M.SC. Physics Shreya & Anukool Yadav 2021

HYDROTHERMAL SYNTHESIS OF TMD NANOSTRUCTURES ALONG WITH ELUCIDATION OF DOUBLE ZONE THERMAL CVD AND PECVD.

A DISSERTATION

SUBMITTED IN FULFILLMENT OF THE
REQUIREMENTS
FOR THE AWARD OF THE DEGREE
OF

MASTER OF SCIENCE
IN
PHYSICS

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MAY, 2021

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CANDIDATE’S DECLARATION

We, Shreya & Anukool Yadav, 2K19/MSCPHY/25 & 2K19/MSCPHY/10, students of **M.Sc. Physics**, hereby declare that the project Dissertation titled “Hydrothermal Synthesis of TMD Nanostructures along with Elucidation of Double Zone Thermal CVD and PECVD”, performed under the supervision of **Dr. Nitin K. Puri** and submitted by us to the Department of **Applied Physics**, Delhi Technological University, Delhi in the fulfillment of the requirement for the award of the degree of Master of Science, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

Shreya

Place: Delhi, India
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CERTIFICATE

I hereby certify that the Project Dissertation titled “Hydrothermal Synthesis of TMD Nanostructures along with Elucidation of Double Zone Thermal CVD and PECVD” which is submitted by Shreya & Anukool Yadav, 2K19/MSCPHY/25 & 2K19/MSCPHY/10, Department of Applied Physics, Delhi Technological University,Delhi in the fulfillment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision. To the best of my knowledge **this work has not been submitted in part or full** for any Degree or Diploma to this University or elsewhere.

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ACKNOWLEDGEMENT

The first and foremost, we would like to express our gratitude to the person whom we are most grateful for, our supervisor of this thesis, Dr. Nitin K. Puri. We are indebted to him for providing us this incredible opportunity to work under his guidance. He has always managed to take time out of his busy schedule to discuss the status of dissertation work and gave positive valuable suggestions to work better. Working under his supervision was truly an unprecedented and incredible experience.

Furthermore, we extend our heartfelt thanks to the Research Scholars of our lab, Ms. Ritika Khatri, Ms. Nikita Jain, and Mr. Anurag Bhandari who guided us at every single step during the whole period of dissertation work. They have always made themselves available for us, whenever we have faced any issue and helped us in every possible way. Working with them was indeed a fun learning experience.

The list couldn't be completed without thanking our parents for their constant support and unconditional love. We highly acknowledge their presence and can't thank them enough using words. Furthermore, we want to thank our friends, Ujjawal, Sharad, Vinay and many others for their presence and support in the times of low motivation.

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ABSTRACT

The scientific world has always been in hunt of opportunities that have the potential to impact not only academia but the industrial world too. It is the result of the quest to explore new technological advances that a new scientific tool in the form of nanotechnology has emerged. It is the science to unravel the properties of the atomic world and to use those properties for revolutionary changes. An example of revolutionary change is the small size of transistors that have influenced the size of computers and thus our lives greatly. The fascinating microscopic world has lots of hidden features in it. Demystifying those features and exploring the unprecedented properties of that world has created new avenues in diverse fields. Before learning the properties of different materials, synthesizing them is a major task. As the future is more about making things smaller and tinier for various applications, the hunt for better methods is always a hot topic of research. Different approaches are used for the synthesis depending upon the factors like the type of precursors, structure, composition and morphology of the product required, and others. Each technique offers a wide range of advantages and disadvantages, thus, learning about them and their usage in some specific conditions is mandatory in this field. In the present work, numerous synthesis techniques viz. Hydrothermal/Solvothermal, Sonochemical, Chemical Vapour Deposition, Sol-Gel, and Chemical Exfoliation are discussed. Their mechanism is briefly discussed along with advantages and disadvantages.

Furthermore, to explore the properties of nanostructures, different attempts of synthesis have been made and reported briefly here. Initially, attempts have been made to synthesize WS_2 nanostructures via Hydrothermal Synthesis at varied conditions. Their observations and results have been discussed and implications have been drawn from the results. After that, to study more about the TMDs and the heterojunctions, attempts have been made to synthesize the nanostructures of ZnO/MoS_2 composite via the Hydrothermal Synthesis. Two approaches have been used here. In one approach, prepared ZnO nanostructures have been put into the procedure of preparation of MoS_2 nanostructures while in the other approach, prepared MoS_2 nanostructures have been put into the procedure of preparation of ZnO. The results of both the approaches and conclusions drawn from them are discussed in further chapters. Eventually, two variants of another technique CVD that are Double Zone Thermal CVD and PECVD present in NRL, DTU, Delhi have been explored and studied. Both the deposition variants i.e., Double Zone Thermal CVD and PECVD offer a wide range of advantages like the uniformity of thin films along with easy accessibility over a wide range of precursors for nanomaterial synthesis. Thus, the principle, working and technical details as well as the advantages and disadvantages associated with the above-mentioned systems are also discussed in the present work.

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CHAPTER 1

INTRODUCTION

Nature has enormous surprises folded within and human beings have always tried to unfold them by delving into diverse disciplines to fulfill their quest. One of the numerous surprises is a world, which is truly alien and fascinating to humanity. If you started guessing that this world is on some other planet or deep into the ocean and entire series of science fiction movies started reeling into your mind, then sorry to say that you are wrong. This world is not elsewhere but in the depth of every single thing. This is the microscopic world that has captivated everyone’s attention and it is none like ours. It has weird properties and phenomena happening there on a smaller scale. This weird world has infinite potential. It harnesses the power of materials to build gadgets of paramount importance by taking the advantage of elements’ intrinsic properties [1].

