Applications of MoS_2 as a Two-Dimensional Material Beyond Graphene

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In 2004 the emergence of graphene sparked interest in studying its unique properties as a possible replacement for silicon in modern electronics. However, due to the absence of a band gap graphene it no longer a candidate for applications to field effect transistors (FETs). However, in graphene's place several materials emerged. Among these materials is molybdenum disulfide (MoS_2) and other transition metal dichalcogenides (TMDs). MoS_2 has been the subject of much research in the past few years and it has been studied for several applications, here application to FETs is of focus.

I. INTRODUCTION

By the end of the last century microelectronics had revolutionized the world, the majority of which are silicon-based devices. Today millions of these silicon-based devices are used in many common electronic devices and have become unavoidable throughout everyday life. Though the first field-effect device was patented in 1925, it was not until 1960 that the first metal-oxide semiconductor field effect transistor was demonstrated [25, 33, 45]. A later, devices were being made with several thousand components on a single chip. From there the progress increased at a rapid rate, a process now known as Moore's law, predicting that for each new generation of memory chip and microprocessor unit, the device size would be reduced by 33%, the chip size would be increased by 50%, and the number of components on a chip would quadruple every three years [38, 45]. This has been proven to be true, and up until recently had shown no signs of stopping. Many times the material limitations were overcome by advances in technology that were seemingly insurmountable and effectively had placed a cap on Moore's law, which ultimately led to new techniques and even more pristine silicon-based materials. However, the limit to oxide thickness has finally placed a maximum on the growth of the silicon-based semiconductor device industy [45]. This impending limit caused many to look for solutions that involved the use of SiO_2 devices and also alternatives to silicon. The result of the latter has given way to a breadth of literature and research that was unforseen a decade ago. The search for alternatives to silicon resulted in research into many new, nontraditional materials. Several notable examples are organic conductors and carbon nanotubes [3, 10]. Arguably one of the most interesting nontraditional materials to come out of such research was graphene.

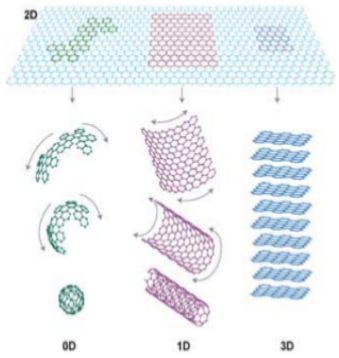

FIG. 1. Graphene can be envisioned in several dimensions. 0-dimensional buckyballs, 1-dimensional nanotubes, or 3-dimensional graphite [42].

II. GRAPHENE AS A NEW TWO-DIMENSIONAL MATERIAL

In 1985, with the discovery of fullerenes, the amount of known carbon allotropes increased [28, 35]. Fullerenes suggested the existence of a one-dimensional form of carbon, known as carbon nanotubes, which were first demonstrated in 1991 [23]. Despite several theoretical studies involving the use of a single layer of graphite, it was not until 2004 that the first monolayer graphene sheet was isolated [39, 40]. In the most basic sense, graphene is simply a single layer of carbon atoms densely packed into a honeycomb lattice. It is used to describe properties of several carbon-based materials (graphite, fullerenes, nanotubes, etc..., see Fig.1) [11, 39, 46]. This was significant because scientists had tried for many years to synthesize monolayers of graphite, though only succeeding in obtaining materials around 10 layers thick [35].

A. Properties of Graphene

To date, graphene's properties have been the focus of much research, both theoretical and experimental. Graphene has many unique properties that have paved the way for new subfields in condensed matter physics (i.e. 'relativistic' condensed matter physics). These

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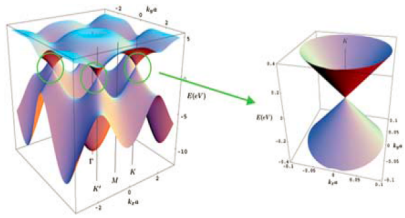

FIG. 2. 3-D representation of the electronic band structure of graphene. The right side shows an enlarged view near the Fermi level in one k point [35].

