Atomically Thin MoS$_2$: A Versatile Nongraphene 2D Material

Y. P. Venkata Subbaiah, K. J. Saji, and A. Tiwari

Two-dimensional inorganic materials are emerging as a premiere class of materials for fabricating modern electronic devices. The interest in 2D layered transition metal dichalcogenides is especially high. Particularly, 2D MoS$_2$ is being heavily researched due to its novel functionalities and its suitability for a wide range of electronic and optoelectronic applications. In this article, the progress in mono/few layer(s) MoS$_2$ research is reviewed by focusing primarily on the layer dependent evolution of crystal, phonon, and electronic structure. The review includes extensive detail into the methodologies adapted for single or few layer(s) MoS$_2$ growth. Further, the review covers the versatility of 2D MoS$_2$ for a broad range of device applications. Recent advancements in the field of van der Waals heterostructures are also highlighted at the end of the review.

1. Introduction

2D materials constitute a unique class of materials in which in-plane atomic bonding is much stronger than that along the out-of-plane direction. These materials are usually artificially derived from layered van der Waals solids.[1] The crystal structure of layered van der Waals solids is composed of one-atom-thick or few-atom-polyhedral layers with tight covalent or ionic bonding along two-dimensions (intralayer) and weak van der Waals bonding along the third dimension (interlayer).[2] The weak van der Waals bonding enables an easy splitting of the layered materials into individual monolayers. The 2D materials differ in their phonon and electronic structure,[1,3] from their bulk phases and exhibit unique and fascinating properties due to the quantum confinement of electrons and the absence of interlayer interactions. Graphene, a single layer of graphite was the first real 2D material.[4,5] However, presently there are a large numbers of layered materials that can be cleaved or grown easily into 2D atomic planes,[6,7] including transition metal dichalcogenides. Figure 1 shows the current library of various 2D materials predicted beyond graphene.[6] The color shading indicates 2D materials that are experimentally stable or unstable in ambient conditions.

Unlike zero-band gap graphene (semimetal),[8] and large band gap hBN (insulator),[9] the 2D transition metal dichalcogenides (sulfides and selenides) have band gaps comparable to conventional Si or GaAs, and thus present a tantalizing prospect of scaling all semiconductor science and technology down to a truly atomic scale. Although these transition metal dichalcogenides (TMDCs) are quite well known for the past few decades for their applications in solid state lubricants,[10] photovoltaic devices,[11,12] and rechargeable batteries,[13] the recent methodologies and concepts evolved from graphene research like exfoliation, transfer, and manipulation of 2D materials have driven interest toward the exploration of layered TMDCs. TMDCs possess hexagonal layers of transition metal atoms (M) sandwiched between two layers of chalcogen atoms (X) with an MX$_2$ stoichiometry. Depending on the different combinations of chalcogen (typically S, Se, or Te) and transition metal (mainly Mo and W) elements, several different kinds of TMDCs are possible. Among the various combinations of TMDCs, MoS$_2$ is the most promising 2D material as its elemental constituents are abundant, nontoxic, and amenable for easy mono/few layer(s) synthesis when compared to their analogous selenides and tellurides.

Despite graphene’s exceptionally high carrier mobility,[14] field-effect transistors (FETs) made from graphene cannot effectively function as electronic switches due to the absence of an electronic band gap.[15,16] 2D MoS$_2$ possesses a relatively high mobility up to 200 cm$^2$/V-s with a high on/off current ratio of $\approx$10$^8$ at room temperature,[17–20] and has a layer dependent band gap with a crossover from indirect (1.2 eV) to direct (1.9 eV) at the bulk to monolayer transition, making this a promising material for efficient electronic,[17,21] and optoelectronic devices.[22–24] The unique electronic band structure and optical properties of monolayer MoS$_2$ are suitable for a wide range of novel functional devices and hence has triggered exhaustive research on this nongraphene material during the last few years.[2,7,25–30] In this paper, we have done a comprehensive review of the state-of-the-art research going on in this area. The review primarily covers the intriguing changes occurring in the physical properties (crystal structure, layer dependent evolution of vibrational and electronic structure and relevant optical properties) of MoS$_2$ when one of the dimensions (specifically the van der Waals dimension) is controlled, followed by the description of various isolation or large-area
growth procedures. Finally, the review outlines many exciting recent device developments in the field of 2D electronics and optoelectronics that include field-effect transistors (FETs), integrated circuits, logic devices, light emitting diodes, photovoltaic devices, and van der Waals heterostructures.

1.1. Crystal Structure of MoS₂

In general, MX₂ compounds can crystallize in more than one 2D structures: the hexagonal (2H), octahedral (1T), and distorted octahedral (1T') structures. Although all these phases consist of a metal atom (M) layer sandwiched between two chalcogenide (X) layers, only 2H phase is semiconducting and other phases are metallic. While the 2H phase is widely studied for electronic applications, the 1T' phase is getting renewed interest since it can exhibit large nonsaturating magnetoresistance, and spin–orbit coupling induced band gap widening and quantum Spin Hall Effect. In the case of MoS₂, the most commonly occurring crystal structure for MoS₂ is hexagonal (2H), which is thermodynamically more stable and has a layered structure with D₆h point group symmetry. Throughout this paper, we consider the 2H phase of MoS₂ unless otherwise specified. In its bulk form, crystal structure of MoS₂ consists of vertically stacked layers that are linked via weak van der Waals forces between the layers, and with strong in-plane covalent bonds between Mo and S atoms. Every single layer of MoS₂ consists of a single sheet of Mo plane sandwiched between two planes of S atoms and forms a 2D hexagonal crystal structure (Trigonal prismatic arrangement) with a D₃h point group symmetry. Each of the single layers has a thickness of \( \approx 6.5 \, \text{Å} \), with the distance between upper and lower sulfur atoms \( \approx 3.2 \, \text{Å} \). The lattice constants of MoS₂ monolayer are reported to be \( \approx 3.22 \, \text{Å} \) with a covalent bond length of Mo-S of 2.43 Å and the S-Mo-S bond angle of \( \approx 80.56^\circ \). The surface of 2D-MoS₂ is free from dangling bonds. A monolayer of MoS₂ has an in-plane stiffness of \( 180 \pm 60 \, \text{Nm}^{-1} \), corresponding to an effective Young’s modulus of 270 ± 100 GPA, which is higher than that of steel (\( \approx 205 \, \text{GPa} \)) as well as of bulk MoS₂ crystal (\( \approx 240 \, \text{GPa} \)). The breaking strength of monolayer MoS₂ is as high as 22 ± 4 GPa, which is between 6% and 11% of its Young’s modulus and hence the monolayer MoS₂ can be deformed and bent to a curvature of radius 0.75 mm without losing its native properties. This exceptional mechanical maneuverability offers the use of MoS₂ in flexible electronic and optoelectronic devices.

1.2. Raman Active Vibrational Modes in MoS₂

Raman spectroscopy is a powerful tool to determine the crystal phase and distinguish between bulk and mono/few layer(s) present in layered van der Waals materials. The group-theoretical analysis of the hexagonal Brillouin zone of single crystal 2H-MoS₂ predicts that there are four first-order Raman active modes, namely: \( E_{1u}^2, E_{1g}^1, E_{2g}^1 \), and \( A_{1g}^1 \) for wave numbers of \( \approx 32, 286, 383, \) and \( 408 \, \text{cm}^{-1} \), respectively. Additionally, there are two IR active modes: \( E_{1u}^2 \) (384 \, \text{cm}^{-1}).
and four silent modes: \(B_{2g}^{12} (58 \text{ cm}^{-1})\), \(E_{2u}^{12} (403 \text{ cm}^{-1})\), and \(B_{2g}^{12} (470 \text{ cm}^{-1})\). The experimental off-resonance[46] and resonance Raman spectra have been extensively studied for bulk 2H-MoS\(_2\).[48,49] The \(E_{2g}^{12}\) mode is caused by the lattice vibration of S-Mo-S layer against other adjacent layers, while the rest of the three modes belong to intralayer vibrations. The \(E_{1g}^{1}\) mode is forbidden in back-scattering operation on a basal plane. \(E_{1g}^{2}\) mode that results from opposite vibration of two S atoms with respect to the Mo atom, and the \(A_{1g}^{1}\) mode that is associated with the out-of-plane vibration of only S atoms in opposite directions are the most sensitive modes to the number of layers present in the film.[50] The Raman shift difference between \(A_{1g}^{1}\) and \(E_{1g}^{2}\) modes (\(\Delta \nu\)) is a characteristic used to identify the number of layers present in MoS\(_2\) specimen. A \(\Delta \nu\) value between 18 and 20 cm\(^{-1}\) indicates the presence of monolayer MoS\(_2\) with the value increasing consistently on increasing the number of layers in the film and reaches \(\approx 25 \text{ cm}^{-1}\) for bulk MoS\(_2\).[3,51–58] (Figure 3c,d).

