A Project Report
On

N doped CVD grown MoS2 decorated with WS2 QDs for broadband photodetection

BY

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Birla Institute of Technology and Science-Pilani, Hyderabad Campus

Certificate

This is to certify that the project report entitled "**N doped CVD grown MoS2 decorated with WS2 QDs for broadband PD**" submitted by **Sukruth S**(ID No**.2020H1400236H**) in partial fulfilment of the requirements of the course BITS G540, Research Practice, embodies the work done by him under our supervision and guidance.

Date: 10th June 2021

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ABSTRACT

Broadband photodetection is critical for biological imaging, communications, and environmental and spectrum monitoring, among other defence and scientific uses. Due to their outstanding optoelectronic properties and significant optical absorbance for their atomic thing thickness, transition metal dichalcogenide semiconductors from the two-dimensional layered materials family have attracted particular attention in recent years for their application in photodetection. In addition, TMDs also have a wide range of optical sensitivity, a configurable bandgap, no dangling bonds, ten large-scale production capabilities using chemical vapour deposition (CVD), and compatibility with complementary silicon metal-oxide-semiconductor.

Theoretically and experimentally, photodetectors based on MoS2 (one of the early TMDs) have also been extensively researched. Several synthetic approaches have been used to create luminous MoS2 nanoparticles since the discovery of their luminosity. As a result, MoS2 was one of the first TMDs to undergo a comprehensive photodetection study. Despite this, the device has always had the disadvantage of having high quantum efficiency or a high switching timing. Several approaches to overcome this disadvantage have been developed in recent years. In this paper, we propose a unique strategy for improving the photoluminescent features of the MoS2 photodetector by combining WS2 QDs with nitrogen doping to create a p-type material.

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Objective

To synthesize an N doped CVD grown MoS2 decorated with WS2 QDs for broadband Photodetection

Work plan

1. A literature review on CVD synthesis of MoS2, the physics and various characterization of MoS2, hydrothermal synthesis of WS2 quantum dots, and thermal evaporation for connections.
2. Fabrication of a single layer of MoS2 wafer followed by P-Type doping.
3. Fabrication of WS2 quantum dots using hydrothermal synthesis and thermal evaporation for contacts on MoS2 now with WS2 QDs.
4. Characterization of the same and calculation of I-V characteristics to obtain parameters like photoresponsivity and specific detection.
5. Documentation of the obtained results.

1. INTRODUCTION

With Moore's law in force for decades, it is more crucial than ever to research new and unique materials to fabricate electronic devices and circuits. Unfortunately, materials like Si and Ge, which were once employed to make devices, have reached their performance and packing limits. In recent years, a novel and inventive method of constructing and synthesizing flexible electronic devices have become a research hotbed. Using 2D materials is one way to get around this problem [1].

Two-dimensional (2D) materials have proven to be a fruitful field for uncovering novel phenomena in condensed matter and a potential platform for pushing the frontier of semiconductor technology beyond Moore's law. This is because they are the thinnest manufactured materials in the universe and have the ultimate limit of thinness in the vertical dimension [2]. Two-dimensional (2D) van der Waals (vdWs) crystals, such as graphene, black phosphorus (BP), silicene, group-IV monochalcogenides, and transition metal dichalcogenides (TMDCs), have a wide range of applications, including electronics and optoelectronics, valleytronics, flexible devices, memory devices, and sensors, due to their unique electrical, mechanical, thermal, and optical properties.

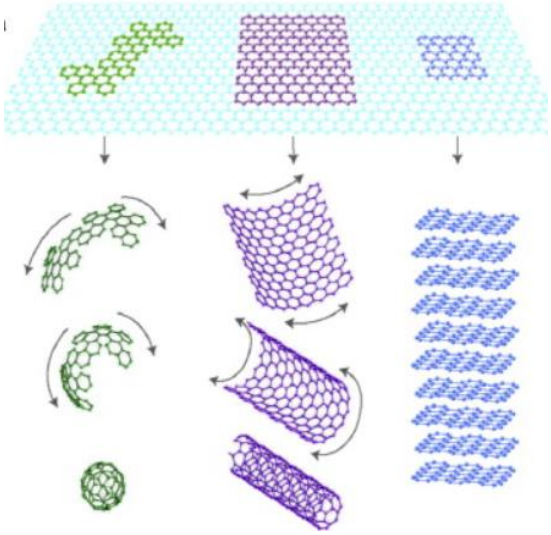

Figure 1. 2D materials representation

Graphene, the most well-known of the two-dimensional materials, has aroused much interest in academia and business. Graphene micro-flakes have long been utilized to make composite materials with outstanding mechanical characteristics. However, the lack of an electronic bandgap has prompted researchers to look for 2D materials with semiconducting properties. Unfortunately, graphene is currently prohibitively expensive to manufacture predominantly, restricting its applicability in products that require mass production. Furthermore, as big graphene sheets are formed, the likelihood of microscopic cracks and other faults in the material increases. Thus, it is required to look at other options when it comes to 2D materials[3-5].