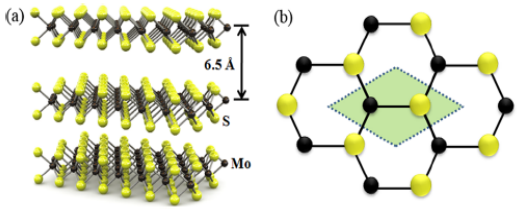

FIG. 3. (a) The atomic structure of layered MoS_2. Different sheets are composed of three atomic layers S-Mo-S, where Mo and S are covalently bonded [43, 57]. (b) Top view of the honeycomb lattice [57].

properties are primarily a result of its low dimensionality and its band structure that allows electrons to mimic relativistic particles [20]. This newly discovered phenomenon has allowed for the study of relativistic effects in condensed matter experiements. This includes the appearance of the atypical quantum Hall effect and the confirmation of other relativistic phonomena [41, 53, 59]. However, it is worth noting that this peculiar band structure can be modified by stacking three or more layers of graphene [35].

For applications to electronics, a material's band gap is of interest. In graphne, however, the conduction and valence bands touch at a single point as shown in Fig.2 [35, 50]. As a result, graphene has no band gap (small band gaps of a few hundred MeV can be introduced in bilayer graphene) [57]. The absence of a band gap is also interesting in the context of the material's optical properties and those implications. The absence of a band gap allows for the absorption of light over a large range of the electromagnetic spectrum, ranging from infrared ($< 1.65\,\text{eV}$) to ultraviolet ($> 3.2\,\text{eV}$), giving potential for electronic-photonic device applications [13, 51, 55].

Graphene's mechanical properties have been of much interest over the last decade. Graphene has a Young's modulus of $\sim 1000\,\text{GPa}$ with a breaking stength that is 13% of that [1, 4]. It can also sustain elastic deformations of 20% due to its two-dimensional nature and it has high pliability [35]. Mechanically, graphene is an exciting material due to the fact it lies in the extreme ranges of some metrics, considering its size and dimensionality.

The mobility in graphene is another property that initially made the material so appealing (and still quite appealing to some degree). Graphene's mobility is about 1000 times that of silicon's [1, 9]. The outstanding crystal quality in large scale (a few microns) is the major contributing factor. Without many defects or imperfections, the electrons can travel long distances, as much as several micrometers, without being scattered even on rough substrates [12, 35]. The average electron mobility obtained in graphene varies depending on temperature, but the graphene's mobility is commonly quoted at around $15,000\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature [42]. Though graphene exhibits a high mobility, the main limiting factor in integration is the lack of band gap in material. This fact does not allow for integration and use in digital transistors. As a result, researchers, though focused still on the potential applications to other devices based upon its optical and mechanical properties, have moved on to other two-dimensional materials for integration in digital circuits. Ongoing research also includes graphene-like nano materials like silicene and germanene, which are the silicon and germanium-based versions of graphene found to show properties that are similar to graphene [6, 49]. These two-dimensional materials are becoming increasingly attractive for a wide-range of applications due to their distinct properties.

III. TRANSITION METAL DICHALCOGENIDES

Graphene is being studied for its unique porperties, however, many other two-dimensional materials are known. Some of the two-dimensional materials being studied in addition to graphene are known as transition metal dichalcogenides (TMDs) [36, 54]. TMDs consist of hexagonal layers of metal atoms (M) in between two layers of chalcogen atoms (X), such that the stoichiometry of the material is MX_2 [57]. The material is dependent on the combination of transition metal, typically one of: Mo, W, Nb, Re, Ni, or V and chalcogen, plus typically one of: S, Se, or Te [54]. These materials are commonly stacked together which involves van der Waals interactions between adjacent sheets and covalent bonding within each individual sheet (see Fig.3) [57]. There are wide variety of properties exhibited by these structures, which include insulator or metal. In addition, they can also display some interesting properties like the topological insulator effect, superconductivity, and thermoelectricity [17, 29, 56, 58].