Nanotechnology is all about the exploration of this enigmatic microscopic world and the potential that it holds to transform the world by unprecedented technological advances. The heart of this science lies in manipulating matter precisely at the atomic scale. It had emerged as a branch of physics initially but now has become the center of various disciplines. It holds the power of transforming our world. [2]. This chapter sheds light on the historical background of this science followed by the fundamental concepts needed to understand it. Furthermore, the applications and implications of this technology in diverse fields have been discussed.

1.1 CLASSIFICATION OF NANOMATERIALS

Nanomaterials are materials in which one or more dimensions are in the nanoscale range. These can be classified into four categories that will be discussed in further sections. To understand the need of exploring different categories, let us go to the example of transistors. We see today, that the electronics world is getting faster and faster by going smaller. Today, billions of transistors can be squeezed in a tiny silicon chip which was beyond imagination, just a few years ago [3]. But, as man's quest is never-ending, scientists try to fit the maximum number of transistors into a small area. This certainly decreases the gap between transistors and after a certain limit, the transistors are so close that they start affecting each other's working. Thus, the need to reduce the surface area of the transistors was felt. These transistors are layered shaped and thus the solution of the above problem appeared in the form of 1-D transistors i.e. nanorods. These vertical transistors have less surface area [4], [5] and thus an opportunity for scientists to squeeze more transistors into a smaller area and making the electronics world even faster.

1.1.1 0-D Nanomaterials

0-dimensional materials (as shown in Fig. 1.1) are the materials in which all three dimensions are confined in the nanoscale range. Quantum dots are 0-D nanostructures that are sometimes referred to as 'artificial atoms' as they can behave like naturally occurring atoms. They are tiny semiconductor particles, just a few nm in size. Because of the quantum phenomena occurring at a small scale, quantum dots have optical and electric properties that differ from larger particles [6]. They have applications in diverse fields. [7]–[9]. However, the process of creating quantum dots

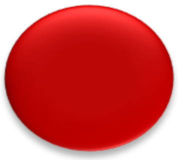


Fig. 1.1 Diagrammatical Representation of 0-D nanomaterials

generates a huge amount of waste and we find ourselves revisiting the environmental concerns [10]. Amazingly though, a low-cost method has been designed to make quantum dots using green leaf extracts, which is an economical method and has non-toxic by-products [11].

Some examples of 0-D materials include Fullerene (C-60), Graphene quantum dots, carbon quantum dots, and others.

1.1.2 1-D Nanomaterials

1-dimensional nanomaterials (as shown in Fig. 1.2) are the materials in which two dimensions are confined in the nanoscale range, while the third dimension is significantly large. Nanowires and nanorods are some 1-D nanostructures. Due to quantum confinement effects, electrons and photons can only propagate through the length in nanowires and nanotubes [12]. This makes them very interesting for nano-electronics and optical applications [13], [14]. These are the smallest structures that can effectively transport electrical carriers. The ratio of surface area to volume in this category of nanomaterials is quite high. This makes them potential candidates.

In nanowires, multi-segment materials can be easily grown which is very difficult in any other kind of materials. Thus, they can be used as the junctions in the nanosystems and this is the biggest advantage of 1-D nanostructures [14]. Nanowires can be made up of metals, semiconductors, oxides, and multi-segments. Carbon nanotubes are the most famous 1-D nanostructures.

Fig. 1.2 Diagrammatical Representation of 1D nanomaterials

1.1.3 2-D Nanomaterials

2-D nanomaterials (as shown in Fig. 1.3) are materials in which two dimensions are relatively large while the third dimension is in the nanoscale range. They have a thickness of just a few atoms. These structures are like thin sheets and are called nanosheets. They include nanofilms, nanolayers, nanocoatings, etc. They are intrinsically thin in a physical sense and that has advantages for electronics and shows quantum confinement behavior. A well-known example of nanosheets is graphene [15]. Beyond Graphene, other 2D materials are Transition Metal Dichalcogenides, Hexagonal Boron Nitride, 2-D Oxides.

2-D nanomaterials form artificial materials when assembled into vertical stacks, called van der Waals heterostructure. The properties of individual layers of these heterostructures can be combined by controlling the sheet order. Using this, electroluminescent devices can be constructed for numerous applications[16]. Modern flexible electronic devices can be build using these van der Waal heterostructures.

1.1.4 3-D Nanomaterials

3D nanomaterials (as shown in Fig. 1.4) are bulk materials having all the dimensions relatively large and no dimension in nanoscale range and thus rightly called equiaxed nanomaterials. Thus, all three dimensions are more than 100 nm in size. These materials can be formed by a cluster of different other types of nanomaterials like

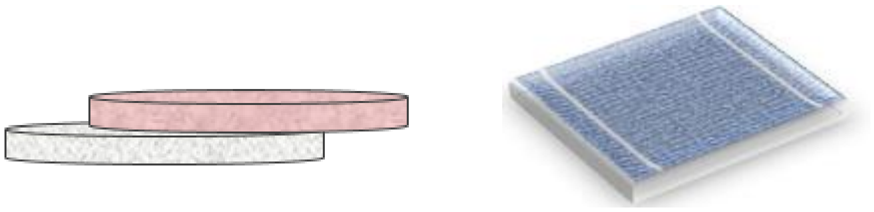


Fig. 1.3 Diagrammatical Representation of 2D nanomaterials

multi-nanolayers, a bunch of nanowires, or dispersed 0-D nanoparticles. Examples of these types of nanomaterials include DNA, viruses, etc.