TMDs (two-dimensional transition metal dichalcogenides) are a new class of materials with features that make them ideal for fundamental research into novel physical phenomena as well as nanoscale sensing and actuation. Transition metal dichalcogenides (TMDCs) are a possible choice because they are semiconductors of the form MX2, where M is a transition metal atom (such as Mo or W), and X is a chalcogen atom (such as S, Se, or Te). The first transistor demonstration and the detection of substantial photoluminescence in MoS2 monolayers have increased the interest in 2D TMDCs. In addition, there are several similarities to TMD and graphene, including noncovalent layer bonding and solid covalent bonding in a plane.

Broadband photodetection is essential for numerous defence and scientific purposes, including biomedicine,

communication and spectrum and environmental monitoring. Due to the excellent optoelectronic capabilities and wide optical absorbance for their atomically thin thicknesses, the transition metal dichalcogenides half-conductors of the two-dimensional coating family have received particular interest in recent years. Under optical devices, a photodetector is an electrical light transforming device. The viability of photodetectors can be determined through one or more of the following performance criteria: high sensitivity or quantum efficiency, quick speed, low noise, and high-dynamic-range. However, there is a considerable performance compromise between quantum effectiveness or sensitivity and speed when building photodetectors[6-8].

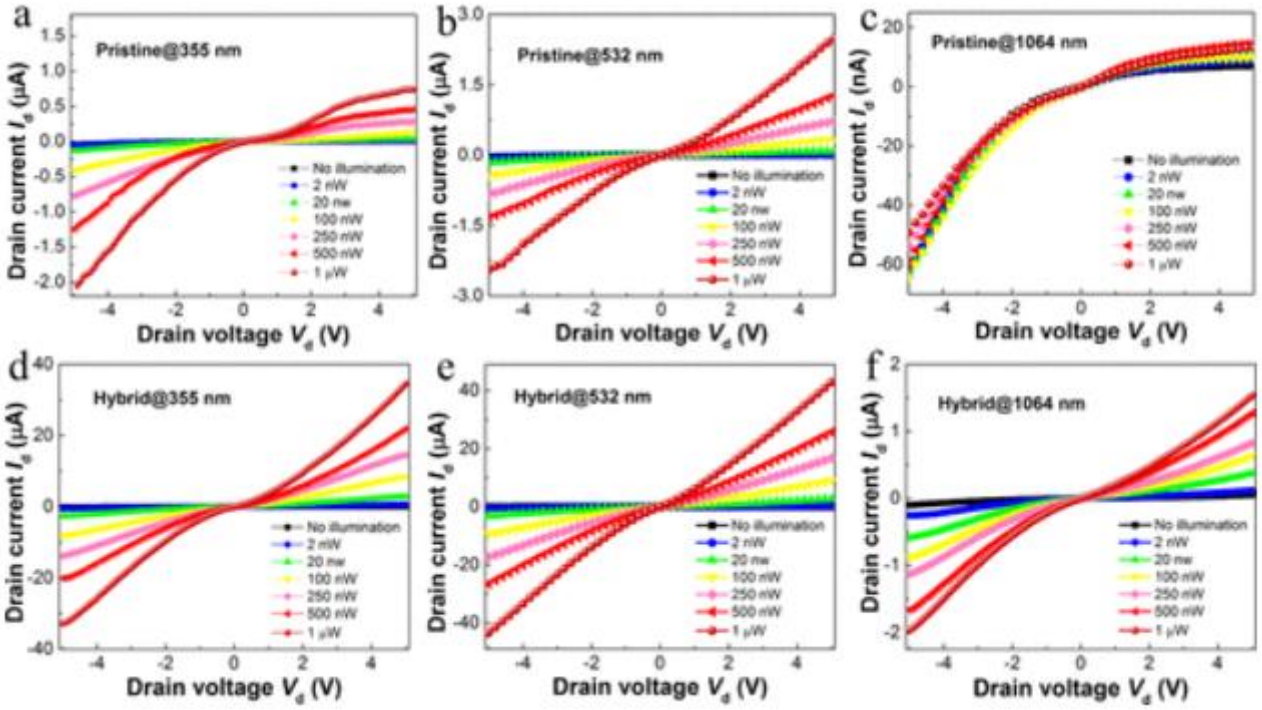

Figure 2. Graph representation of Broadband photodetector for various wavelengths (a)-(f)

