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Transition Metal Dichalcogenides: A Review

Sumi Bhuyan
Department of Physics
Digboi College
Digboi, India

Abstract:- The remarkable findings of graphene has again led to the renewed interest in two dimensional inorganic system, transition metal dichalcogenides (TMDCs). Its fascinating structural property, with strong in plane bonding and out of plane interactions helps in exfoliating two dimensional layers of single unit cell thickness. Bulk TMDCs has been studied over a decade, but its recent advances in nanoscale fabrication and exfoliation mechanisms, layered samples have shown promising applications in optics and electronics industry. Bulk TMDCs having an indirect band gap changes into layers of direct band gap and are promising candidate for photodetectors, transistors and electroluminescent devices. In this review article I will discuss about the different fabrication techniques, optical properties and its future prospect of MoS_2.

I. INTRODUCTION

Transition Metal Dichalcogenides (TMDCs) are the oldest know materials which can be classified from semiconductors to insulators [1]. Out of all TMDCs, MoS_2 is one of the oldest one. Comprehensive studies has already been made of this system but its relevance is most prominently observed in today's material technology because of its advances in sample fabrication, optical study, transfer of layers, manipulation of 2D materials and the expertise gained in studying 2D layered system like graphene. This article deals with a review on the growth of different TMDCs along with brief discussion about its optical properties. The number of publications on TMDCs per year is exponentially increasing. Because of its flexible band gap engineering technique, growers are increasingly taking interest in manufacturing thin films by both sandwiching different materials with TMDC layers, as well as exfoliating TMDCs upto single layers with different capping elements to enhance both electrical and optical properties [2]. A total of 60 different TMDCs are known at present, out of which two-thirds are layered materials. Most of the layered TMDCs are synthetic in nature, whereas some are naturally occurring like MoS_2. Bulk MoS_2 crystals are prepared by chemical vapour method from MoS_2 powders. WSe_2 crystals are made from elemental W and Se powders by chemical vapour deposition. Numerous review article has been published throughout every year and readers can opt to look out for the references for further understanding about TMDCs.[3-10]

II. SAMPLE PREPARATION

A) *Mechanical exfoliation:*

Mechanical exfoliation is most used technique to obtain the cleanest and high purity layers of TMDCs. In this process, flakes of bulk crystals are peeled of by an adhesive tape by the method of mechanical exfoliation. These freshly cleaved thin flakes are now brought in contact with a substrate and further rubbed against the adhesive tape to peel off thin layers of TMDCs on the substrate. On removal of the scotch tape, single and multi-layered TMDCS remain on the substrate. This sample preparation is useful to make fundamental study on the properties of layered TMDCs, but it is not useful in large scale sample fabrication due to non-uniformity in sample size. . Fig. 1 shows the image contrast of both bi layered and monolayered MoS_2 prepared in our lab.

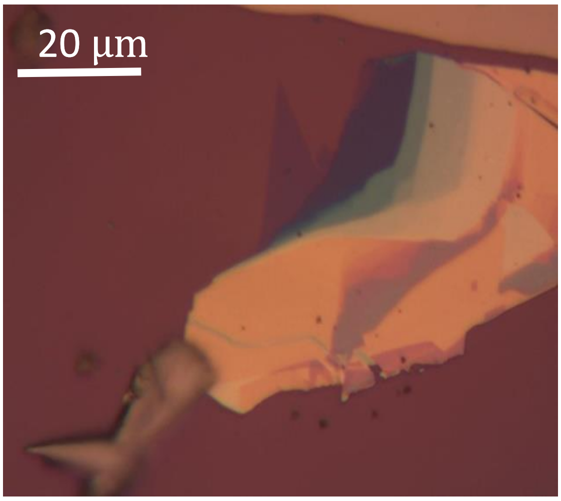

Fig.1: Monolayer MoS_2 was obtained by mechanical exfoliation on to SiO_2/Si substrate.

B) *Liquid Exfoliation:*

To obtain large quantities of layered nanosheets, liquid exfoliation is promising. The intercalation of TMDCs with ions makes them suitable for liquid exfoliation. In case of large scale layered MoS_2 preparation, the bulk MoS_2 is submerged in a solution of butyl lithium in hexane, which results in Li intercalation of MoS_2, followed by treatment with water. On treatment with water, hydrogen gas is released pushing the layers apart. This process produces quantities in the submicrometer sized monolayers in grams [5].