Several in-depth experimental studies have been performed to understand the evolution of vibrational modes in MoS\(_2\) as the thickness of the specimen is reduced to a single monolayer.[43,49,52,59–62] When the layer number increases, the inter-layer van der Waals forces in MoS\(_2\) suppress vibrations, resulting in a higher restoring force acting on atoms,[52] and hence both \(A_{1g}^{1}\) and \(E_{1g}^{2}\) modes are expected to stiffen (blueshift). However, recent layer dependent Raman studies,[43,52] have shown that while the out-of-plane \(A_{1g}^{1}\) mode is consistent with the predicted stiffening with increasing layer number, the \(E_{1g}^{2}\) mode softens (redshift) instead of the expected blue-shift due to the dominant long-range Coulombic

\[ A_{2u} (470 \text{ cm}^{-1}) \]

\[ B_{2g}^{12} (58 \text{ cm}^{-1}) \]

\[ B_{1u}^{12} (403 \text{ cm}^{-1}) \]

\[ B_{2g}^{12} (470 \text{ cm}^{-1}) \]
interlayer interactions in multilayer MoS$_2$. It has also been observed that the full width at half maxima for the $A_{1g}$ mode increases on going from bulk to monolayer whereas the value for the $E_{1g}^{2g}$ mode remains unaffected.\cite{43,52} In a recent report, Terrones et al.\cite{63} showed that in the case of monolayer MoS$_2$ films, due to the lack of inversion symmetry, the out-of-plane and in-plane Raman modes should be represented by $A_{1g}'$ and $E'$, respectively. However, in most of the earlier literature even for monolayer MoS$_2$, peaks are indexed as $A_{1g}$ and $E_{1g}^{2g}$.

1.3. Electronic Band Structure of MoS$_2$

Knowledge of electronic band structure is essential for understanding the electronic and optical processes in various electronic and optoelectronic devices. The electronic band diagram of graphene has a linear energy dispersion around the K point and exhibits a zero band gap.\cite{64,65} The gapless electronic band structure of graphene makes it unsuitable for fabricating efficient FETs. The electronic band structure of bulk and monolayer MoS$_2$ calculated from first principles is shown in Figure 4a, which indicates a parabolic dispersion.\cite{51,67} The valence band maximum (VBM) centered at the $\Gamma$ point and the conduction band minimum (CBM) located midway in the $\Gamma$–K direction constitutes an indirect band gap of 1.2 eV for bulk MoS$_2$.\cite{3,68} The direct excitonic bands at K Brillouin point remain almost unaffected as the number of layers in the film decreases, while the conduction band states between $\Gamma$ and K and the valance band states at the $\Gamma$ point move apart and cause a widening in indirect excitonic transition that results in a direct band gap for monolayer MoS$_2$ (Figure 4b). Although, the direct excitonic states at the K point remain almost unchanged, there is a slight increase in the direct band gap by about 0.05–0.1 eV.\cite{67,69} In conclusion, the bands at the $\Gamma$ point and midway between $\Gamma$ and K points vary significantly on going from bulk to monolayer and establish a direct K–K band transition with a gap of $\approx$1.9 eV for monolayer MoS$_2$. The ultimate crossover from indirect to direct band gap nature is quite intriguing and can be accounted for by a combined effect of quantum confinement, long range Coulombic effects, and a change in the hybridization between $p_z$ orbitals in S atoms and $d$-orbitals in Mo atoms.\cite{3,35,51,70}

Density functional theory (DFT) calculations showed that as the Mo layer is sandwiched between two S layers, the conduction band states of $d$-orbitals in Mo atoms at the K point are relatively unaffected by interlayer coupling; however, the states near the $\Gamma$-point, are severely affected due to combinations of the antibonding $p_z$ orbitals in S atoms and the d orbitals in Mo atoms.\cite{51,69}
As discussed in Section 1.3, the band gap of MoS$_2$ changes from indirect to direct band gap during the transition from bulk to monolayer. During this transition, the exciton binding energy also changes drastically showing an increase from $\approx 0.1$ eV in bulk to 1.1 eV in monolayer samples. Bulk MoS$_2$ is an indirect band gap semiconductor and produces an insignificant photoluminescence. However, a changeover to a direct band gap material in its monolayer form, yields...
a gigantic photoluminescence, about $10^4$ times higher than that of bulk. Despite this, still the reported values, lying between $10^{-3}$ and $10^{-6}$ for few-layer MoS$_2$ samples and up to $4 \times 10^{-3}$ for monolayer MoS$_2$ samples, are far behind the near unity values expected for direct band gap semiconductors.[$^9$]

The photoluminescence spectra of MoS$_2$ exhibits two excitonic peaks denoted as A (≈1.9 eV) and B (≈2.05 eV) around the K zone[$^{1,51}$] (Figure 4c). These peaks are shown to originate from the direct excitonic transitions at the K zone, with the energy splitting (≈0.15 eV) resulting from the combined effect of interlayer coupling and valence band spin–orbit coupling.$^{[3,69]}$ The photoluminescence of MoS$_2$ is also quite significantly affected by the type of substrate, doping, and ionic liquid gating. For example, Li et al.$^{[76]}$ demonstrated the effect of substrate on photoluminescence of monolayer MoS$_2$. They showed that by choosing the substrate, different amounts of charges can be induced into the monolayer MoS$_2$, that can in-turn modify the relative intensities of the charged exciton (trion),$^{[77]}$ and neutral exciton.$^{[58,76,78]}$ Mouri et al. showed that the solution-based chemical doping can also be an effective route to alter the photoluminescence by the adsorption of p-type and n-type dopants by switching the recombination process between exciton and trions.$^{[79]}$ In another study, Li et al. showed that the magnitude of the photoluminescence can also be increased by using ionic liquid gating which passivates the surface states and traps charges that act as recombination centers.$^{[79]}$ Using this approach they reported almost a 300% enhancement in the photoluminescence intensity (Figure 4d).

2. Methods of Synthesis

There are two major synthesis routes, which have been readily utilized for synthesizing MoS$_2$ monolayers. The first one is based on exfoliation techniques and usually results in very small area flakes. While, the second route is based on vapor deposition techniques and can result in large area growth of monolayer MoS$_2$.

2.1. Exfoliation Techniques

Exfoliation is the most widely employed method for preparing monolayer or few layer MoS$_2$ samples. The fragile van der Waals forces (40–70 meV),$^2$ across the interlayer allow easy isolation of layered materials into mono or few layer(s) using exfoliation techniques. There are two subclasses of exfoliation techniques namely micromechanical exfoliation and chemical exfoliation.

2.1.1. Micromechanical Exfoliation

In 1999, a micromechanical approach was used for the first time by Lu et al.$^{[80]}$ to obtain thin graphite sheets from the patterned highly oriented pyrolytic graphite. Later, in 2004, Novoselov et al.$^{[1,4]}$ demonstrated the perfect isolation of truly 2D single layer flakes of graphene using the same approach. The micromechanical cleavage involves, a fresh surface of a layered crystal being either rubbed against another substrate surface or pressed against the “scotch tape,” which leaves a combination of single or few layer flakes attached to the substrate or “scotch tape.” For synthesizing mono/few layer(s) MoS$_2$, bulk MoS$_2$ single crystal is pressed against an adhesive scotch tape and subsequent repeated exfoliation leaves the flakes adhered to it, which are then transferred to substrates.$^{[3,17,22,49,51,52]}$ As these monolayers are highly transparent, the transferring substrate must be a thick (opaque) dielectric layer (usually 200–300 nm of SiO$_2$ on Si). The color contrast under optical microscope (Figure 5a) between the substrate and mono/few-layer helps to identify the formation of single/few layer MoS$_2$.$^{[17,18,51,52,78]}$ Subsequent AFM height profile measurements (Figure 5b) provide the information about the number of layers in the specimen.$^{[39,43,59,81]}$ Although micromechanical exfoliation technique is quite simple and produces high quality flakes, the yield of this technique is extremely low and results in irregular shaped flakes with high percentage of few layers than perfect monolayer of MoS$_2$. Gacem et al. proposed a modified micromechanical exfoliation technique with anodic bonding to produce high quality and larger size single-layer and few-layers 2D materials.$^{[82]}$