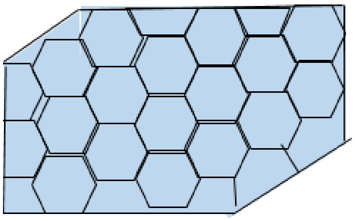


Fig. 1.4 Diagrammatical Representation of 3-D nanomaterials

1.2 SCIENTIFIC BACKGROUND

As discussed in the previous section, TMDs are vastly explored two-dimensional nanomaterials due to their exceptional properties that will be discussed in the coming sections. However, it is essential to know at the point that how these materials came into the picture. Thus, in this section, the properties, importance, and historical background will be discussed.

1.2.1 Graphene

Before learning about TMDs, there is a dire need to know about the most famous and first-ever two-dimensional material, Graphene. Monolayer Graphite is known as Graphene and it is the strongest of the materials ever known [17]. Approximately, it is hundreds of times stronger than steel yet flexible. It is an excellent conductor and conducts electricity better than copper. In previous times, it was believed that 2-D nanomaterials are not stable and thus, can't be produced. But, it was in 2004, when graphene was synthesized successfully and left the scientists' community awestruck. Since then, it has been exploited to find applications in diverse fields. And rightly, it has changed the scenario of the electronics industry which further put the world in a digital race.

However, the zero band gap in Graphene created a gigantic issue while learning its usage in some applications like switches and others. This limitation of graphene baffled scientists and they tried to find a solution to the above problem. Two different solutions were suggested to overcome this limitation. One was to increase its bandgap by various means while the other one was to find new analogous materials with higher bandgap showing semiconducting behavior. The efforts were made to increase the bandgap of graphene layers but changing its bandgap changed its properties as well, which didn't solve the problem [18], [19].

Thus, the second solution, which was to find the analogous materials, was implemented, and eventually, TMDs came into the picture as analogous materials with semiconducting character. After that, research has been started to learn about their applications in different fields including sensing, electronics, optical, and others.

1.2.2 Transition Metal Dichalcogenides

TMDs or Transition Metal Dichalcogenides are materials that have thickness relatable to Graphene along with exceptional semiconductor properties.

TMD layers consist of metal atoms, such as Molybdenum or Tungsten and this layer is stuck between two layers of chalcogen atoms like Sulfur, Selenium, etc. The adjacent layers are bound together very weakly and thus layers can slide over each other. This is the reason, why these materials are widely used for solid lubrication. They have hexagonal structures, which resemble graphene.

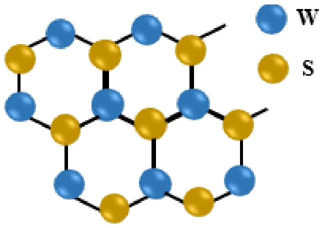


Fig. 1.5 Schematic hexagonal structure of WS_2

TMD monolayers have direct bandgap [20], [21]. While for multilayer TMD, like bilayer or trilayer, the bandgap is indirect. Thus, there is a need to separate monolayers from bulk. To do this, there are numerous techniques that will be further discussed in Chapter 2.

Two of the TMD materials, Tungsten Disulfide (as shown in Fig. 1.5) and Molybdenum Disulfide are studied for the completion of this thesis work. The synthesis mechanism, properties, and results of the synthesized nanostructures of both materials will be discussed in further chapters.

1.3 APPLICATIONS

These discoveries in the field of nanotechnology have a very promising future where the arrangement of atoms in the desired way can show some amazing results. There are a large number of pieces of evidence that show how the world’s smallest materials are changing our lives including the nano-machines that defeat the cancer cells, tiny computer chips, a few inches long high definition cameras, and others. There is no limit to the extent, to which nanotechnology can change the world by technological advances. It holds numerous mysteries and infinite possibilities within. Advances have been made in diverse fields including mechanical, medical, chemical, computing, and others. There are several applications of nanotechnology in diverse fields. Few of the applications are discussed here.

1.3.1 Nano-medicine

The idea of subatomic disease-fighting machines has been in science fiction for decades. So, this idea is not a new one but would have come a lot closer to experimentally making this idea a reality in the past decade. This sounds like a new perfect solution to many modern problems. But let’s just explore how, when, and where science fiction meets facts and what challenges may lie ahead. Nanotechnology is already heavily incorporated into medical tools. Nano-medicine is a very important application of nanotechnology in medicine. It’s used for disease prevention, diagnosis, and treatment.

Nano-medicine is the era of the nanobot. Nanorobots are tiny packages that complete tasks at the desired locations inside the human body in an automated way. Currently, water-soluble drugs are widely used in the medical field for all kinds of treatments, but, they are far from a perfect solution and present numerous difficulties in the treatment. Through these nano-bots, scientists can directly have access to a specific area of the body and can provide better and fast treatment by releasing drugs at the desired location directly. They also hold the potential to replace the pacemakers completely by treating the heart cell directly. They are super durable and can theoretically operate for years without any damage [24].