This compromise can be reduced using 2D photodetectors and 2D photodetector synthesis transitional metal dichalcogenides. Various photodetectors, including single, few, and several layer photodetectors, were constructed, and studies were performed with various IV transfer metals as Re, Se and Sn. In photodetectors, MoS2 and WS2 individually showed promise, but they were always linked to disadvantages like high single performance characteristics. On the other hand, these wafers, synthesized by CVD, display great quantum effectiveness or exceptional sensitivity[2]. Thus, a new method to increase the performance of MoS2 can be done using quantum dots.

CVD is a general name for a group of processes that need a solid substance to be deposited at a gaseous stage and sometimes mimics physical vapour deposition (PVD). Chemical vapour deposition is the procedure by which a volatile precursor is introduced into a chamber (typically under vacuum). The chamber is heated to a precursor gas that reacts on the desired coating at reaction temperature and is divided on the surface area of the result. Over time, the coating material is built on the surface and coats the whole exposed region[11].

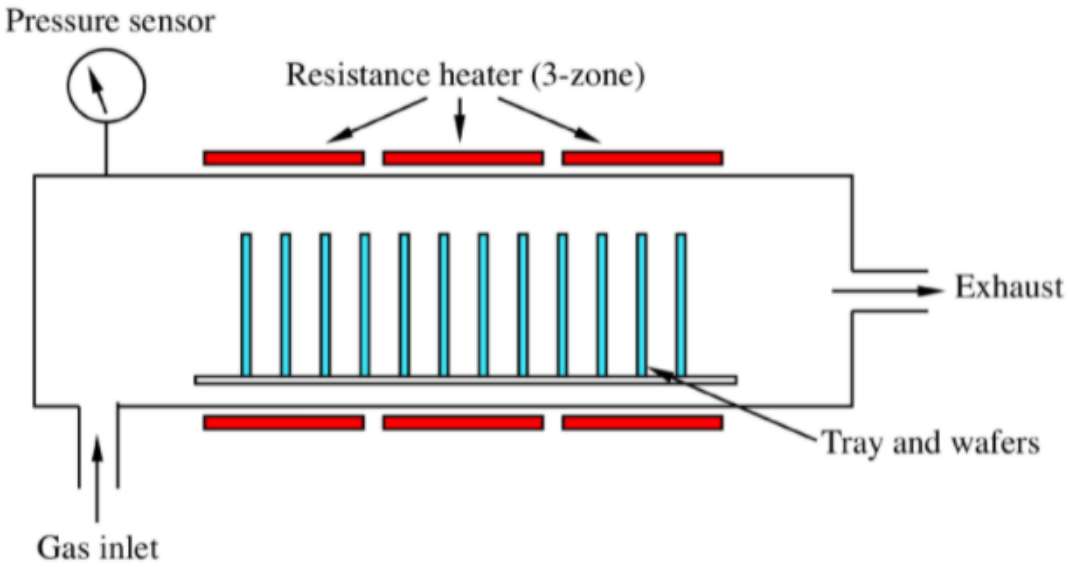

Figure 3. A typical low-pressure hot-wall CVD reactor for coating silicon substrates is shown schematically.

Quantum dots (QDs) are semiconductor particles a few nanometers in size, having optical and electronic properties that differ from larger particles due to quantum mechanics. They are a central topic in nanotechnology. Because of the peculiar optical features, especially luminescence, quantum dots (QDs) are frequently used for imagery, labelling and sensing in biological systems[10]. In general, less than ten nanometers are achieved by manipulating the TMDs to several nanometers, TMD Quantum dots (TMD QDs) showing distinctive features resulting from rim and quantum containment effects. QDs have been widely researched among the TMD families of QDs (W, Mobility, WS), MoS2 and Mobility, and QDs with ultrasmall dimensions, high volume ratios of the surface, active border sites and bandages.