There are also some reports on layer by layer laser thinning,$^{[83]}$ thermal annealing,$^{[84]}$ and plasma (Ar$^+$) thinning,$^{[85]}$ of mechanically exfoliated MoS$_2$ few layers to obtain high yield of monolayer MoS$_2$ samples with good shape control and improved lateral sizes. However, despite their success in controlling the thickness down to monolayer, prolonged exposure to radiation in laser thinning and thermal thinning techniques causes rougher morphology. Compared to laser and thermal thinning, the Ar$^+$ plasma thinning has been shown to be a more reliable technique, with much less surface roughness.$^{[85]}$

2.1.2. Chemical Exfoliation

Layered TMDCs can be prepared by chemical exfoliation techniques also known as liquid-phase exfoliation.$^{[86,87]}$ Liquid-phase exfoliation, in general, involves the separation of layered materials through intercalation or dispersion followed by sonication to yield single and few layer flakes.$^{[86,88]}$ Liquid-phase exfoliation methods are convenient and result in materials big enough to be usable in various thin film applications.$^{[89]}$ The simplest lithium ion intercalation method uses the concept of lithium ion insertion between the MoS$_2$ layers to widen the gaps between the layers, often using n-butyllithium in hexane as the lithium source. The subsequent addition of water removes the lithium, and a sonication process allows the layers to separate and be retrievable.$^{[90,93]}$ Organic solvents such as methanol, ethanol, and isopropyl alcohol as well as rapid heating in vacuum at around 600 °C can also be used instead of lithium intercalation to separate the layers of MoS$_2$. Although these liquid methods (both lithium intercalation as well as organic solvents, etc.) are simple, they are rather time consuming (taking up to 3 days), sensitive to environmental conditions, and either produce a low yield with incomplete separation or result in structural deformations of the 2H-MoS$_2$
(hexagonal) to 1T-MoS$_2$ (octahedral),[73,92] due to excess intercalation of lithium ions. The high-yield production of single-layer MoS$_2$ using liquid exfoliation has been demonstrated by Zeng et al. [92] using a controllable electrochemical lithiation process, which is different compared to the conventional lithium intercalation process.[73] However, due to the nature of the complex electrochemical process, its scope is limited. A mixed solvent strategy has been suggested by Zhou et al. using a low boiling point solvent mixture of 45 vol% ethanol in water. They obtained a yield of $0.018 \pm 0.003 \text{ mg mL}^{-1}$ for MoS$_2$ nanosheets ($=2–4 \text{ nm}$), which is $\approx$13 times higher than that with pure ethanol and 68 times higher than that with pure water.[93] More recently, Coleman et al.[86,87] succeeded in obtaining suspended flakes of various TMDCs, including MoS$_2$, with a high yield ($=0.3–0.5 \text{ mg mL}^{-1}$). They initially sonicated the MoS$_2$ powder in two different types of solvents with varying surface tensions: (1) N-Methyl-2-pyrrolidone (NMP),[86] and (2) aqueous surfactant sodium cholate.[87] The resultant dispersions were centrifuged and the supernatant was decanted. The results showed a good stabilization and prevented the 2D nanosheets from aggregating during the slow solvent evaporation. Furthermore, the use of organic/inorganic solvents avoids structural deformations and is insensitive to environment, and may potentially be scaled up to obtain large quantities in hybrid sheets. An improvement of up to $0.8 \text{ mg mL}^{-1}$ yield with sizes varying from 50–700 nm has recently been reported by Yao et al.[88] using aqueous sodium dodecyl sulfate solution as a surfactant in combination with ball milling and sonication. Despite solvent and surfactant exfoliated MoS$_2$ being efficient means for producing higher concentrations of flakes, bilayer and few layer flakes are far more abundant than single layer flakes. Additionally, the dispersed concentrations are still below $1 \text{ mg mL}^{-1}$ with lateral flake sizes found to be around 200–400 nm, which are not large enough for practical applications. A drastic enhancement in the concentration of exfoliated MoS$_2$ (around $40 \text{ mg mL}^{-1}$) with increased flake sizes up to 700 nm has recently been reported by O’Neill et al.[94] using N-Methyl-2-pyrrolidone as the solvent with a controlled sonication time between 23 and 60 h and a centrifugation rate of 1500 rpm. The longer sonication times (60–140 h) caused a reduction in the flake sizes to 400–200 nm due to the sonication induced scission. These results demonstrate that controlled centrifugation coupled with sediment recycling can be an effective route to separate dispersed MoS$_2$ nanosheets by size (Figure 5c–e). The color of the resultant dispersions varies strongly with the final centrifugation rate, which can be used to confirm that the size of the nanosheets has indeed changed.

2.2. Vapor Deposition Techniques for Large Area Growth of MoS$_2$

Exfoliation techniques remain simple and reliable techniques to demonstrate the concepts and features of 2D materials and devices for research. However, it is very important to develop large area growth methods to synthesize mono or few layer(s) TMDCs in order to extend the applicability of 2D materials from flake scale to wafer scale. Vapor-based deposition techniques, both chemical vapor deposition as well as physical vapor deposition, have been explored recently for such purpose.

2.2.1. Chemical Vapor Deposition

The 2D MoS$_2$ growth procedure by chemical vapor deposition (CVD) normally involves either a single step vapor phase
co-deposition of solid precursor and sulfur onto adjacent/top mounted insulating substrate at elevated temperatures, or a two-step process that involves precursor deposition on desired substrate (mostly insulators or metals) followed by vapor phase sulfur annealing. So far, the growth of MoS$_2$ by CVD technique has been explored using the following five different types of Mo sources: MoO$_3$, ammonium thiomolybdate [(NH$_4$)$_2$MoS$_4$], metallic Mo, MoCl$_5$, and MoS$_2$.

**Chemical Vapor Deposition Using MoO$_3$ Precursor**: Balendhran et al. were among the first few groups to demonstrate the growth of atomically thin MoS$_2$ using codeposition of MoO$_3$ and sulfur onto quartz substrates at 750 °C. Codeposited films were annealed in the excess of sulfur for 180 min at 830 °C to achieve MoS$_2$ layer. Lee et al. reported the CVD growth of large area monolayers of MoS$_2$ on amorphous SiO$_2$ substrate. Their experimental setup consisted of a reaction chamber with two adjacent ceramic boats loaded with MoO$_3$ powder and sulfur powder. The upside down SiO$_2$/Si substrate was mounted on the top of the MoO$_3$ boat and the chamber was heated to 650 °C in a nitrogen atmosphere. Their results demonstrated that the growth of MoS$_2$ is very sensitive to substrate pretreatment. Mann et al. employed a CVD setup analogous to that used by Lee et al. for the growth of small areas of MoS$_2$ monolayers using MoO$_3$ and sulfur powders as the Mo and sulfur sources, and found that heating the tube furnace for 3 min (till the sulfur melts) results in the best deposition. Their transport measurements showed an n-type conductivity with a bit poor mobility of 0.26 cm$^2$ (V-s)$^{-1}$. Lin et al. proposed a modified method to synthesize wafer-scale MoS$_2$ thin layers by using a two-step thermal annealing process. Initially, the ultrathin films of MoO$_3$ were thermally deposited on c-plane sapphire substrates at the rate of 0.05 nm s$^{-1}$ followed by a first anneal in a H$_2$/Ar environment at 500 °C for 60 min followed by a second anneal in a sulfur environment at 1000 °C for 30 min. Their results showed that the two-step process is more suitable for obtaining higher carrier mobility.

than the one step direct sulfurization process (Figure 6b). In a later study, Ji et al.\cite{108} reported epitaxial growth of centimeter scale monolayer of MoS$_2$ on nearly lattice matched mica substrates using low pressure chemical vapor deposition (LPCVD). A slightly different approach was employed by Wang et al.\cite{99} who used thermally evaporated MoO$_3$ as the starting material, which was then reduced in a sulfur vapor followed by the layer-by-layer sulfurization of the reduced MoO$_2$ micro plates before finally obtaining MoS$_2$ flakes with a rhomboidal shape and a domain size of $\approx 10\ \mu$m. Many similar fabrication routes of MoS$_2$ sulfurization have been adopted recently by various research groups for achieving large area growth of monolayer MoS$_2$.\cite{100–104}

### Chemical Vapor Deposition Using Thermolysis of Ammonium Thiomolybdate

Thermolysis of ammonium thiomolybdates, (NH$_4$)$_2$MoS$_4$ has also been explored to synthesize 2H-MoS$_2$\cite{105–108}. For example, Liu et al.\cite{109} reported the growth of large area, high quality MoS$_2$ layers on sapphire and SiO$_2$/Si substrates by this technique. In their study the thermal decomposition of (NH$_4$)$_2$MoS$_4$ solution was performed by first annealing it in an Ar+H$_2$ atmosphere at 300 °C under a pressure of 1 Torr for 60 min followed by a second annealing in an Ar+H$_2$ atmosphere at 1000 °C under a pressure of 500 Torr for 30 min. Initially, 0.25 g of solid (NH$_4$)$_2$MoS$_4$ was added to 20 mL dimethylformamide (DMF) to form the ammonium thiomolybdate solution. The sapphire or SiO$_2$/Si substrates were dipped vertically into the ammonium thiomolybdate solution to form an ultrathin film of (NH$_4$)$_2$MoS$_4$. This process was followed by a two-step annealing as shown in Figure 6c to produce high quality, thin layers of MoS$_2$. During the annealing process, the (NH$_4$)$_2$MoS$_4$ films decomposed into NH$_3$, H$_2$S, and MoS$_2$ before finally forming MoS$_2$. The presence of H$_2$ is essential during annealing in order to avoid oxidation, and it was noticed that the direct annealing of (NH$_4$)$_2$MoS$_4$ films in an inert atmosphere with sulfur did not produce high quality MoS$_2$ films.