A. Properties of MoS_2

As discussed in Sec. II A, pristine graphene has no band gap. Though it is possible introduce a band gap in bilayer graphene and graphene nanoribbions, the appeal of many TMDs is that they have direct band gaps which make ideal candidates for electronic material applications [57]. One such example of a semiconducting TMD is MoS_2 (molybdenum disulphide). TMDs, and more specifically MoS_2 and the properties it exhibits, have been studided to some extent for several decades with electrical measurements dating back to the 1960s [14, 16]. However, as of late there has been renewed interest in several TMDs are their potential applications.

Like graphene, and many other two-dimensional materials, MoS_2 has a Young's modulus that is comparable to steel ($\sim 205\,\text{GPa}$) [47]. The Young's modulus of single-layer MoS_2 is $\sim 270\,\text{GPa}$. The Young's modulus of bulk MoS_2 is $\sim 240\,\text{GPa}$. The fact that monolayer MoS_2 has a higher Young's modulus than its bulk material counterpart is thought to be mostly due to defects in the material, interlayer sliding or the absence of stacking faults in monolayer samples [30]. In a further study it was found that the Young's modulus of multilayer MoS_2 ranging in thickness from 5 to 25 layers was $330 \pm 70\,\text{GPa}$ [8]. In addition, both single and bilayer MoS_2 have a breaking strength of about 6% and 11% of their Young's modulus, respectively [4]. This is an indication that MoS_2 is quite flexible compared to other commonly used engineering materials (stainless steel $\sim$ 0.4%, kevlar $\sim$ 2.6%) [18].

As stated before, MoS_2 and some other TMDs are appealing for applications, specifically for use in integrated circuits and logic applications (see sec.V for more on applications). Monolayer MoS_2 has an indirect band gap of $1.8\,\text{eV}$ and few layer (bulk) MoS_2 has a direct band gap of $1.3\,\text{eV}$ [15, 21, 26, 34, 57]. This change in transition from an indirect band gap semiconductor to a direct band gap semiconductor is shown in Fig.4. The unusual electronic structure of mono and few-layer MoS_2 which ultimately results in some unique optical properties, are due to the composition of the material's conduction and valence bands. The valence band maximum at the Γ point shifts downward to the K point of the Brillouin zone as the number of layers decreases [34, 48]. The change in the band structure as a function of the amount of layers is due to quantum confinement and the change in hybridization between p_z orbitals on S atoms and d orbitals on Mo atoms [32, 34, 48]. Using quantum mechanical modeling systems to investigate the many-body electronic structure of MoS_2 (density functional theory), it has been shown that the conduction band states at the K point are primarily the result of d-orbital electrons localized on the Mo atoms in between layers and are relatively unaffected by interlayer coupling [22, 52]. Conversely, states near the Γ-point

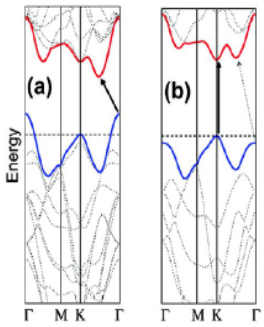

FIG. 4. Calculated band structures of bulk (a) and monolayer (b) MoS_2 and the arrows indicate the lowest energy transition [48].

are strongly affected by interlayer coupling due to the effects of antibonding p_z-orbitals on the S atoms and the d orbitals on the Mo atoms [48]. The result of this is that the states near the K-point are, for the most part, unchanged while the states near the Γ-point are shifted, causing the change from an indirect to a direct band gap as the amount of layers of the material is decreased.