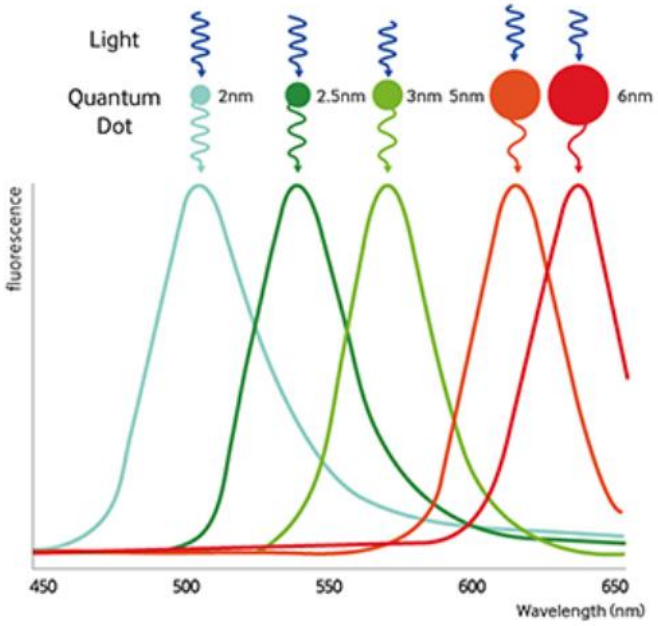

Figure 4. Graph representing the luminescence vs atomic size for a typical quantum dot atom.

Although TMD QDs have gained special attention from scientific and technological communities, research is still in the lead phase. The structure of nanosheets was most of the study on nanostructured TMDs.

Concerning TMD QDs, a more significant investigation is urgently needed of their synthesis, characteristics and applications in biological systems. Up to now, there have been some relevant review reports for catalysis and energy applications for TMD nanoparticles, MoS2 QDs, low-dimensional TMDs and TMD QDs.

This report proposes the fabrication of a hybrid photodetector using MoS2 CVD synthesized wafer and WS2 deposited QDs and describes the various characteristics such as XRF, PL, and Raman.According to the knowledge of the author there is no other report which is working on the hybrid photodetectors of this design.

2. LITERATURE SURVEY

While several papers deal with the induvial synthesis and characterization of MoS2 and WS2, very few papers deal with the quantum dots of WS2 deposited onto MoS2. Therefore, this study has aimed to make a systematic move in filling the holes in the proposed device by incorporating ideas from these texts.

S.No	Publication and Year	Paper and Author	Content	Limitation
1	19th December 2019	Coupled Charge transfer Dynamics and Photoluminescence Quenching in Monolayer MoS_2 Decorated with WS_2 Quantum Dots Larionette P. L. Mawlong, Abhilasha Bora & P. K. Giri	By coating the monolayer MoS2 (1L-MoS2) with WS2 quantum dots (WS2 QD), this work studied the tunability of the photoluminescence (PL). Chemical vapour deposition and liquid exfoliation procedures are used to make direct bandgap 1L-MoS2 and WS2 QDs. .	This article concentrates on the manufacture method, which is very specialised and necessitates the use of expensive salts, which is not practical. As a result, the scientists do not describe the optical behaviour or photodetector characteristics.
2	18th December 2020	Quantum Dots synthesis and application Jaison Jeevanandam, Satheesh Kumar Balu, Swetha Andra, Michael K. Danquah, Manisha Vidyavathi and Murugesan Muthalagu	The numerous ways for manufacturing quantum dots, as well as their related physical and chemical characteristics, are discussed in this series of studies. Nanocomposites are also explored, as well as their current uses in numerous industries, because they are made by combining diverse materials with quantum dots.	These studies give a broad overview of QD synthesis, however they do not go into detail on how to classify the QDs that have been created.
3	30th April 2021	High-performance photodetector and its optoelectronic mechanism of MoS_2/WS_2 vertical heterostructure Xin Lin, Fang Wang, Xin Shan, Yinping Miao, Xudong Chen, Meng Yan, Lifang Zhang, Kai Liu, Jun Luo, Kailiang Zhang	The transfer approach successfully prepares the MoS2/WS2 vertical heterostructure. The MoS2/WS2 heterostructure photodetector has a high on/off ratio (around 108) and electron mobility (12 cm2V-1S-1). At the same time, the MoS2/WS2 photodetector has a photoresponsivity of 298 A/W and a photoresponse speed of 9 ms.	The synthesis of WS2 and MoS2, but not of QDs, is explored.

3. METHODOLOGY

CVD Process

In a simple CVD process, the following are the steps:

- In the reaction chamber, a predetermined mixture of gas and diluent inert gases is introduced with the default flux rate;
- the gas species is transferred to the substrate;
- the reactants are adsorbed to the surface of the substratum;
- the reactants undergo chemical reactions with the film substrate;
- Furthermore, the by-products of the reactions are desorbed and evacuated from the reactant.

The reactant gases react with the substrate material on or near the wafer surface and during the chemical vapour process during the gas phase of the reactor atmosphere. Heterogeneous reactions occur preferentially on the heated surface of the wafer where high-quality films are produced, starting at the substratum surface.