Shi et al.\cite{110} employed an alternative approach based on reduced graphene oxide (rGO)\cite{111} that could act as a good template for MoS$_2$ nanoflakes. Their method used (NH$_4$)$_2$MoS$_4$ solution together with rGO dissolved in an organic solution. They demonstrated the epitaxial synthesis of MoS$_2$ nanoflakes over graphene covered Cu foil at a relatively low temperature of 400 °C. Their idea was based on the fact that the planar surface of CVD grown graphene (CVD-G) is free from dangling bonds. This coupled with its weak van der Waals forces could play an important role for achieving a better growth of MoS$_2$. A low dose of (NH$_4$)$_2$MoS$_4$ with the solvent lead to the island growth of MoS$_2$ on the graphene substrate, as the dose of precursor increased, the isolated MoS$_2$ islands packed into continuous MoS$_2$ nanosheets through coalescence.

### Chemical Vapor Deposition Using Mo Precursor

Zhan et al.\cite{96} employed a different CVD route based on a metallic Mo precursor followed by vapor phase sulfurization to achieve large area growth of single or few layer(s) MoS$_2$ films on SiO$_2$ substrate. Initially, a thin layer of Mo ($\approx 1–5\ \text{nm}$) was predeposited using e-beam evaporation onto SiO$_2$ followed by sulfurization under a $N_2$ atmosphere at 750 °C for 10 min. The experimental setup consisted of a two-zone reaction quartz tube, in which Mo coated films were placed into ceramic boats at the center of the hot zone while the sulfur powder was loaded onto another ceramic boat and placed up-wind in the low temperature zone ($\approx 113\ ^\circ\text{C}$). The resulting CVD grown MoS$_2$ films showed resistivities of $1.46 \times 10^4$ to $2.86 \times 10^2\ \Omega\ \text{cm}$ with mobilities ranging from 0.004 to 0.04 cm$^2$ (V·s)$^{-1}$ with a p-type behavior. Laskar et al.\cite{112} successfully grew large area, single crystal MoS$_2$ films by sulfurization of e-beam evaporated Mo films deposited on c-axis oriented sapphire substrates and found that the high temperature growth between 900 and 1100 °C yields high quality, epitaxially oriented, single crystal MoS$_2$ films. These films exhibited a high field effect mobility of $12 \pm 2\ \text{cm}^2$ (V·s)$^{-1}$ with an n-type behavior. Recently, Lee et al.\cite{113} demonstrated a CVD method of sulfurization of e-beam evaporated Mo films using a gas phase sulfur precursor (H$_2$S) to realize wafer scale, uniform MoS$_2$ films with absolute control over the number of layers (Figure 6d). The thickness of the MoS$_2$ film was controlled by varying the thickness of the metal film. The electron beam evaporated Mo films were placed in a tubular quartz chamber and then heated to 750 °C under argon flow (50 sccm). The injection of H$_2$S/H$_2$/Ar (1:5:50) reaction gas mixture over 15 min converted the Mo into a MoS$_2$ film. During the deposition, the chamber pressure was maintained at $3.1 \times 10^{-1}$ Torr. The introduction of H$_2$ was noted as an essential step to avoid the oxidation of predeposited metal film. Orofino et al.\cite{114} followed a slightly different approach that involved the reaction of DC magnetron sputtered Mo film with a sulfur vapor (from the solid sulfur powder). Their method successfully produced centimeter scale MoS$_2$ sheets on MgO substrates with grain sizes varying from 50–200 nm. Very recently, Ahn et al.\cite{115} demonstrated a low-temperature synthesis of large area, few layer MoS$_2$ directly onto polyimide (PI) substrates by starting with electron beam evaporated Mo using plasma enhanced chemical vapor deposition (PECVD) in the ambience of H$_2$S. This was the first report of the direct deposition of wafer scale 2D MoS$_2$ onto flexible substrates (at temperatures between 150 and 300 °C) without using a transfer method.\cite{81,111} These films exhibited an average mobility of 3.7 cm$^2$ (V·s)$^{-1}$. The low temperature PECVD approach opens a new pathway for the synthesis of 2D materials directly onto plastic substrates, and can be extended for the fabrication of transparent flexible semiconductor devices with high quality and uniformity.

### Chemical Vapor Deposition Using MoCl$_5$ Precursor

Yu et al.\cite{116} reported the growth of monolayer and bilayer MoS$_2$ films on SiO$_2$, sapphire, and graphite substrates using MoCl$_5$ and sulfur precursors at relatively high temperatures (>$800\ ^\circ\text{C}$). They showed that the number of layers in the resulting MoS$_2$ films can be precisely controlled by modifying the amount of MoCl$_5$. The as-grown films showed an n-type behavior with a field effect mobility varying in the range $0.003–0.3\ \text{cm}^2$ (V·s)$^{-1}$. More recently, McCready et al.\cite{54} demonstrated the synthesis of large area monolayer heterostructures comprising of MoS$_2$/graphene on SiO$_2$/Si substrate using MoCl$_5$ and S precursors (Figure 6e). In that study, the graphene was grown on Cu foil and then transferred onto the SiO$_2$/Si substrate. The schematic diagram of their experimental set up is depicted in Figure 6e.

### Chemical Vapor Deposition Using MoS$_2$ Precursor

Wu et al.\cite{117} used MoS$_2$ precursor to obtain high optical quality monolayer MoS$_2$ on a variety of insulating substrates (SiO$_2$, sapphire, and...
The growth was carried out in a horizontal quartz tube furnace with MoS$_2$ powder as the source placed at the center of the furnace which was heated to 900 °C with Ar as the carrier gas. Substrates were kept at ≈650 °C and were placed far from the center of the tube. The triangular shaped islands of MoS$_2$ monolayers with side lengths up to ≈25 µm were obtained by this method. A slightly modified method was proposed by Luo et al.[23] which involved the direct decomposition of MoS$_2$ at 900 °C (Figure 6f). They successfully grew large areas of double layer MoS$_2$ on SiO$_2$ substrates and found that the films were highly sensitive to photo illumination.

Although CVD is a promising technique and is capable of producing large area MoS$_2$ films, the CVD grown MoS$_2$ mono/few layer(s) are still poor in quality and their carrier mobilities are significantly low[53,96,109] compared to exfoliated flakes due to the high temperature growth processes that induce various kinds of defects in the final sample.[103,118–120] Therefore, there is a need for developing alternative synthesis methods capable of producing high quality and large area MoS$_2$ thin films with a good control over the number of layers.

2.2.2. Physical Vapor Deposition

In a recent study, Late et al.[121] employed a relatively less explored physical vapor deposition technique, specifically pulsed laser deposition (PLD), for producing nearly stoichiometric nanostructures of MoS$_2$ on a tungsten tip as well as on Si substrates. Their method involved the laser ablation of a MoS$_2$ target prepared from MoS$_2$ powder. The deposition was carried out at 700 °C under Ar atmosphere with a pressure of 1 × 10$^{-2}$ mbar and a laser energy density of 2 J cm$^{-2}$.[24] Later, Loh et al.[122] studied the growth mechanism of few layer MoS$_2$ on variety of metal substrates (Cu, Ni, Al, Ag) using PLD and demonstrated that the highly crystalline few layer MoS$_2$ can be grown on Ag substrates using a laser energy density of 5 J cm$^{-2}$, but not on other metallic substrates due to either excessively strong or poor ad-layer substrate interactions. However, the growth of semicrystalline few layers MoS$_2$ was achieved on Al substrates by adjusting a longer deposition time coupled with very high laser energy density of 20 J cm$^{-2}$, suggesting that the substrate interactions can be screened out by increasing the supply of Mo and S atoms at the surface by using large laser energies. In a subsequent study, Serrao et al.[57] reported PLD grown highly crystalline few layers MoS$_2$ thin films consisting of monolayers on 5 × 5 mm$^2$ substrates of Al$_2$O$_3$ (0001), GaN (0001), and SiC-6H (0001). Similarly, RHEED-assisted pulsed laser deposition of layered MoS$_2$ on c-sapphire has also been demonstrated recently.[56] In a more recent study, Siegel et al. reported the PLD growth of centimeter scale, atomically thin MoS$_2$ thin films on c-sapphire, using large laser energies. In a subsequent study, Siegel et al.[123] reported the PLD growth of centimeter scale, atomically thin MoS$_2$ thin films. They demonstrated that the number of monolayers in the MoS$_2$ film can be precisely controlled down to a single monolayer (ML) by just controlling the number of incident laser pulses. The schematic process starting from MoS$_2$ powder to the growth of centimeter scale 1 monolayer (ML), 2 ML, 3 ML, 4 ML, 10 ML, and 60 ML is shown in Figure 7.

