

Applications of MoS₂ as a Two-Dimensional Material Beyond Graphene

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An article usually includes an abstract, a concise summary of the work covered at length in the main body of the article.

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I. INTRODUCTION

II. GRAPHENE AS A NEW TWO-DIMENSIONAL MATERIAL

A. The Discovery of Graphene

By the end of the last century microelectronics had revolutionized the world, the majority 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 [24, 31, 43]. A decade after the first device, 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 [36, 43]. This 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 industry [43]. This impending limit caused many to look for solutions that involved the use of SiO₂ devices and also alternatives to silicon. The result of the latter has given way to a breadth of literature and research that was unforeseen a decade before. 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.

In 1985, with the discovery of fullerenes the amount of known carbon allotropes increased [26, 33]. 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 [37, 38]. 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 several carbon-based materials (graphite, fullerenes, nanotubes, etc..., see Fig.1) [11, 37, 44]. 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 [33].

B. 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 properties are primarily a result of its low dimensionality and its band structure that allow electrons to mimic relativistic particles [20]. This newly discovered phe-

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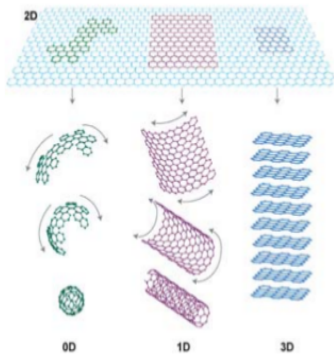


FIG. 1. Graphene can be envisioned in several dimensions. 0-dimensional buckyballs, 1-dimensional nanotubes, or 3-dimensional graphite [40].

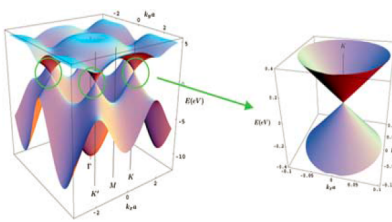


FIG. 2. 3D representation of the electronic band structure of graphene. The right side shows an enlarged view near the Fermi level in one k point [33].

nomenon has allowed for the study of relativistic effects in condensed matter experiments. This includes the appearance of the atypical quantum Hall effect and the confirmation of other relativistic phenomena [39, 51, 57]. However, it is worth noting that this peculiar band structure can be modified by stacking three or more layers of graphene [33].

For applications to electronics a material's band gap is of interest. In graphene, however, the conduction and valence bands touch at a single point as shown in fig. 2 [33, 48]. As a result graphene has no band gap (small band gaps of a few hundred MeV can be introduced in bilayer graphene) [55]. The absence of a band gap is also interesting in the context of the material's optical properties and the implications of these. 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, 49, 53].

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 strength that is 13% of that [1, 4]. It can also sustain elastic deformations of 20% and due to its two-dimensional nature it has a high pliability [33]. Mechanically, graphene is

an exciting material due to the fact that 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 here. Without many defects or imperfections the electrons can travel long distances, as much as several micrometers, without being scattered even on rough substrates [12, 33]. The average electron mobility obtained in graphene varies depending on temperature, but the most commonly measured value is $\mu = 100,000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ with values up to $\mu = 500,000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ obtainable at low temperatures [18]. 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.

III. TRANSITION METAL DICALCOGENIDES

Graphene is being studied for its unique properties, 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) [34, 52]. 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 [55]. The material is dependent on the combination of transition metal, typically one of: Mo, W, Nb, Re, Ni, or V, and chalcogen, typically one of: S, Se, or Te [52]. 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) [55]. 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, 27, 54, 56]. Ongoing research also includes graphene-like nano materials like silicene and germanene, which are the silicon and germanium-based versions of graphene and are found to show properties that are similar to graphene [6, 47]. These two-dimensional materials are becoming increasingly attractive for a wide-range of applications due to their distinct properties.

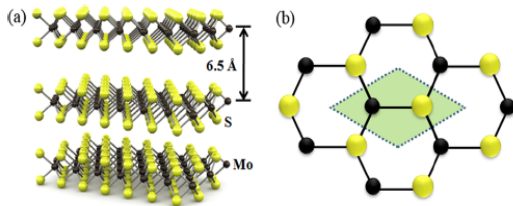


FIG. 3. (a) The atomic structure of layered MoS₂. Different sheets are composed of three atomic layers S-Mo-S, where Mo and S are covalently bonded [41, 55]. (b) Top view of the honeycomb lattice [55].

A. Properties of MoS₂

As discussed in sec. II B, pristine graphene has no band gap. Though it is possible to introduce a band gap in bilayer graphene and graphene nanoribbons, the appeal of many TMDs is that they have direct band gaps which make them ideal candidates for electronic material applications [55]. One such example of a semiconducting TMD is MoS₂ (molybdenum disulphide). TMDs, and more specifically MoS₂ and the properties it exhibits have been studied 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 and their potential applications.