Synthesis of MoS2

Different approaches can be utilized to make a single MoS2 layer. These tactics can be classified between downstream and downstream in two categories. First, the exfoliation of a single or a few layers of bulk is familiar with top-down approaches. Second, moS2 layers are the chemical and physical vapour deposition methods most typically used at the bottom-up (CVD and PVD).

There are several techniques to make one MoS2 layer. Both policies can be classified into two categories: upstream and downstream. In top-down procedures, single or few bulk layers are frequently used as a mechanical, solvent or chemical exfoliation. MoS2 layers are the chemical and physical vapour deposition methods (CVD and PVD) most typically used.

CVD of MoS2 using MoO3 or MoCl5 as the precursor

This technique commonly vaporizes and converts solid MoO3 or MoCl5 into MoS2 as powders through reacting at high temperatures with S steam (> 800 °C). First, MoO3 or MoCl5 will vaporize the furnace in the hottest zone (T>800 °C). Then, the heating poWder of the sulphur vapour and the vapour with the Ar flow is added to the system. Finally, the precursors would react to MoS2, which is then placed on the substratum.

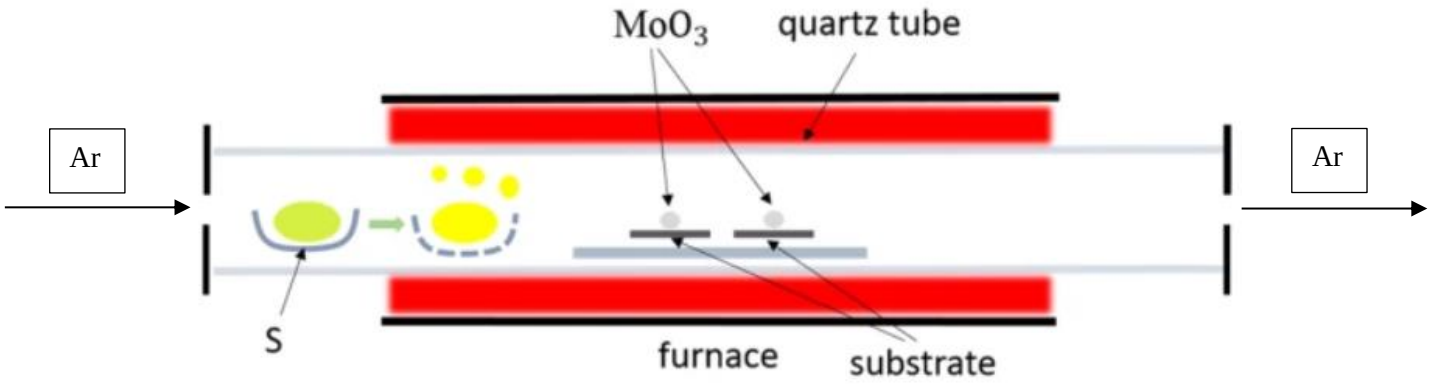

Figure 5. Chemical Vapor Deposition of MoS2

CVD of MoS2 using (NH4)2MoS4 as the precursor

The conversion of (NH4)2MoS4 to MoS3 at 120~360 °C is known as the thermolysis of ammonium thiomolybdates [(NH4)2MoS4) in the N2 atmosphere. A higher temperature (> 800 °C) is required to convert MoS3 to MoS2 afterwards. Conversion of (NH4)2MoS4 in the presence of H2 to MoS2 happens at a lower temperature (425 °C) was also reported. Nevertheless, in H2 at over 500 °C, MoS2 decomposes into Mo. Two steps involve a change in this technique. The substratum is first dipped in a solution with (NH4)2MoS4 and then heated at 500°C in the Ar/H2 atmosphere. In an ar/s environment at 1000°C or higher to generate MoS2, people cured the sample to achieve a more excellent crystallinity.

CVD of MoS2 using Mo Metal and S Powder as the Precursors

Sulfurization of Mo thin films also synthesized MoS2 layers. This technique involves evaporation or sputtering of a thin sheet Mo (1 to 5 nm thick). The Mo film is subsequently subjected to high-temperature Sulphur vapour (750 °C).

Synthesis of WS2

The WS2 QDs water solutions were synthesized using a simple and one-step hydrothermal method. The synthetic technique is summarised in Figure 6. Up-pure water dissolved 0.066 grammes of Na2WO4·2H2O for 12.5 mL with an additional 5-minute ultrasound. Then the ph changes to pH with 0.1 M HCl were added to 6.5. L-cysteine was injected into 0.00242 g solution in the following steps, and 15 minutes after ultrasonography, 50 mL of water were added. It was then transformed for stainless steel into a Teflon-lined 100 mL autoclave and reacted 190°C over 46 hours. The surfactants containing WS2 QDs were centrifuged for 20 minutes, at a rate of 10,000 rpm, after the autoclave naturally cooled. The QD product from WS2 has been collected and then cooled to 4°C.