Another technological advancement is a high-definition camera that is just a few inches long in size, encapsulated like a capsule. It has quite a bright future in the field of medicine. It can be directly engulfed like a drug capsule and provide high pixel images. With the help of those images, scientists can directly look for the problem in the body and can more precisely work upon them. They can be more advanced in the future, where instead of taking images within a time interval, they can make long videos of 360 degrees and can give a better overview of the internal system and specific issues. Though it seems some part of science fiction, hopefully, going to be a stunning reality soon.

1.3.2 Nano-electronics

The crazy advances in electronics have left everyone awestruck. A tiny wafer contains an unbelievable number of sophisticated machines made up of different materials like Gallium, Germanium, Arsenic, and many others. The trend and advances of new tinier gadgets have captivated everyone’s attention from the scientific as well as the non-scientific world. Today, a gigantic amount of information can be stored in a microchip, just a few inches long consisting of billions of transistors in an area of only a few microns. The storage of the same data would have taken an entire building, long years back. Semiconductors, a strange class of elements holds large credit for this evolution. The race to miniaturize began 500 years ago. Since then, miniaturization started another era of the electronic revolution and has changed our lives completely [25]–[27].

CHAPTER 2

SYNTHESIS TECHNIQUES

All the technological advancements of the future that seem impossible right now can indeed become a reality by the discoveries of today. These discoveries in the field of nanotechnology have a very promising future where the arrangement of atoms in the desired way can show some amazing results. Synthesis of these nanomaterials is in itself a huge topic of research where the change in a single parameter like temperature can also make a difference in the structure and morphology of the product [28]. There are various synthesis techniques with different working principles which give very different products at specific conditions. The hunt for new tiny gadgets creates a need for new and better synthesis techniques to get products of high purity and controlled dimensions.

There are two different types of approaches: (i) Top-Down Approach, (ii) Bottom-Up Approach. Both of these approaches have different principles, advantages, disadvantages and methodologies. All the synthesis techniques, whether physical or chemical, fall under either of these categories. In this chapter, we will shed light on these two approaches. Furthermore, various synthesis techniques are discussed here mentioning their principle.

2.1 TOP-DOWN APPROACH

It involves miniaturization. In this approach, synthesis is usually started with large bulkier material, and then its size is reduced to the desired level using various techniques like cutting, etching, etc. Generally, the starting material in this approach is in solid form. The flowchart depicting the process is shown in Fig. 2.1.

The advantages of this approach can be summarized as:

(i) Large-scale production of nanomaterials is easily possible.
(ii) Chemical purification is not required in this approach.

Along with advantages, there are several disadvantages also while using this approach. Some of them are:

(i) An only a limited number of structures can be formed by this approach.
(ii) Control over deposition parameters here is very difficult.
(iii) It is much costlier than the bottom-up approach.

Some examples of the Top-Down Approach are the Solid State Reaction Method, Lithography Techniques, Liquid Phase Exfoliation Method, and others.

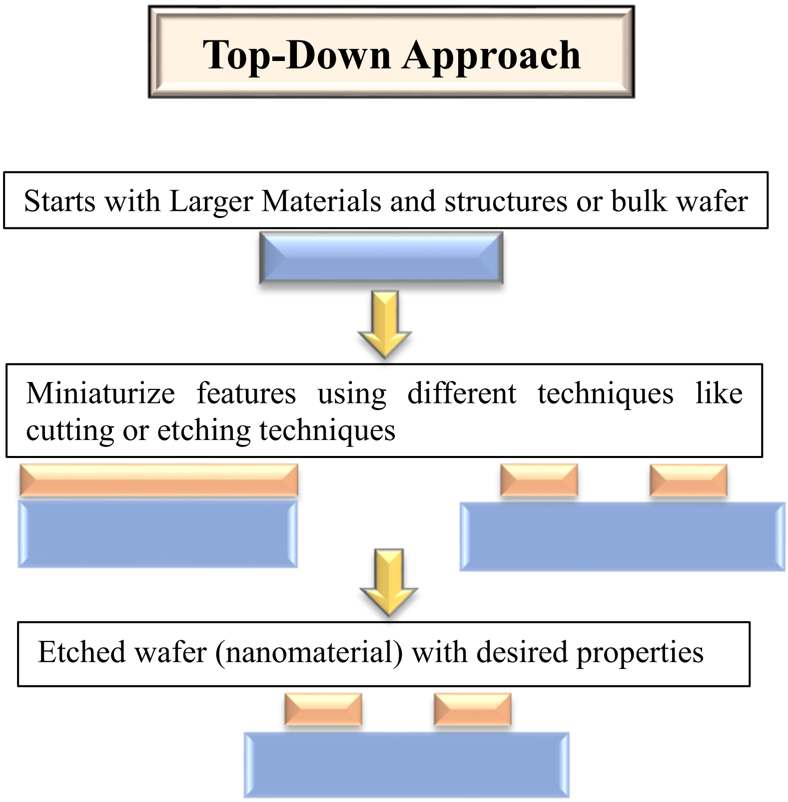


Fig. 2.1 Flowchart depicting Top-Down approach

2.2 BOTTOM-UP APPROACH

In this approach, synthesis takes place by atom-by-atom deposition of nanomaterials or layers of nanomaterials on the desired substrate. In this approach, the starting material or precursor is generally in the liquid or gaseous phase. Here, we start with tiny structures, and their controlled deposition results in the desired structure. The flowchart depicting the process can be shown in Fig. 2.2.

