinations of heterostructure have been fabricated for the Photo detector based on transition metal dichalcogenides and black phosphorus. MoS_2/WSe_2,[41] black phosphorus/ MoS_2,[42] is often used. GaTe/MoS_2 heterostructure has a high photo-detecting capability.[43]

Biosensor

Two-dimensional materials are suitable for biosensing devices due to their ultra-sensitivity to environmental changes.[44] It can also be used in DNA differentiation ability. In MoS_2 it is also sensitive to the pressure of moisture and oxygen, which restrict their application in aqueous solutions. Heterostructuring can be used to increase stability and sensitivity. A study demonstrates the usefulness of graphene/ MoS_2 heterostructure for label-free selective detection of DNA hybridization by the photoluminescence intensity changing of MoS_2.[45] The top layer of graphene helps in avoiding the contact between MoS_2 layer and moisture. Also, it works as a host of the DNA owing to its biocompatibility. The detection ability of graphene/MoS_2 sensor is almost 1 atto mole (10^{-18} mole) with few minutes of fast response time, displaying the potential of ultrasensitive DNA detection using two-dimensional heterostructure.

Solar Cells

A solar cell comprises a junction of two materials with opposite charge carriers, allowing efficient carriers to separate the photo-generated electron-hole pairs at the interface to incorporate the photovoltaic effect. These interfaces can easily be fabricated by Schottky or p-n junction in two-dimensional heterojunctions. The main question was if it is possible to achieve enough solar energy conversion within such a thin layer.[46] To answer that question, Bernardi and his team had studied the photovoltaic effect of two-dimensional heterojunction. Theoretically, they also studied the Schottky barrier between MoS_2/WS_2 stacking heterostructure. Their study shows that even the atomically thin active layer can produce power conversion efficiencies close to 1% or a power density up to 2.5 MW/kg. A two-dimensional heterostructure solar cell is more efficient than an existing solar cell.[47]

Thermoelectric Devices

The thermal conduction restricts the dissipation of heat in two-dimensional heterostructure in the vertical direction. The temperature gradient can be fabricated in few-layer two-dimensional materials or vertical heterostructure. Researches have been done in this field, and it was found that on graphene/h-BN/graphene heterostructure,[48] applies a temperature gradient on top and bottom graphene layers and measures the thermoelectric voltage, the heterostructure display a Seebeck coefficient of about -99μV/K. With thermal and electrical conductance, the power factor (S^2G) of $1.51*10^{-15}$ W/K^2 and thermoelectric figure of merit=$1.05*10^{-6}$ can be derived even though the thermoelectric energy conversion efficiency is low in this device. But it is anticipated that progress can be made shortly.[49-50]

Light Harvesting and Detection Devices

The restacking and exfoliation of 2D material opens up a flexible path-way towards designing and manufacturing a new age of optoelectronic devices. Due to graphene's broadband and ultrafast response, there had been significant interest in graphene-based photo-detection devices, despite the gapless nature of graphene. Unfortunately, due to relatively low absorbance of a single layer of graphene restrict its photo-responsivity, but this can be improved by van der Waals integration. In contrast, many monolayer TMDs have intrinsic band gaps and also strong absorption. These properties make TMDs attractive building blocks for making van der Waals heterostructure devices for high-speed and broadband detection with high efficiency and photoconductive gain.

To manufacture tunable photo-detectors, three basic types of van der Waals heterostructure have been examined. The first device, vertical graphene-TMD-graphene heterostructure, has been manufactured as a broad-area photodiode for highly effective phonon harvesting and photocurrent generation.[51]

Light Emitting Devices

In addition to light harvesting and detection, van der Waals heterostructure has also been explored for electrically induced light emission. Single-layer TMDs, like MoS_2 and WSe_2 have been used to make laterally defined light emitting p-n diodes. But light emission from the lateral p-n junction device is restricted by the 1D junction interface. Thus vertically stacked van der Waals heterostructure is more favorable since the photoactive area is defined by the large 2D overlapping area. Like photo-detection, electroluminescence was observed in single-layer MoS_2p-type silicon and MoS_2-WSe_2 vertical heterostructure. However, current injection in such heterostructure is still restricted by lateral contacts and lateral carrier transport owing to the depletion of the ultrathin 2D semiconductors. Light emission is typically localized to one rough edge of the junction in place of the entire overlapping area. It is essential to design the van der Waals heterostructure devices with vertical current injection for making a broad-area LED using van der Waals heterostructure.[52]

Energy Storage Device

Since electronic conductivity, the number of intercalation sites, and stability during extended cycling are essential for manufacturing effective and high-performance energy storage devices. Although individual 2D materials like graphene display some of the needed properties, none can offer all the properties required to maximize energy density, power density, and cycle life. It is believed and predicted that stacking different 2D materials into heterostructure could open up a possibility to construct electrodes that would combine the advantages while discarding the shortcomings of the individual building blocks.[53]

Nanogenerator

Obtaining energy from the environment is the focus of the scientific community for the past few years. Graphene nanogenerator has been demonstrated by Huikai Zhong [], which is based on moving Van der Waals heterostructure made between graphene and 2D graphene oxide. This nanogenerator can convert mechanical energy into electricity with a Voltage output of around 10 Mv. 2D Boron nitride was also demonstrated to be an effective material for moving van der Waals heterostructure nanogenerator. The exploration of nanogenerators will be important for better understanding the origin of the flow-induced potential in nanomaterials.[54]

CONCLUSIONS

The 2D Van der Waals heterostructure (VDWH) are interesting for their device applications and understand the fundamental physics and chemistry behind it. Using the theoretical tools, e.g., density-functional theory calculations, their heterostructures are extensively studied. However, experimental studies are limited due to various constraints, controlled synthesis restriction, and lattice mismatch to avoid defect creation which can deteriorate the properties of these heterostructures. Being two-dimensional, these are highly applicable for various device applications, and many times the figures of merit of these devices are comparable to the three-dimensional devices. Indeed, 2D VDWH is an open field of research as many applications are yet to be explored, e.g., spintronic, memory devices etc., and there is much scope for improvement in the already synthesized VDWH devices.

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