3. Device Applications

One of the main benefits of MoS$_2$ compared to graphene is its nonzero band gap. Specifically, graphene has a zero band gap;
it is semimetallic in nature, which means even though it has a very high mobility, transistors made from it cannot be effectively turned off. MoS₂, however, has a nonzero band gap and acts as a semiconductor, which means it is a suitable candidate for applications in electronic and logic devices as its conductivity can be modulated. Additionally, although MoS₂ exhibits an indirect band gap in the bulk phase, when its thickness is reduced to a single monolayer its band gap becomes direct. This implies that monolayer MoS₂ can also find application in optoelectronic devices. Furthermore, due to the 2D nature of MoS₂, electrostatic control of the material also becomes viable that can allow for the creation of low power electronic devices and short channel FETs. This section gives an overview of the progress made in electronic and optoelectronic device technology using mono/few layer MoS₂ films.

3.1. Field Effect Transistors Based on MoS₂

The most fundamental component of modern electronic devices is the field effect transistor (FET). Steady advances and progress in semiconductor manufacturing technology, particularly in lithography, have allowed the reduction of transistor sizes to just a few nanometers. The latest breakthrough of Intel’s 3D device processors has a 14 nm node in silicon-based metal-oxide-semiconductor field effect transistors (MOSFETs). Despite the many desirable advantages like cost reduction, fast switching, and lower power consumption associated with the size reduction of transistors, scaling much further beyond 14 nm has limitations due to quantum mechanical tunneling between the drain and the source of the transistors as well as due to joule heating.[23] In order to make nanometer-sized devices that are free from short-channel effects, it is necessary to use thinner gate oxides as well as thinner channel materials. This can be easily understood by looking into the Poisson equation modeled for natural length[123]

\[
\lambda = \sqrt{\varepsilon_a \varepsilon_m d_a / \varepsilon_m}
\]

In the above equation, \(\varepsilon_a\) and \(\varepsilon_m\) are dielectric constants of the channel material and the gate oxide, whereas \(d_a\) and \(d_m\) correspond to the thicknesses of channel and the oxide layer, respectively. The 2D van der Waals materials are considered as an excellent choice for channel material and it is expected that by using these materials, it will be possible to continue miniaturization much beyond the physical limits of current silicon-based technology.[25-27]

The first mechanically exfoliated MoS₂-based FET was reported by Novoselov et al. in 2005,[5] soon after their pioneering work on graphene. They found, however, that the material displayed a low mobility of \(\approx 3 \text{ cm}^2 \text{ (V-s)}^{-1}\) and a relatively low on/off ratio. The issue of lower mobility in single layer MoS₂ transistors was addressed by Radisavljevic et al.[17] by using a high-k dielectric material, HfO₂. To date, this report is treated as the first successful demonstration of a switchable transistor using single layer MoS₂. In their work, an exfoliated MoS₂ monolayer was transferred onto a silicon substrate covered with 270 nm thick SiO₂. HfO₂ was used as the top gate oxide. The measured top gate width was reported as 4 µm and top gate length, source to gate, and gate to drain spacings were 500 nm (Figure 8a,b). The top gated MoS₂ FET demonstrated significant improvement in the mobility \(> 200 \text{ cm}^2 \text{ (V-s)}^{-1}\) with a drain current on/off ratio of \(10^6\) and a subthreshold swing (SS) of 74 mV dec⁻¹ (Figure 8c). The device showed a maximum on-current of 10 µA (2.5 µA µm⁻¹) and a transconductance of 4 µS (1 µS µm⁻¹). Yoon et al.[124] performed subsequent simulation studies to estimate the ultimate performance limit of top gated MoS₂ monolayer transistors using HfO₂ as the top gate dielectric material \((L_g = 15 \text{ nm} \text{ and } t_{ox} = 2.8 \text{ nm})\), analogous to the previous experimental device. The simulation results (Figure 8d) predicted a high on-off ratio \(>10^{10}\) and sharp switching (SS \(\leq 60 \text{ mV} \text{ dec}^{-1}\)) with excellent short channel behavior (drain induced barrier lowering as low as 10 mV V⁻¹).

In a subsequent experimental study, Lembke and Kis demonstrated a high performance transistor with a mobility of \(1090 \text{ cm}^2 \text{ (V-s)}^{-1}\) at a drain voltage of 20 mV[125] which is the highest mobility reported so far for monolayer MoS₂ transistors. This high value was understood to be due to full-channel gating. Furthermore, their transistors exhibited almost two orders of magnitude enhancement in the on-current (250 µA µm⁻¹) compared to previous reports. The high on-current in these transistors can support large current densities, close to \(5 \times 10^7 \text{ A cm}^{-2}\), which is 50 times higher than the critical current density of copper. This is understood to be due to much stronger intralayer Mo-S covalent bonds in 2D MoS₂ than metallic bonds. Besides, its success for digital electronics applications[126-128] the above results demonstrate that monolayer MoS₂ could also be an interesting candidate for analog circuit applications as it could provide better power gains and support larger current densities as well. More recently, Krasnozhon et al.[129] tested the operational radio frequency (RF) performance of top-gated monolayer, bilayer, and trilayer MoS₂ transistors in the gigahertz range of frequencies, where commercial devices are operated. The results of these MoS₂ RF-FETs show an intrinsic transconductance higher than 50 µS µm⁻¹, a saturation of drain-source current, and a voltage gain larger than 1 up to 5 GHz frequency. Trilayer MoS₂ FETs have shown a cut off frequency as high as 6 GHz. Although the performance of the RF-MoS₂ FETs are rather limited, further modification in device geometry and material processing could lead to the realization of full potential of 2D semiconductors for low-cost and flexible, high-frequency analog current and voltage amplifiers as well as high-frequency logic circuits. Considering the potential of single layer MoS₂ transistors for forming short channel FETs, there have been many studies where various different kinds of gate dielectrics such as Al₂O₃,[130,131] ionic liquid,[132-134] and polymer gated dielectrics[135,136] were utilized. The use of Al₂O₃ dielectric in a bottom gate multilayer MoS₂ FET device gave rise to a mobility of 100 cm² (V-s)⁻¹[137] that was significantly elevated to 170 cm² (V-s)⁻¹ and 517 cm² (V-s)⁻¹ for top-gated and dual-gated single layer MoS₂ FET devices, respectively.

A common characteristic of charge carriers in 2D materials is their low effective mass, which helps fast charge transport across the material and hence the high field effect mobility in FETs. However, low effective mass also implies low density of states near the band edges, which leads to high contact resistance at 2D material-metal interfaces because of the reduced
availability of states for effective charge injection. None of the metal-MoS₂ interfaces are completely Ohmic and hence the formation of Schottky barriers at the metal/channel interface causes substantial reduction in the device mobility due to high contact resistance. There have been proposed methods, either using a low work function material, or surface doping in the contact region via chemical/molecular doping, in order to achieve highly transparent tunneling contacts. Alternatively, Perera et al. introduced electrostatic doping through use of an ionic liquid (Figure 8e) as the top gate to achieve low resistance MoS₂/metal tunneling contacts. This study demonstrated remarkable enhancement in the mobility from ≈100 to 220 cm² (V-s)⁻¹ when the temperature decreased from 180 K to 77 K (Figure 8f). Moreover, the use of an ionic liquid as the dielectric material resulted in ambipolar operation in contrast to the commonly observed n-type behavior.