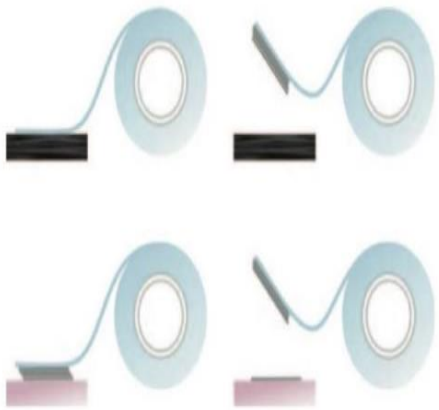

Fig. 2: Schematic of micromechanical cleavage by scotch tape method. Figure is taken from reference [12].

C) Chemical Vapour Deposition:

For various applicative purposes it is necessary to fabricate materials with large area and CVD seems to be a crude way of fabricating uniform monolayers of large area. CVD was highly used for fabricating MoS_2 initially, although with this technique many other TMDCs are fabricated. CVD technique can be used in two different ways, one is a two step growth process, another is a one step growth process. In two step growth route, Mo precursors are initially deposited on substrates and then sulphurised by passing SO_2 to form desired MoS_2 thickness. In one step growth process, both Mo and S are simultaneously introduced in presence of a carrier gas and allowed to react to form MoS_2 layers on the substrates. The layers formed are of considerable size, of the order of mm. Fig.3 shows the schematic of both the two step growth route and one step growth route of MoS_2 fabrication.

D) Electronic structure:

Band structure calculations of TMDCs play an important role in identifying the routes of different physical properties of layered TMDCs. The first principle DFT calculations is the most used band structure calculation method. Whereas Bethe-Salpeter method is used to obtain information from the optical spectra. Electronic structure calculations provide information about the evolution of band structure from bulk to layered materials. In case of bulk MoS2, the band structure is an indirect one, with the valence band maximum lying at Γ point and conduction band minimum at a low-symmetry point of the Brillouin zone. Whereas in case of layered MoS2, both the valence band maximum and conduction band minimum shift together to K point in the Brillouin zone, forming a direct band gap of energy 1.71 eV, while its optically measured to be 1.92eV[11]. Bandstructure of bulk MoS_2 and layered MoS_2 is shown in Fig. 4

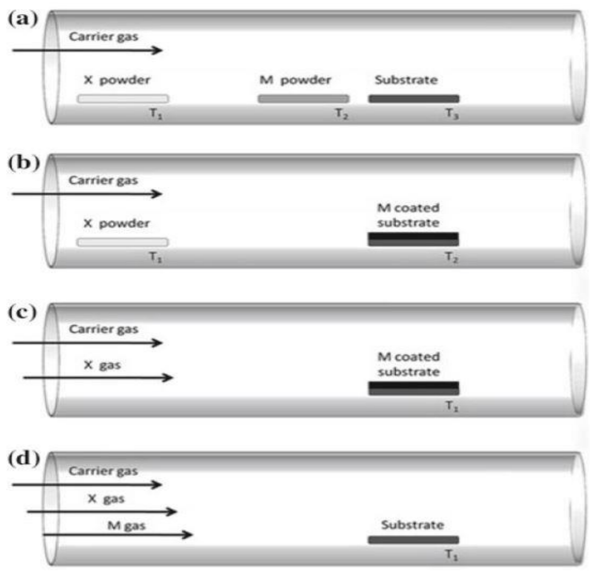

Fig. 3: a) Schematic showing monolayer growth of MoS_2 by vapour phase where metal (M) and chalcogen (X) powders used. b) Substrate coated with metal oxide and X powder c) Metal coated substrate and X used as gaseous precursor d) Both M and X used as gaseous precursor.