Carrier mobility in two-dimensional TMDs are affected by scattering. The amount by which the scattering affects the mobility is dependent on a number of factors, namely: material thickness, carrier density, effective mass, temperature and electronic and phonon band strucutre [52]. The main sources of scattering in 2-D TMDs are acoustic and opitcal phonon scattering and Coulomb scattering [2, 44].

IV. MECHANICAL EXFOLIATION AND CHARACTERIZATION OF MOS_2 NANOSHEETS

Several methods exist that can be used to prepare atomically thin nanosheets of MoS_2 (and other TMDs). Among these several methods are mechanical exfoliation, chemical exfoliation, chemical vapor deposition and sonication [57]. The method of mechanical exfoliation used to synthesize monolayer and few-layer MoS_2 is very similar to the method use by Geim et al. to synthesize their samples of graphene from 3-D graphite [40].

To date, mechanical exfoliation remains the best method to synthesize MoS_2 crystals of the highest quality. The process involves taking bulk MoS_2 crystals and peeling thin layers from the bulk material using some adhesive material. Commonly, the adhesive material is Scotch tape, though there have been variations such as a silicone stamp [7]. This leaves a number of flakes attached to the surface of the adhesive. The flakes that are attached to the adhesive are then placed onto a substrate using instruments like plastic tweezers to further separate the flakes from the adhesive material.

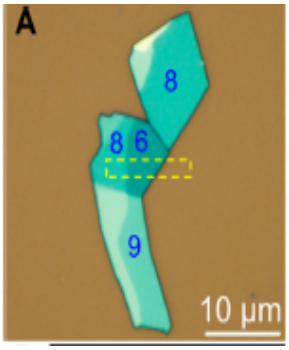

FIG. 5. Color image of a MoS_2 deposited on a 90 nm SiO_2/Si substrate. The digits indicate the layer numbers of MoS_2 nanosheets [31]

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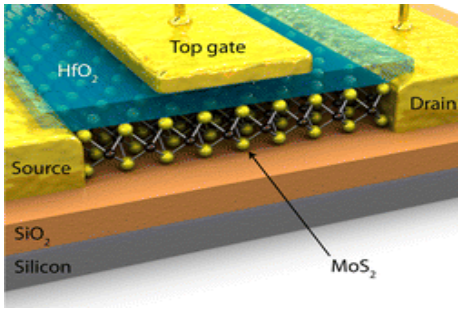

FIG. 6. Schematic view of a MoS_2 transistor with Au leads and encapsulated in 30 nm thick high κ dieletric HfO_2 acting as a top-gate dielectric [30, 43].

The process results in mono and few-layer flakes of MoS_2 being deposited on the substrate [31]. In addition to mono and few-layer flakes of MoS_2 being deposited on the substrate, the most common substrate being SiO_2/Si, a quantity of thicker flakes of MoS_2 are deposited as well [5]. This is demonstrated in Fig.5, showing the varying thicknesses of MoS_2 flakes on a substrate. As a result a method is needed to further differentiate between the flakes of varying thicknesses on that have been deposited on the substrate before any type of fundamental research can be done on the material.

Determining the size of synthesized two-dimensional materials is inherently challenging due to the small sample sizes. Several methods have been developed throughout the years to indentify and characterize these materials. The method used is dependent on the desired properties of the material that are of interest. For locating and subsequently determining the thickness of MoS_2, optical microscopy is one techinique that does well to identify single and multi-layer flakes [5]. In addition, to identify the thickness of these flakes, a common technique involves the use of atomic force microscopy (AFM).

V. APPLICATIONS OF MOS_2 TO FIELD EFFECT TRANSISTORS

MoS_2 exhibits unique properties that make it an interesting candidate for several applications. Some of these applications include optoelectronic devices, namely devices that can interact with, detect, or control light. The electronic structure of MoS_2 is what makes it interesting for this application. In addition, MoS_2 is of interest for molecular sensing applications [52]. As compared to graphene, MoS_2 is appealing in this context because of the natural band gap and as a result it is an an ideal candidate for use in field effect transistors (FETs).