There are numerous advantages of synthesizing the nanomaterials using this approach which can be summarized as follows:

(i) Fewer defects are introduced while the material is synthesized using this approach

(ii) The structures obtained are more homogeneous

(iii) The parameters involved in the deposition can be well controlled

(iv) It is more economical and produces less waste.

However, like any other technique, it has some disadvantages too, which are:

(i) Large scale production is difficult if we use this approach

(ii) Chemical purification of nanoparticles is required to remove any contamination introduced during synthesis.

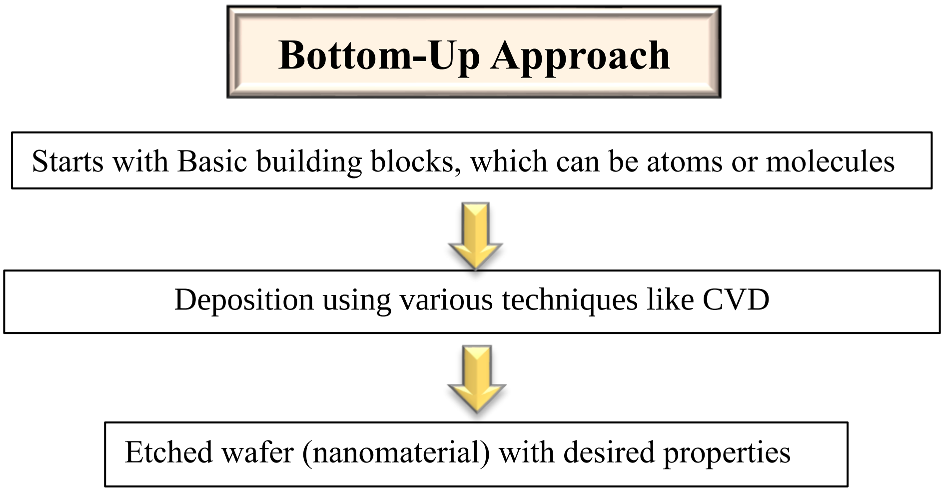


Fig. 2.2 Flowchart depicting Bottom-Up approach

2.3 HYDROTHERMAL/SOLVOTHERMAL SYNTHESIS

These are two promising inorganic synthesis methods that involve the synthesis via chemical reaction as shown in Fig. 2.3. (a). These are the green processes as the reaction takes place in a sealed reactor known as Autoclave shown in Fig. 2.3. (b). The autoclave is generally made up of metal and is employed with Teflon or alloy lining to protect it from highly corrosive solvent.

These processes offer numerous advantages over other techniques apart from being the green processes:

(i) These are relatively low-cost processes
(ii) These are environment-friendly processes as they takes place inside a sealed reactor
(iii) High purity products are formed in these reactions [29].

In the hydrothermal method, the solvent used is water while the solvothermal process uses aqueous and non-aqueous organic solvents like ethylene diamine, ethanol, diethylenetriamine [30], [31], polyethylene glycol [32], etc.

Furthermore, the solvothermal process has some additional advantages over the hydrothermal process:

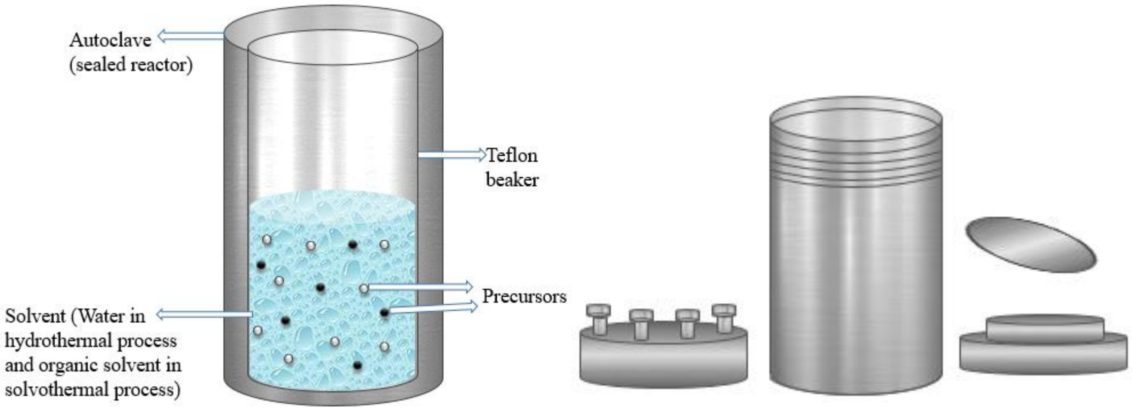


Fig.2.3. (a). A diagrammatical representation of Hydrothermal/Solvothermal Synthesis. **(b).** A diagrammatical representation of an autoclave in Nanomaterials Research Laboratory (NRL), DTU, Delhi, India.

(i) It requires relatively low temperature and pressure

(ii) Precursors which are sensitive to water can be used in this process

(iii) The crystallinity of products formed is very well controlled in this process.

2.4 SONOCHEMICAL SYNTHESIS

This is a method which neither requires high temperature and pressure nor long reaction times. In this process, the precursors are mixed and put together in solution form and then the sonochemical treatment is given. It involves passing ultrasonic waves through the solution using an ultrasonicator as shown in Fig. 2.4. In this way, the hotspots are generated which can achieve very high pressure and temperature. The hotspots are the places where the reaction takes place at sufficiently high temperature and pressure conditions and the products are formed [33]. It is a powerful tool for the synthesis or modification of nanomaterials where even a little variation in the reaction conditions can lead us to the change in morphologies and compositions of the product formed.