Like graphene, and many other 2D materials, MoS₂ has a Young's modulus that is comparable to steel (~ 205 GPa) [45]. The Young's modulus of single-layer MoS₂ is ~ 270 GPa. The Young's modulus of bulk MoS₂ is ~ 240 GPa. The fact that monolayer MoS₂ 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 [28]. In a further study it was found that the Young's modulus of multilayer MoS₂ ranging in thickness from 5 to 25 layers was 330 ± 70 GPa [8]. In addition, both single and bilayer MoS₂ have a breaking strength of about 6% and 11% of their Young's modulus, respectively [4]. This is an indication that MoS₂ is quite flexible compared to other commonly used engineering materials (stainless steel $\sim 0.4\%$, kevlar $\sim 2.6\%$) [19].

As stated before, what MoS₂ 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 MoS₂ has an indirect band gap of 1.8 eV and few layer (bulk) MoS₂ has a direct band gap of 1.3 eV [15, 21, 25, 32, 55]. 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 MoS₂ which ultimately results in some unique optical properties are due to the composition of the material's conduction and valence bands. The valence band

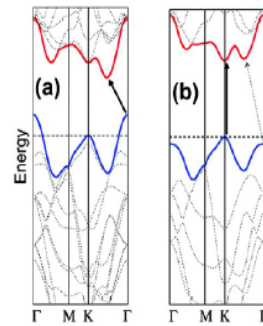


FIG. 4. Calculated band structures of bulk (a) and monolayer (b) MoS₂ and the arrows indicate the lowest energy transition [46].

maximum at the Γ point shifts downward to the K point of the Brillouin zone as the number of layers decreases [32, 46]. 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 [30, 32, 46]. Using quantum mechanical modeling systems to investigate the many-body electronic structure of MoS₂ (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, 50]. Conversely, states near the Γ -point 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 [46]. 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 structure [50]. The main sources of scattering in 2D TMDs are: acoustic and optical phonon scattering and Coulomb scattering [2, 42].

IV. MECHANICAL EXFOLIATION AND CHARACTERIZATION OF MoS₂ NANOSHEETS

There exist several methods that can be used to prepare atomically thin nanosheets of MoS₂ (and other TMDs). Among these several methods are mechanical exfoliation, chemical exfoliation, chemical vapor deposition, and sonication [55]. The method of mechanical exfoliation used to synthesize monolayer and few-layer MoS₂ is very similar to the method used by Geim et al. to

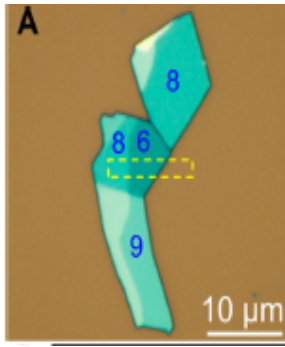


FIG. 5. Color image of a MoS_2 deposited on a 90 nm SiO_2/Si substrate. The digits indicate the layer numbers of MoS_2 nanosheets [29]

synthesize their samples of graphene from 3D graphite [38].

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 on this such as a silicone stamp, instead [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. The process results in mono and few-layer flakes of MoS_2 being deposited on the substrate [29]. 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 synthesized two-dimensional materials is inherently challenging due to the small sample sizes. Several methods have been developed throughout the years to identify 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 technique 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).

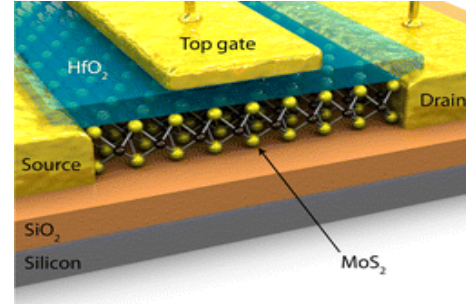


FIG. 6. Schematic view of a MoS_2 transistor with Au leads and encapsulated in 30 nm thick high κ dielectric HfO_2 acting as a top-gate dielectric [28, 41].

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 [50]. As compared to graphene, MoS_2 is appealing in this context because of the natural band gap and as a result it is 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, drain, gate, and often a substrate. The source is where the carriers enter the channel, the drain is where carriers leave the channel, the gate regulates the channel conductivity, and the substrate serves mainly to bias the transistor into operation [35]. The channel material

VI. STATE OF THE ART

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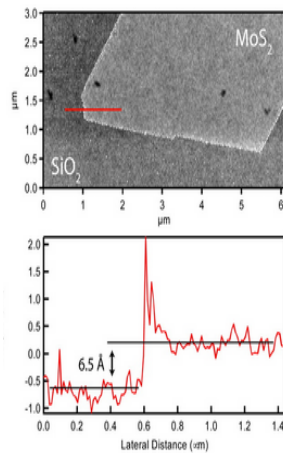


FIG. 7. The top image is an AFM image of single layer MoS_2 , the bottom image is the corresponding height profile [28].

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