Even though the use of an ionic liquid gate in MoS₂ FETs is highly successful, the instability of the liquid body causes a hindrance for all practical purposes. This critical problem associated with liquids has recently been resolved by gelation. An ionic gel is capable of combining the flexibility of an organic polymer dielectric with the high performance of an ionic liquid. In more recent studies, the use of polymer-based electrolytes has also been demonstrated. The capping of the polymer electrolyte (PE), consisting of poly(ethylene oxide)
(PEO) and lithium perchlorate (LiClO$_4$), on top of MoS$_2$ devices has driven a threefold enhancement in the mobility of MoS$_2$ FETs owing to significant reduction in the resistance at the MoS$_2$/metal interface and dielectric screening at the channel/dielectric interface.\textsuperscript{135} Bao et al. showed that multilayer MoS$_2$ FETs on polyethylene methacrylate (PMMA) exhibits an ambipolar behavior with a high mobility of 470 cm$^2$ (V·s)$^{-1}$ for electrons and 480 cm$^2$ (V·s)$^{-1}$ for holes.\textsuperscript{136}

There are some other methods, like phase engineering,\textsuperscript{147,148} and insertion of graphene,\textsuperscript{149} which have been explored for reducing contact resistance at metal–2D semiconductor interfaces. Kappera et al. reported a contact resistance of 200–300 $\Omega$·µm, at zero gate bias, by locally inducing metallic 1T phase of MoS$_2$ on semiconducting 2H phase.\textsuperscript{147} Such phase engineering approach, where inducing a metallic phase of the same semiconducting material reduces the contact resistance, has been found effective in reducing the contact resistance in other 2D systems as well.\textsuperscript{148} Leong et al. demonstrated that insertion of an etched graphene as a buffer layer at metal-MoS$_2$ interface can lead to low contact resistance.\textsuperscript{149} They achieved a contact resistance of 200 $\Omega$·µm with nickel-etched-graphene electrode on MoS$_2$.

3.2. Integrated and Logic Circuits Based on MoS$_2$

The transistors based on single layer/few layer(s) MoS$_2$ show promising mobility, high on/off current ratio, and record current density. These appealing transistor device characteristics enable 2D MoS$_2$ to be a potential candidate for consideration toward building digital circuits comprising of Boolean logic gates and memory components. In this direction, Radisavljevic et al.\textsuperscript{126} and Wang et al.\textsuperscript{127} have demonstrated research scale logic circuits based on exfoliated single layer and bilayer MoS$_2$. The first logic device, composed of two single-layer transistors connected in series fabricated on a single flake of monolayer MoS$_2$, was demonstrated as the most basic logic gate: a logic inverter, capable of converting logic state 0 (low input voltage state) into logic state 1 (high output voltage state) (Figure 9a–c). Connecting two transistors in parallel and using an external resistor as a load, a NOR gate was realized (Figure 9d). In a later report, Wang et al.\textsuperscript{128} presented large scale integrated circuits based on CVD grown, single layer MoS$_2$. The devices included fully integrated inverters and NAND gates operated in depletion mode. The demonstration of two types of universal logic gates, NAND and NOR, enables the realization of all other possible logic gates (AND, OR, XOR, etc.) using combinations of NAND gates or NOR gates.\textsuperscript{126,127} This is indeed an important step toward 2D nanoelectronics.

A static random access memory (SRAM) element has also been demonstrated using a pair of cross-coupled inverters.\textsuperscript{127} This memory cell has two stable states, 0 and 1 at the output, and can be set to logic state 1 (or 0) by applying low (or high) voltage to the input. Coupling the high conductivity of graphene with the unique semiconducting properties of 2D MoS$_2$, Bertolazzi et al.\textsuperscript{150} demonstrated an all-2D nonvolatile memory cell based on MoS$_2$/graphene heterostructures with a floating gate design. The device included not only a 2D channel (MoS$_2$), but also 2D source and drain contacts (graphene strips) and floating gate (few layer graphene). The information storage and erasing process can be understood from its transfer characteristics performed in two sweeping directions (Figure 9e) and energy band diagram of the memory device in program and erase states (Figure 9f). The large hysteresis (memory) window of 8 V allows the charging (program state) and discharging (erase state) of a floating gate that corresponds to the control gate sweeping direction from −15 to +15 V and from +15 to −15 V, respectively. The dynamic behavior of the switching between the program state and the erase state was achieved through the application of voltage pulses to the control gate at a drain-source bias of 50 mV. A maximum program/erase (P/E) current ratio of 10$^4$ of the nonvolatile memory device not only allows easy readout of the device state, but also enables multilevel storage. The successful operation of these initial prototype memory cells will pave the way for efficient and scalable devices through the engineering of blocking oxide layers using 2D oxides. In addition to the demonstration of a wide range of digital and logic circuits based on single layer MoS$_2$ FETs, analog circuits such as a small signal amplifier with a room temperature gain of four has also been reported using single layer MoS$_2$ transistors.\textsuperscript{151}

3.3. Optoelectronic Devices

The presence of a direct band gap in the visible frequency range, coupled with its high carrier mobility makes monolayer MoS$_2$ an ideal candidate for various optoelectronic device applications like light generation (LEDs), light harvesting (solar cells) and light sensing (photodetectors).\textsuperscript{122,124,104,152} Several research scale prototype optoelectronic devices based on single or few layer MoS$_2$ have already been demonstrated. A brief description of these devices is given below.

3.3.1. Photodetectors

The sizable, thickness dependent band gap of MoS$_2$ nanosheets along with its large surface-to-volume ratio enable efficient light detection over a wide range of wavelengths from ultraviolet (UV) to the near infrared (NIR).\textsuperscript{153,154} The irradiation of photons of energy greater than the band gap of a semiconductor gives rise to a photocurrent upon the separation of photogenerated electron–hole pairs (excitons) through an applied or built-in field. There are two fundamental designs for semiconductor-based photodetectors: phototransistors (applied field or gate control) and photodiodes (built-in field).

The very first single layer MoS$_2$ photodetector device, a phototransistor, was fabricated by Yin et al.\textsuperscript{155} (Figure 10a,b). This device exhibited an increased photocurrent for excitation wavelengths below 670 nm with good photosensitivity of 7.5 mA W$^{-1}$ (Figure 10c,d), which is very high compared to graphene-based transistors’ photosensitivity (1 mA W$^{-1}$).\textsuperscript{156} Also, the transition speed for current rise (OFF to ON) or current decay (ON to OFF) is quite fast (50 ms) which reveals a fast response/recovery speed of single layer MoS$_2$ phototransistors. However, the response/recovery rate in these devices is still far lower than graphene transistors (tens of picoseconds),\textsuperscript{157} which is accounted by the lower mobility of these back
gated phototransistors (0.11 cm² (V-s)^{-1}). Lee et al. demonstrated transparent top gated phototransistors based on mono-, bi-, and trilayer MoS₂ nanosheets. The bi- and trilayer transistors showed good photoresponse to red, green, and UV light due to their respective band gaps of ≈1.65 and ≈1.35 eV, whereas monolayer MoS₂ transistor barely responded to red light due to its comparatively equal gap (≈1.82 eV), but was still sensitive to green and UV lights. The thickness modulated linear mobility values were estimated to be as high as 80, 27, and 10 cm² (V-s)^{-1} with longer response and recovery times of 1.5, 1, and 0.3 s respectively for single, double, and

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**Figure 9.** a) Schematic of integrated circuit consisting of two top-gated transistors connected in series and b) cross-sectional view of the single layer MoS₂ transistor together with electrical connections. c) Output voltage as a function of input voltage for integrated MoS₂ inverter and d) Output voltage characteristics for different combinations of input voltage for NOR gate logic circuit based on single layer MoS₂ transistor. e) Transfer characteristics of floating gate transistor in two sweeping directions with large hysteresis memory window of 8 V and f) simplified band diagram of the memory device in program and erase states. a–d) Reproduced with permission. Copyright 2011, American Chemical Society. e,f) Reproduced with permission. Copyright 2013, American Chemical Society.
triple-layer transistors. In a later study, Choi et al.\textsuperscript{[154]} demonstrated ultrasensitive bottom gate (Al\textsubscript{2}O\textsubscript{3}) multilayer MoS\textsubscript{2} photodetectors with high photoresponsivity (>100 mA W\textsuperscript{−1}) for a wide range of wavelengths from UV to the NIR. They suggested that the narrow band gap of multilayer MoS\textsubscript{2} is more advantageous than single layer MoS\textsubscript{2} for wide range light detection and also that the bottom gate configuration is more viable for commercial fabrication than using a high-K material for a top gate.