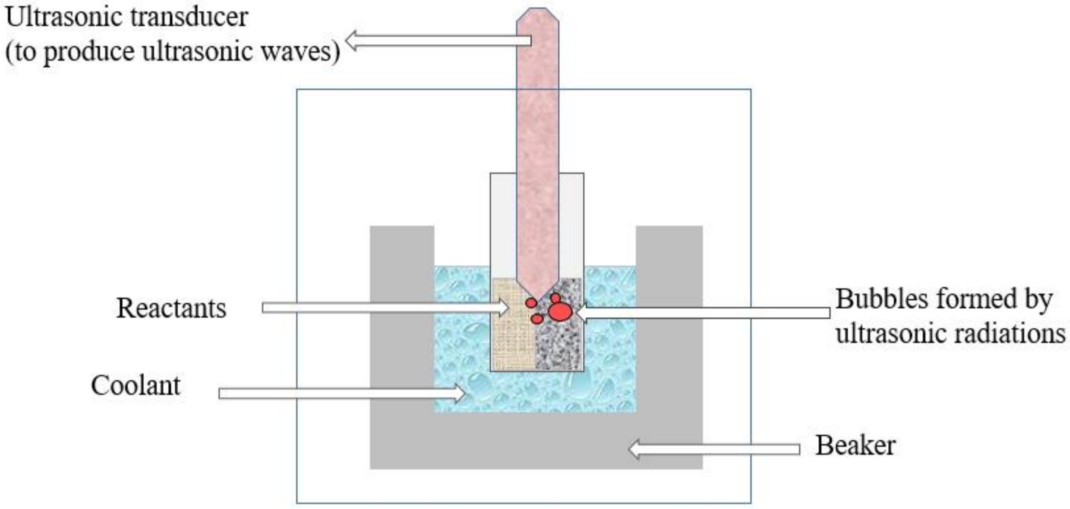


Fig.2.4. A diagrammatical representation of Sonochemical Synthesis.

2.5 CHEMICAL VAPOUR DEPOSITION

It is a vacuum deposition method that involves a chemical reaction inside a vacuum chamber. It is used for the production of various materials like alloys, carbides, oxides, nanoparticles, etc. Layers of materials are deposited on a solid surface called substrate below atmospheric pressure i.e., vacuum. There are many types of CVD's namely Thermal CVD, Metal-Organic CVD (MOCVD), Plasma Enhanced CVD (PECVD), Atomic Layer CVD (ALCVD) [34], [35], etc. The technical details and working of the above two instruments are reported in detail in one of our publications, *"Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage"*, accepted in 'Lecture Notes in Mechanical Engineering'. This bottom-up approach involves the deposition of one or more stable solid films on a substrate at high temperatures by a suitable chemical reaction. A detailed discussion on the same technique is presented further in Chapter 5.

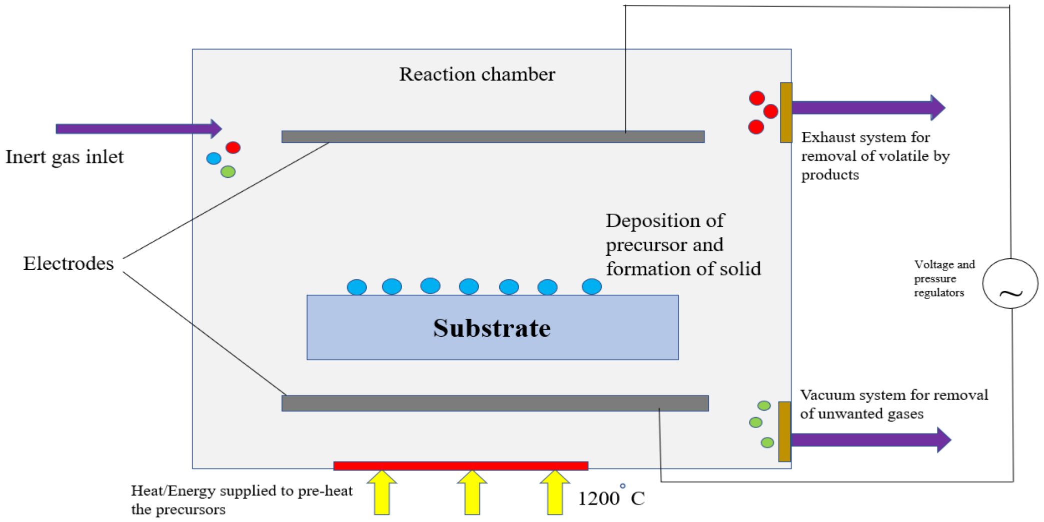


Fig. 2.5. A diagrammatical representation of Chemical Vapour Deposition.

2.6 SOL-GEL SYNTHESIS

This method falls under the bottom-up approach of nanomaterials synthesis in which we start with small atoms and molecules and build up solid nanostructures. It is an inexpensive, wet-chemical technique, used to synthesize ceramic thin films, fibers, and powders at low temperatures, generally nanotubes of silica and TiO_2 [36].

This method was first studied and explained by a chemist named J.J. Ebelmen on silica gels in the mid-19th century (around 150 years ago). The Sol-gel method, as is evident from the name, involves two materials i.e., ‘sols’ (solid particles suspended in liquid) and ‘gels’ (porous network of particles having liquid between the pores). First, sols are formed inside a liquid which is then connected after some process to form a network of gels. The liquid then gets evaporated and we are left with the powder or thin-film formation [37].