FETs are the most fundamental component of modern electronic circuits. These components are used primarily as a switch in digital circuits. Typically, FETs are composed of a source and a drain that serve as contacts for the channel, the area that connects them [37]. The channel has thin dieletric coating and has a metal electrode at the top, the top gate. By changing the carrier density through the use of this electrode one can control the channel's conductivity. Fig.6 shows a schematic of a single-layer MoS_2 FET, illustrating the positioning of the drain, source, top gate, and the commonly used SiO_2/Si substrate. A side image of a similar FET is shown in Fig.7, here the relative thicknesses and positions are shown more clearly. One of the ideal properties for a transistor channel would include high charge carrier mobility, a higher mobility would allow for fast switching between on and off states [30]. Another property that is necessary for use in transistors is the presence of a band gap, which eliminates the use of graphene, even though it exhibits high mobility the lack of a band gap does not allow for the fabrication of transistors that could be switched on or off.

The use of gate dielectric is of importance in FETs in the context of mobility. Electrical measurements of single layer MoS_2 have shown a room temperature mobility in the range of $0.5 - 3\,cm^2V^{-1}s^{-1}$, whereas the mobility of bulk MoS_2 under room temperature conditions is measured in the range of $200 - 500\,cm^2V^{-1}s^{-1}$ [14, 19, 40]. However, by using HfO_2, a material that has a high κ, the room temperature mobility of single layer MoS_2 can be increased to around $200\,cm^{-1}V^{-1}s^{-1}$. In addition, this device showed a current on/off ratio near 10^8 [43]. Here on/off ratio is referring to the ratio of value of current needed for the device to be considered switched on as compared to the value of current needed for the device to be considered switched off. The reported mobility of monolayer MoS_2 is much lower than that of graphene or Si [27]. This fact presents a problem for use in high-performance applications that could limit the use of MoS_2 to low power devices.

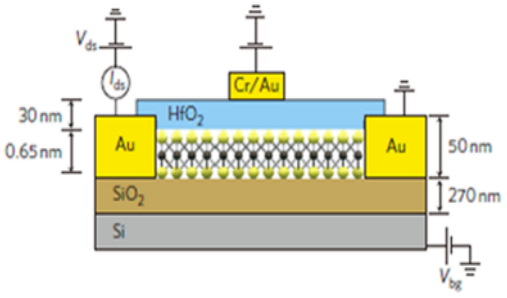

FIG. 7. A cross-sectional view of the monolayer MoS_2 FET of thickness 6.5 Å. The monolayer is separated from the top gate by 30 nm of HfO_2 [57].

VI. CONCLUSIONS AND FUTURE WORK

The field of condensed matter physics as it pertains to two-dimensional materials has grown rapidly in the previous years. Graphene offers some potential applications based upon its unique properties. However, the lack of a band gap led researchers to search for other materials that would allow the devices it comprised to be switched on and off. This, in part, renewed research in TMDs, and among them MoS_2, which had previously been studied to some extent.

MoS_2 has an electronic structure that is interesting, the band gap for few-layer MoS_2 is indirect and the band gap increases and becomes a direct band gap for monolayer MoS_2. In addition, MoS_2 exhibits high current on/off ratios. The presence of a relatively large band gap and a high current on/off ratio led to the study of MoS_2 as a material in FET channels.

To date, there is much ongoing research that looks to address some of problems that still remain in the study of MoS_2 as a two-dimensional material and its applications. One such problem that needs to be addressed in the coming years is improvements in mobility. The low mobility measurements in MoS_2 FETs are limits to the applications such FETs can be used for. Theoretial predictions show that mobility could still be imporved significantly [24]. Much of the challenge in this problem lies in decreasing the scattering.

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