Figure 10. a) Atomic force microscopy image of exfoliated monolayer MoS\textsubscript{2}. b) Optical microscopy image of first monolayer MoS\textsubscript{2} phototransistor with Ti/Au metal contacts for source and drain. c) The photocurrent (I\textsubscript{ph}) of transistor as a function of excitation wavelength for fixed optical power of 80 µW. d) Variation in photoresponsivity with gate voltage at V\textsubscript{ds} = 1 V and constant optical power of 80 µW. The device shows maximum photoresponsivity of 7.5 mA W\textsuperscript{−1} for gate voltage of 50 V.\textsuperscript{[155]} e) Photograph of CVD MoS\textsubscript{2} monolayer grown on graphene/SiO\textsubscript{2}/Si. f) Schematic representation of graphene/MoS\textsubscript{2} phototransistor with source and drain contacts (Ti/Au = 5 nm/80 nm). g) Photoresponse and h) photogain characteristics of graphene/MoS\textsubscript{2} phototransistor as a function of power densities.\textsuperscript{[104]} a–d) Reproduced with permission.\textsuperscript{[155]} Copyright 2012, American Chemical Society. e–h) Reproduced with permission.\textsuperscript{[104]} Copyright 2014, Nature Publishing Group.
In a later study, Zhang et al.\textsuperscript{[158]} studied the performance of CVD grown monolayer MoS\textsubscript{2} phototransistors in ambient conditions. This study demonstrated that the photoresponsivity and photogain of the devices are severely affected by the surface accumulation of air adsorbates, which diffuse toward the MoS\textsubscript{2}/SiO\textsubscript{2} interface. The decrease of phototransistor performance was theorized to be due to the adsorbates from the air acting as p-type dopants and leading to the dominance of p-type behavior, rather than n-type as is seen under vacuum. These p-type dopants on the surface or at the MoS\textsubscript{2}/SiO\textsubscript{2} interface impose additional coulomb potential, which interacts strongly with the out of plane $A_{1u}$ mode, resulting in an abnormal increase in carrier scattering. Extensive Raman analysis of MoS\textsubscript{2} monolayers has been done with laser exposure under an Ar ambient to confirm the p-type doping of air and its effects on MoS\textsubscript{2} Raman modes. Surprisingly, Lopez-Sanchez et al.\textsuperscript{[159]} demonstrated an improved responsivity (1.04 A W\textsuperscript{−1}), photogain (up to 24), and fast response/recovery times (40 50 $\mu$s\textsuperscript{−1}) with the use of trilayer MoS\textsubscript{2} in Au—MoS\textsubscript{2}—Au photodetectors.\textsuperscript{[164]} The reason for the faster response times/recovery times were attributed to the decrease of contact spacing from 8 to 4 $\mu$m, which induces a higher electric field at the Au/MoS\textsubscript{2} interface under the same applied bias. In addition, PDs based on p-Si/n-MoS\textsubscript{2} heterojunction have also been tested. However, these yielded lower rise and fall times of 0.3 ms compared to conventional MSM PDs. In a later study, Jariwala et al.\textsuperscript{[165]} demonstrated a gate-tunable p–n heterojunction photodetector through the integration of p-type single-walled carbon nanotubes and n-type MoS\textsubscript{2} monolayer. Their photodetector exhibited an ultrafast photoresponse time (<15 $\mu$s) and a high spectral responsivity (≈0.1 A W\textsuperscript{−1}) at 650 nm.

### 3.3.2. Light Generation and Harvesting

In 1939, R.S. Ohl from Bell Labs accidentally discovered the p–n junctions during the purification process of Si crystals.\textsuperscript{[164]} This pioneering discovery led to the development of a variety of optoelectronic devices for light generation (LED), light harvesting (solar cells), and detection of light (photodetectors). To date, efficient LEDs and solar cells employ technology that involves epitaxial III-V alloys or multielemental materials (such as CIGS) due to the lack of simple materials having a direct band gap in the visible spectrum. Recently, atomically thin TMDCs of molybdenum disulfide (Mo) and tungsten (W) have opened up fantastic avenues for novel optoelectronic device designs due to the presence of a finite and direct band gap in these materials.\textsuperscript{[6,25,26]} The first report on electroluminescence (EL) from single layer MoS\textsubscript{2} was presented by Sundaram et al.,\textsuperscript{[22]} in metal-MoS\textsubscript{2} Schottky junction through a hot carrier injection process. Although this study was considered a breakthrough for light emitting applications, the EL was locally confined and the high threshold power required for light emission and poor carrier-to-photon conversion efficiency ($10^{-5}$) made these devices almost impractical. The reason for locally confined EL in lateral metal-MoS\textsubscript{2} junctions was attributed to the full depletion of the monolayer that prevents the efficient carrier injection across the entire monolayer. To achieve broad area EL, vertical p–n structures were proposed that can enable threshold-free recombination. In this way, Lopez-Sanchez et al.\textsuperscript{[167]} introduced a novel, vertical 2D-3D heterostructure diode composed of monolayer MoS\textsubscript{2} (n-type) and p-Si for EL devices and solar cells. The rectifying behavior of MoS\textsubscript{2}/p-Si diode (Figure 11(a)) indicated that all related optoelectronic operations could be achieved using the combination of atomically thin MoS\textsubscript{2} and a 3D semiconductor. The application of a forward bias induces light emission, resulting mainly from radiative recombination in MoS\textsubscript{2}, as radiative recombination in Si is less significant due to its indirect gap (Figure 11(b)). Moreover, the EL is active over a large area (Figure 11(c,d)) compared to previously local-gated electroluminescence\textsuperscript{[22]} in
metal-MoS₂ Schottky junctions and exciton-related EL confined at the heterojunction edge of MoS₂/p-Si. The observation of large area emission is attributed to the hydrogen passivation of the Si, resulting in the formation of a true junction between MoS₂ and p-Si. The heterojunction was also operated as a solar cell and showed a maximum light-to-electrical power conversion efficiency of 4.4%. There are also some other reports on ultrathin MoS₂ PV devices; however, those reports are mainly based on multilayer MoS₂ nanosheets. Recently, Tsai et al. reported the photovoltaic operation over a large area using monolayer MoS₂ with p-Si to form a type-II heterojunction. Such a heterojunction photovoltaic device achieved a power conversion efficiency of 5.23%, which is the highest value reported among all monolayer TMDC-based solar cells (Figure 11e,f).

The results show that monolayer MoS₂/Si solar cells hold promise for the integration of 2D materials with commercially available Si-based electronics and optical devices. Combining the advantage of high optical absorption of graphene and WS₂, Bernardi et al. studied the performance of 1 nm thick solar cells based on MoS₂/Graphene and MoS₂/WS₂ bilayer. Their computational studies showed that such bilayer solar cells can reach over 1% power conversion efficiency in just 1 nm thickness, thus holding a packing power density of 2.5 MW Kg⁻¹, a value far superior to any known ultrathin solar cells.

Although MoS₂ has distinctive optical properties for strong light-matter interaction, the lack of controlled doping strategies and the difficulty in achieving hole conduction in monolayer MoS₂ hinders the fabrication of atomically thin...
homogeneous p–n junctions.\cite{127} Earlier attempts to demonstrate the formation of stable MoS$_2$ p–n junction devices by using electric double layer gating\cite{140} or creating p-doped MoS$_2$ by efficient plasma treatment\cite{173,174} was not feasible as these liquid gating and plasma treatments can damage the atomically thin structure. The exploitation of intrinsically p-type TMDCs having different band gaps and work functions\cite{175} led to van der Waal p–n heterostructures of p-WSe$_2$/n-MoS$_2$, which are promising for applications in optoelectronic devices such as light emitting diodes\cite{152} solar cells\cite{176,177} and photodiodes.\cite{178}

### 3.4. Valleytronic Applications

Single layer MoS2 has attracted tremendous attention recently because of its potential application in valleytronics.\cite{179–181} Valleytronics is a new paradigm of electronics that utilizes materials in which the conduction (valence) band exhibits two or more minima (maxima) at equal energies but at different momentum values.\cite{182–184} Thus, in addition to charge and spin, these materials have an additional degree of freedom to play with.\cite{185} Valley polarization in these materials is achieved by controlling the number of charge carriers in the valleys. Devices based on selective valley conduction are termed as valleytronic devices. Monolayer MoS$_2$ is considered a promising material for valleytronic device applications since its conduction band and valence band edges have two energy degenerate valleys at the corners of the first Brillouin zone.\cite{179–181} Moreover, unlike graphene, the breaking of inversion symmetry, strong spin–orbit coupling and existence of a direct band gap are added advantages in the case of monolayer MoS$_2$.