The basic process of this technique (as shown in Fig. 2.6) involves the conversion of solvent-dissolved precursors into colloids (1-1000 nm in size) via some basic reactions like hydrolysis, polycondensation, or polyesterification. Precursor particles used as initial materials can be metal salts like metal alkoxides or metal chlorides. Catalysts are also used in some reactions to increase the rate of hydrolysis. If the environment has an acidic catalyst, then hydrolysis is slow which causes the formation of linear molecules and if it is basic, then the process is fast, and heavily-branched polymeric chains are obtained. The next step is gelation or precipitation that is connecting the colloids formed to obtain a 3-D, highly viscous, bigger cluster of

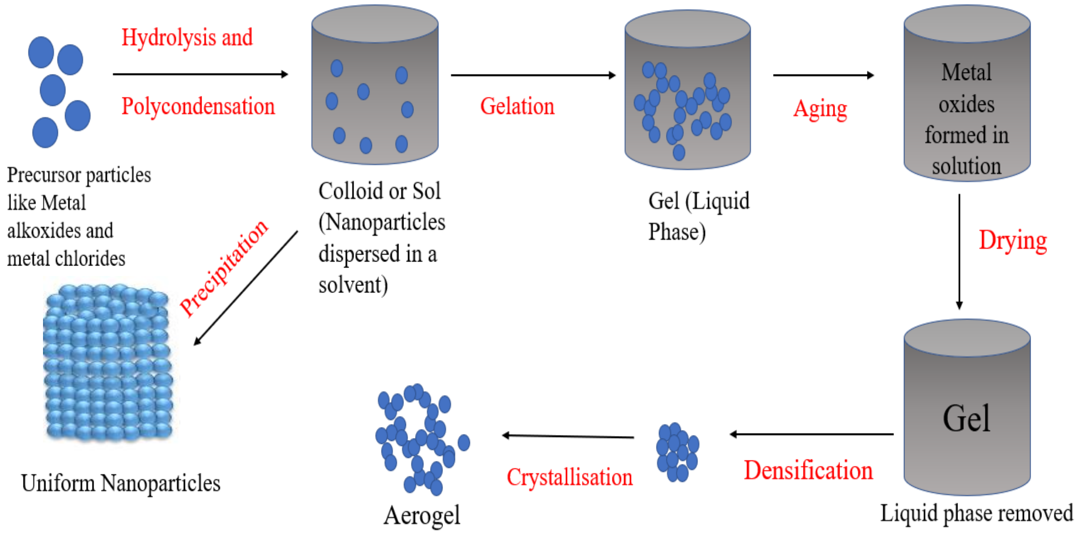


Fig. 2.6. A diagrammatical representation of Sol-Gel Synthesis.

nanoparticles i.e., gel. Gelation majorly depends upon the physical conditions of the network like size and cross-linking of the structures. Aging or syneresis of the gel is done next for many hours or days, where the gel continuously thickens, transforms, and gains enough strength to prevent cracking. Now, extra liquid is extracted out via drying followed by further densification. Under supercritical drying conditions, the highly porous structures may even form aerogels. The last step is the crystallization of the network structures after which the desired nanoparticles are obtained [38].

There are several advantages of the process, which may be summarized as follows:

(i) This method requires less energy consumption leading to less pollution (extensively used in nuclear fuel preparations) and is generally used to generate highly pure and highly dense ceramic and glass materials.

(ii) In this synthesis method, we can obtain desired products even at low temperatures as the reaction rates decrease since the precursors are generally dissolved at atomic scales leading to lowering of the reaction temperatures [39].

(iii) Uniform and small-sized nanoparticles can be obtained with good control over the material's composition.

(iv) We can coat over large and complex surfaces easily.

(v) This method can protect the materials from corrosion as a thick coating can be developed.

(vi) It is an efficient, simple, and cost-effective method of high-quality nanoparticle synthesis.

Along with advantages, there are some disadvantages too, associated with the technique which are as follows:

(i) The raw materials or the precursors are sometimes costly.

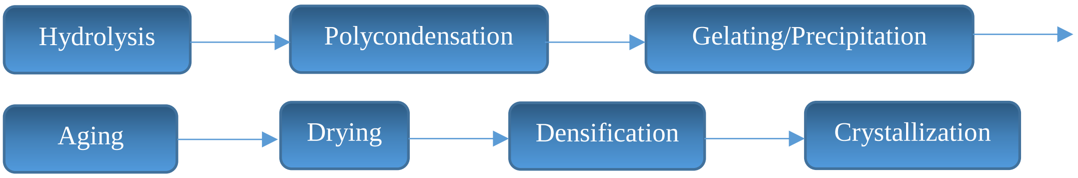


Fig. 2.7. A flowchart of the steps of Sol-gel synthesis

(ii) The synthesis is time taking, compared to other synthesis techniques.
(iii) It uses some toxic organic solutions.
(iv) Impurities may persist in the form of hydroxyl or carbon groups.

2.7 CHEMICAL EXFOLIATION METHOD

In general, exfoliation falls under the category of the top-down approach of nanoparticle synthesis which is done to form layered graphene structures from graphite molecules. Exfoliation can be of major two types: Mechanical exfoliation and Chemical exfoliation. Mechanical exfoliation is a low-cost technique that can be done at room temperatures but the scaling is very poor so generally chemical exfoliation is preferred [40].