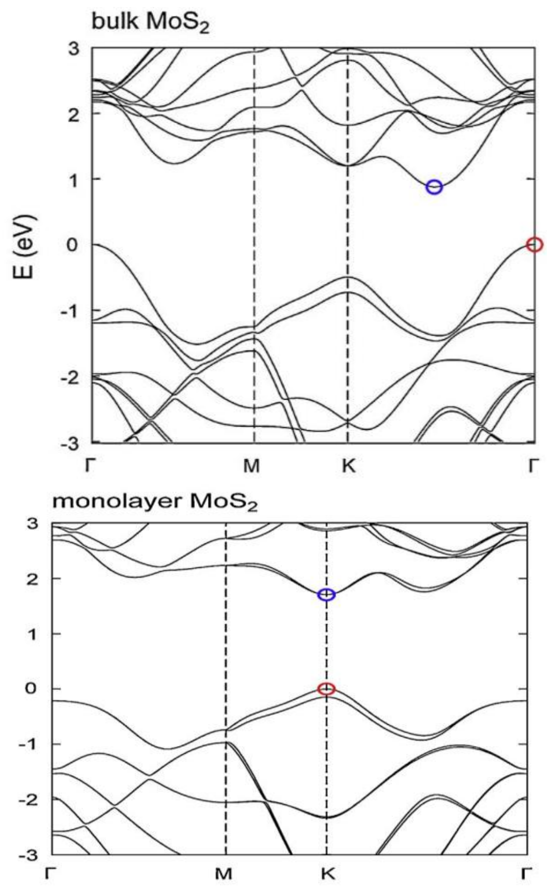

Fig. 4: Electronic band structures of (a) bulk MoS2 and (b) monolayer MoS2 calculated from first principles using density functional theory (DFT) within the generalized gradient approximation (GGA) [11]

E) Optical properties:

The monolayered TMDCs are different from the bulk ones, although the composition remains same. The bandstructure changes from being indirect to direct as we move from bulk to single layers. It was first seen in MoS_2, where the band gap energy changed from 1.2eV to 1.8 eV at room temperature. Sufficiently high photoluminescence was observed from monolayers of MoS_2, which indicates that such monolayers can be suitable candidates for photodetectors, LEDs, lasers, optical switch, modulators, displays among others. The first MoS_2 phototransistor showed photo resistance of about 7.5mW/A. The photoresistance can be tuned to different wavelengths by stacking MoS_2 of different thickness. It was also seen that the MoS_2 based photodetectors had low dark current noise compared to usual Si Avalanche diode. Optoelectronic devices based on TMDC were the first to exploit the spin valley coupling. P-N junctions are created by assimilating both MoS_2 and WSe_2 gated by liquid electrolytes and used as LEDs. On application of in plane electric field, valley symmetry breaking of electrons and holes occurs, resulting in emission of circular polarized light. Heterostructures of different TMDCs can be fabricated to use it as solar cells, phototransistors etc[11]. PL Spectra of mono layer MoS_2 at low temperature is shown in Fig 5.

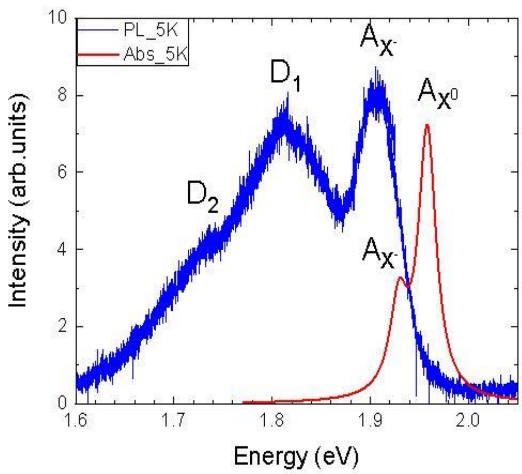

Fig. 5: Blue line shows the PL spectrum of MoS_2 monolayer obtained at 5K where D1, D2 are due to transition from defect states and A_X^- is due to trion. The red spectra is the absorption spectra theoretically calculated from the reflectance contrast. A_X^- is due to trion and A_X^0 is the exciton peak. The trion peaks are stokes shifted as compared to its position in absorption spectra.

III. CONCLUSION

The unique properties of TMDCS like direct band gap, intersesting electronic properties, optical transparency makes it a suitable candidate for next generation optoelectronics industry. To continue the pace of progress a lot of issues still needs to be addressed and more studies needs to be made by the scientific community .

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