The most challenging task in valleytronics research is to identify a suitable technique to address the carriers in different valleys separately. Schemes based on inversion symmetry breaking, which can lead to circular dichroism in different k-space regions, have been suggested by many researchers.\cite{185,186} Since monolayer MoS$_2$ does not have an inversion symmetry, selective photoexcitation by circularly polarized light can be used as a means of controlling the valley population.\cite{187,188} Carriers in different valleys can be addressed by controlling the angular momentum of the excitation photon (i.e., helicity of the light). Photons with a given circular polarization excite the electrons of only a particular spin. Because of the strong spin–orbit interaction in MoS$_2$, the momentum of the electrons, which are excited by the photons, is determined by their spin. Therefore, right and left circularly polarized light can selectively populate two different valleys in monolayer MoS$_2$. Moreover, it has been shown that in bilayer MoS$_2$, the inversion symmetry can be broken by an external electric field applied normal to the plane. This leads to a potential difference between the individual layers and allows the control of valley polarization.\cite{189}

Despite the promising nature of single and bilayer MoS$_2$ for valleytronic applications, the technology is still in infancy. Much more research is needed to develop techniques for selectively populating the valleys and also for selectively detecting the corresponding valley polarized current.

### 3.5. Multilayer van der Waals Heterostructures

The multilayer van der Waals structures are created by stacking various 2D atomic crystals on top of each other with a chosen sequence.\cite{6,190} The resulting stack represents an artificial van der Waals material analogous to Lego blocks—where each block is an individual 2D material\cite{6} (Figure 12a). The concept of designing artificial heterostructures has been demonstrated experimentally by stacking graphene/hBN or graphene/MoS$_2$/graphene (GMG) or graphene/MoS$_2$/metal (GMM) to realize vertical field effect transistors (VFETs), and superlattices (Figure 12b).\cite{191–196} The use of hBN in conjunction with graphene produces high electronic quality heterostructures\cite{197,198} but causes an insufficient on/off current ratio due to hBN’s larger band gap (≈5.97 eV). Larger on/off ratios would be expected for a graphene/MoS$_2$ VFET, owing to MoS$_2$’s smaller band gap as compared to hBN. The earliest experiments on MoS$_2$-based heterostructures were conducted by Britnell et al.\cite{192} utilizing a vertical stack consisting of graphene/MoS$_2$/graphene (GMG) for tunneling field effect transistors. In that report, the authors demonstrated two different types of graphene-based heterostructures with few layer hBN or MoS$_2$ acting as the insulating tunnel barrier. Tunneling transistors utilizing MoS$_2$ exhibited three orders of magnitude higher on-off ratio (≈10$^4$) compared to those utilizing hBN-based (≈50).

Yu et al.\cite{199} designed an n-channel VFET by sandwiching few-layer MoS$_2$ between monolayer graphene and an ohmic-contact metal top electrode (GMM). The optimized VFET delivered a high on-current density of up to 5000 A cm$^{-2}$, which is 3–5 orders of magnitude greater than the recently reported vertical tunneling transistor\cite{195} and graphene barristor,\cite{200} while retaining a high on-off ratio of >10$^4$ (Figure 12c,d). Under negative $V_{sd}$ regime the Schottky barrier at the contact between graphene and MoS$_2$ plays a dominant role in current modulation, whereas under positive $V_{sd}$ conditions the top metal–MoS$_2$ contact plays the primary role in determining the current modulation (Figure 12e). An extensive study was conducted to further understand the charge transport mechanism in their VFETs by considering three different device configurations that included a graphene–MoS$_2$–graphene tunneling barrier (GMG TB), a graphene–MoS$_2$–graphene Schottky barrier (GMG SB) and a graphene–MoS$_2$–metal (Ti) Schottky barrier (GMM SB) with variable MoS$_2$ thicknesses. It was found that the charge transport mechanism in the GMG heterostructures and their variants depends on the thickness of the MoS$_2$ layer, consistent with the earlier reports.\cite{192} For ultrathin MoS$_2$ layers (<4 nm), the tunneling current is the dominant component in charge transport, whereas for thicker MoS$_2$ films (4–40 nm), thermionic emission current is the dominant component.

In a later report, Myoung et al.\cite{201} showed that the current on-off ratio of the vertical graphene field-effect transistor can be enhanced by up to 10$^6$ by replacing the top graphene electrode (Gr$_T$) by an armchair or zigzag graphene nanoribbon (AGNR or ZGNR), which is one order larger than their conventional GMG heterostructures. The improvement in the current on-off ratio of graphene/MoS$_2$/AGNR was attributed to the one-dimensional nature (van Hove singularity) of AGNRs. Myoung et al.\cite{201} also exploited the magnetic properties of atomically thin MoS$_2$ by calculating the spin-dependent
tunneling current through a magnetic MoS$_2$ (m-MoS$_2$) in GMG heterostructures (Figure 12f). Their calculations predicted that the graphene/m-MoS$_2$/graphene heterostructure can act as a spin-filter for holes due to the difference in spin-splitting near the K-valley of m-MoS$_2$. The spin splitting is about 50 times larger in the valence band ($\delta v \approx 145$ meV) than in the conduction band ($\delta c \approx 3$ meV). The large spin-splitting energy in the valence band leads to a strong spin-polarization in the hole tunneling current, $P_j \approx 0.9–0.97$ (Figure 12g,h). Most recently, Huo et al.\cite{178} demonstrated vertical heterojunctions comprising of p-WSe$_2$/n-MoS$_2$, which are shown to exhibit distinct rectification behavior as well as ambipolar conduction with an n-type on/off ratio of $10^2$ and a p-type on/off ratio exceeding $10^4$ from the p-channels of WSe$_2$ and n-channels of MoS$_2$.

In addition to the earlier demonstrations of graphene/MoS$_2$-based vertical heterostructures for novel electronic applications, these heterostructures have also been exploited for optoelectronic device applications by making use of the direct band gap of MoS$_2$. Yu et al.\cite{204} used vertically stacked GMG and GMM heterostructures to obtain highly efficient, gate-tunable photocurrent generation and photodetection. They demonstrated that the amplitude and polarity of the photocurrent in the gated vertical heterostructures can be readily modulated by the electric field of an external gate to achieve a maximum external quantum efficiency of 55% with corresponding photoresponsivity of $\approx$0.22 A W$^{-1}$ and faster response times (<50 $\mu$s).
Most recently, MoS₂-graphene-metal hybrid structures were demonstrated to work as multifunctional photoresponsive memory devices with a room temperature photoresponsivity of up to $5 \times 10^8 \text{ A W}^{-1}$ [205], which is the highest to date among the graphene-based photodetectors. Similar to graphene/MoS₂ PDs, a novel semiconducting PD consisting of MoS₂-WS₆ has been shown to exhibit a high photoresponsivity of 1.42 A W⁻¹ [190]. A novel heterostructure based on MoS₂ PDs comprising of p-type black phosphorus/n-type monolayer MoS₂ has also been demonstrated recently [206]. These p–n diodes exhibit gate-tunable current-rectifying characteristics and show a maximum photoresponsivity of 418 mA W⁻¹ at 633 nm with a photovoltaic energy conversion of 0.3% upon illumination. This successful concept demonstration and realization of a variety of multilayer van der Waals heterostructures show great promise to design truly atomic scale, functional heterostructures, and circuits.

4. Conclusions and Outlook

In this review, we have highlighted the recent findings and key studies on the synthesis and fundamental properties of atomically thin MoS₂ that are relevant in context to their potential application in the next-generation electronic and optoelectronic devices. Most of the reports in this field so far are based either on mechanically exfoliated MoS₂ flakes or on CVD grown MoS₂ films. The exfoliation methods produce device quality flakes; however, the extremely smaller size of the flakes and low yield makes them unsuitable for large area applications. CVD is a promising technique for producing large area devices. However, the CVD grown MoS₂ mono/few-layer films are poor in quality and their carrier mobility is significantly low. Thus, significant improvements in the growth processes capable of producing high quality and large area MoS₂ ultrathin films is needed for making further progress in this field. Moreover, a majority of the MoS₂-based devices reported till date exhibit unipolar (n-type) conduction and there is no control over intrinsic doping levels in MoS₂. Controllable doping strategy to achieve ambipolar conduction in monolayer MoS₂ is highly desirable. Several doping strategies such as, substitutional doping, edge sites doping, surface adsorption doping and electrostatic doping have been proposed recently [207–212], but, there still remains a challenge to maintain doping stable and efficient. Another major challenge in this field is the high contact resistance encountered at the source and drain end of the metal/MoS₂ interface, which severely affects the final mobility of the device. There have been number of studies to address the above challenge by exploring various different contact materials having different work functions (Au, Pt, Ni, Ti and Sc) [119,140,213,214], but, still much more work is needed in this area to solve the problem completely. Similarly, more research is needed on van der Waals heterostructures to fully understand the concept of junction formation in atomically thin layers. In summary, over the last few years, atomically thin MoS₂ has emerged as an alternate to graphene. Lot of exciting work is going on in this area and it looks like that this is just a matter of time when the technology based on these 2D materials will replace the present silicon based CMOS technology.

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