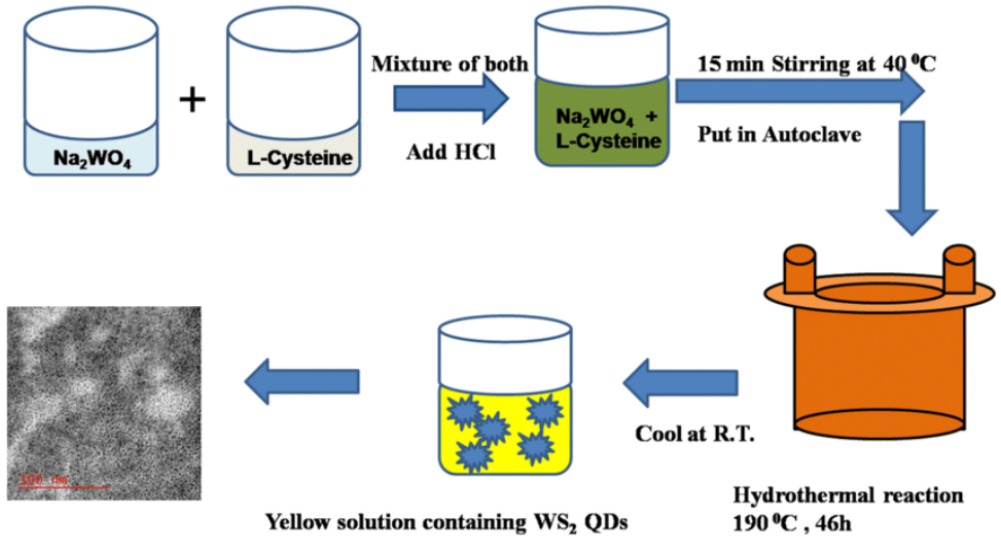

Figure 6. WS2 QDs preparation schematic illustration

4. CHARACTERIZATIONS

In this report, we concern ourselves with five characterizations to determine the various parameters of the obtained sample.

XRD

X-ray powder diffraction (XRD) is a quick analytical technique that may offer unit cell measurements and is used chiefly for crystalline material phase identification. The material being analyzed has been thinly powdered and homogenized, and the bulk composition has been estimated on an average basis. The discovery of cryptic crystalline materials is the most typical use of X-ray powder diffraction (e.g. minerals, inorganic compounds). Identifying unknown solids is critical in geology, environmental science, material science, chemistry, and biology.

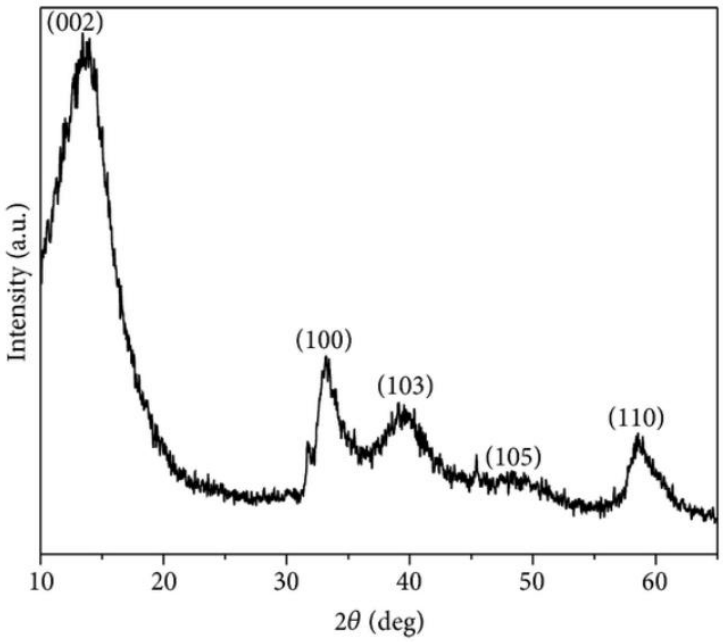

Figure 7. XRD of the MoS2.

XPS

X-ray examination Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) analyses the elements constituting the sample surface, its structure, and chemical bonding state by irradiating x-rays on the sample surface and analyzing the kinetic energy of the photoelectrons released from the sample surface.

Furthermore, the chemical shift induced by the electron state surrounding the atoms to be studied, such as atomic valence charges and interatomic distances, is typically more significant than that found in AES, making the relative ease with which the state of chemical bonds can be determined another advantage of XPS.

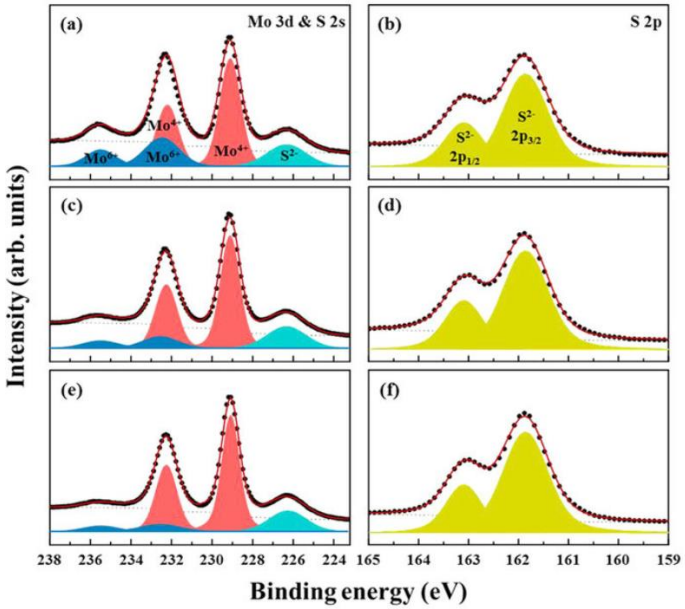

Figure 8.X-ray Photoelectron Spectroscopy

SEM

The scanning electron microscope (SEM) may investigate and characterize a wide range of photonic materials. From extremely conductive samples to insulating materials, there is something for everyone. This flexible instrument is used in a variety of applications. Secondary electron imaging, backscattered electron imaging, X-ray examination (both qualitative and quantitative), electron channelling patterns for investigating crystalline materials, charge collecting techniques for semiconductor samples, and cathodoluminescence are some of the techniques available.

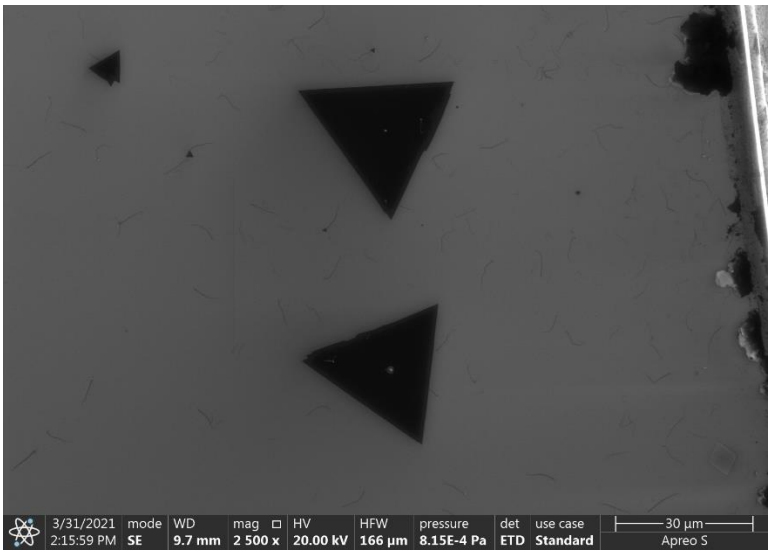

Figure 9. SEM of MoS2

PL

Photoluminescence (PL) is an optical phenomenon in which semiconductors release light when they are exposed to light with an intensity more significant than the energy band difference of the semiconductor. According to the PL process, excited electrons created by optical excitation will revert to the ground state and release photons. PL measurements, including steady-state and time-resolved PL spectra, PL decay, and PL quantum efficiency (PLQE), are routinely employed to study the essential radiative characteristics of semiconductors.

In semiconductors, power-dependent PL measurements may be used to investigate radiative bimolecular recombination, nonradiative trap-assisted monomolecular recombination, and nonradiative Auger recombination. In addition, temperature-dependent PL experiments, such as thermally triggered delayed fluorescence, are frequently employed to investigate phonon-assisted recombination (TADF). Because the concentration of dopants in host-guest systems can alter radiative recombination, PL measurements may also be used to track the rate of energy transfer and the concentration of dopants.

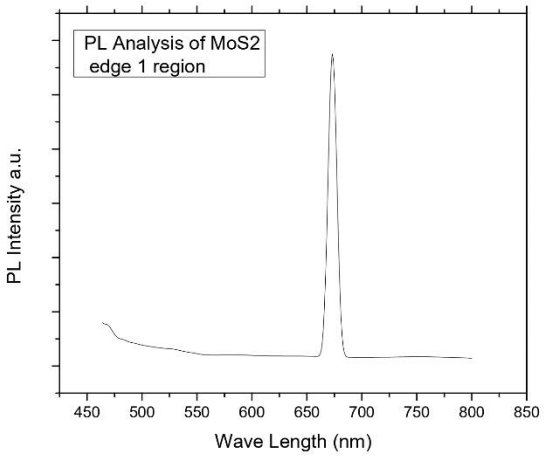

Figure 10. PL of MoS2

RAMAN

Raman spectroscopy is a method that classifies molecules, analyses chemical bonding, describes microstructures of materials, and measures thermal conductivity by measuring the frequency shift of inelastically scattered light from the sample based on their distinct vibrational characteristics (fingerprints). Smekal predicted the Raman scattering phenomenon, which is the basis of Raman spectroscopy, in 1923, and C.V. Raman found it experimentally in 1928. Raman spectroscopy is a non-destructive chemical analysis tool that may reveal details about the chemical composition, phase and polymorph, crystallinity, and molecular interactions. It is dependent on the interaction of light with a material's chemical bonds.

The intensity and wavelength direction of Raman dispersed light are seen in a Raman spectrum, which has a range of peaks. Person bonds such as C-C, C=C, N-O, C-H, and groups of bonds such as benzene ring breathing mode, polymer chain vibrations, lattice modes, and so on lead to a particular molecular bond vibration.

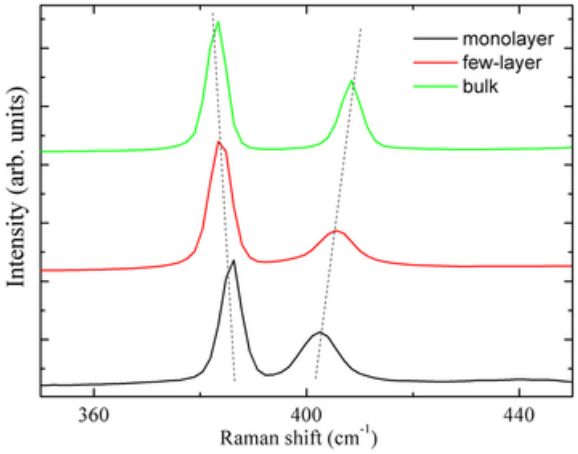

Figure 11. Raman characterization for MoS2

XRF

X-ray fluorescence (XRF), an analytical technique, may be used to assess the chemical composition of a wide range of sample types, including solids, liquids, slurries, and loose particles. X-ray fluorescence may also be used to determine the thickness and composition of layers and coatings. It can detect elements ranging from beryllium (Be) to uranium (U) at concentrations of 100 parts per million to less than one part per million. XRF, like optical emission spectroscopy (OES), inductively coupled plasma (ICP), and neutron activation analysis, is an atomic emission method (gamma spectroscopy). These approaches are used to determine the wavelength and intensity of 'light' (in this case, X-rays) emitted by energized atoms in the sample. Fluorescent X-rays with discrete energy typical of the elements present in the sample are released when an X-ray tube is bombarded with the primary X-ray beam.

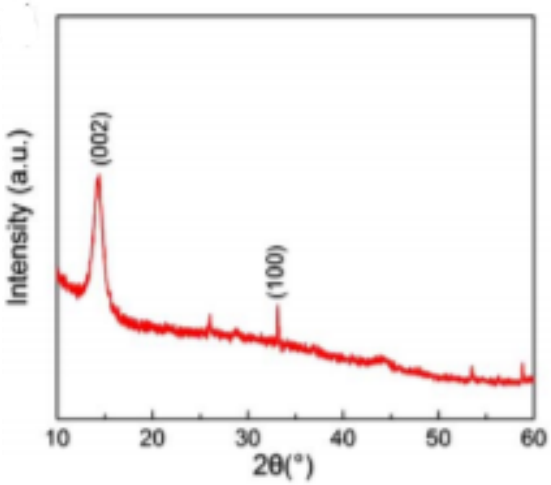

Figure 12.XRF of MoS2

5. RESULTS

MoS2 photodetector was synthesised and was doped with nitrogen to produce a p type MoS2.Various characterisation of the N-doped MoS2 wafer was done to determine the performance parameters of the wafer. WS2 quantum dots was synthesised hydrothermally and will be used to improve the performance further.

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