In chemical exfoliation synthesis, reduction of interlayer forces takes place followed by the formation of intercalated compounds. After this, the material is exfoliated in the presence of oxygen by rapid heating. This synthesis mechanism (as shown in Fig. 2.8) produces a large amount of graphene at low temperatures [41]. Exfoliation is a phase transition, which takes place when there is a layer to solvent molecule charge transfer and a minimum mixing enthalpy at well-defined elevated temperatures.

The process starts with the reduction of interlayer forces of graphite sheets by overcoming inter-planar Vander-wall forces using energetic ultrasound vibrations followed by dispersion and exfoliation. Graphite molecules are dispersed in a liquid that acts as a solvent and has similar values of surface energy as that of graphite. Then,

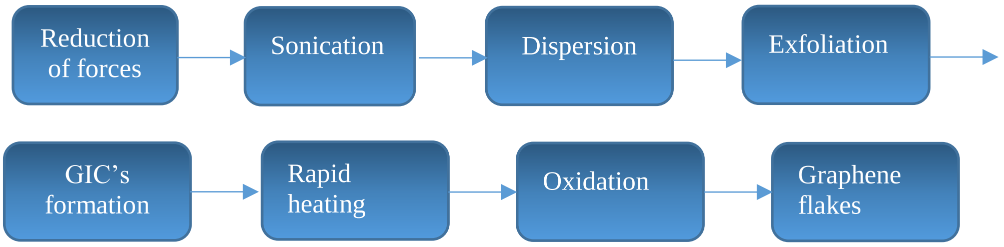


Fig. 2.8. A flowchart of the steps of Chemical Exfoliation

the dispersed solution of graphite is exfoliated followed by sonication using Hummer's method (oxidation of graphite using oxidizing agents) causing the formation of an intercalated compound (GIC's). Exfoliation occurs as a result of the transfer of charge from solvent to layers of graphite material leading to charging of graphite sheets which depends upon the composition of the solvent [42]. Then rapid heating and oxidation are done after exfoliation which leads to the decomposition of graphite flakes and the formation of a colloidal solution of graphene oxides (GO) from which Graphene is extracted.

CHAPTER 3

SYNTHESIS

3.1 CHEMICALS AND MATERIALS

Tungsten hexachloride (WCl_6), Thioacetamide or TAA (C_2H_5NS) and Ammonium Molybdate Tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) with 99.98% purity were purchased from Sigma Aldrich. Zinc acetate ($ZnC_4H_6O_4$) and Sodium Hydroxide (NaOH) were purchased from Thermo Scientific. Thiourea (CH_4N_2S) was purchased from SRL Pvt. Ltd. Acetone was purchased from Rankem. Ethanol was purchased from Merck. We have used Milli-Q water, (18.2 MΩ cm) as the solvent during our synthesis. All the chemicals used here had an analytical grading and were taken without any further purifications being done.

3.2 WS_2 NANOSTRUCTURE SYNTHESIS

WS_2 nanostructures were synthesized via the Hydrothermal method and their phase was checked using XRD characterization. Fig. 3.1. gives an outline of the hydrothermal process used for WS_2 nanomaterial synthesis in NRL lab, DTU, Delhi, India.

We first weighed the salts/precursors i.e., Tungsten Hexa-chloride and TAA, and added them to two different beakers containing water as solvent. Beakers were then kept for magnetic stirring at room temperature (27-30° C) with varied revolutions per second for 1 hour for mixing of salts in water. Two different approaches were followed for the synthesis of WS_2 nanostructures. In one approach of synthesis, the TAA solution was added dropwise into WCl_6 solution after one hour while in the other approach, the WCl_6 solution was added into TAA solution. After this, the mixed solutions were kept for stirring for 1 hour. The pH of the solutions was regulated and optimized to the values ranging from 6 to 8 which was initially 2 by adding liquor ammonia drop by drop. The solution mixtures were then transferred to Teflon-lined autoclaves of different capacities and kept in the oven for 20-24 hours at 220°C. Then centrifugation and washing of samples was done using De-ionized Water (DI) and ethanol, 3 times with each. Drying of samples was done at 60°C in an oven for 24 hours. Then the samples were sent for XRD analysis. We tried 5 reaction attempts to synthesize the materials at varied conditions. In the following Table 3.1. we have summarized all 5 reaction attempts and their physical optimization conditions.

Table 3.1: Reaction attempts summary for WS_2 synthesis

Sample	Precursor name	Amount (g)	DI water (mL)	Stirring conditions	pH
S1 (TAA into WCl_6)	WCl_6	0.522	30	stirred at 250 rpm, 30°C	Initial: 2
	TAA	0.6	30	stirred until fully dissolved	Final: 6
	TAA was added into WCl_6 and the mixture was stirred at 350 rpm at 30°C.				
	Solution mixture kept at 220°C for 24 hours in a 100 mL Teflon-lined autoclave.				
S2 (WCl_6 into TAA)	WCl_6	0.522	18	stirred at 350 rpm, 27°C	Initial: 2
	TAA	1.000	17	stirred at 250 rpm, 27°C	Final: 8
	WCl_6 was added into TAA and the mixture was stirred at 350 rpm at 27°C.				
	Solution mixture kept at 220°C for 24 hours in a 50 mL Teflon-lined autoclave.				
S3 (TAA into WCl_6	WCl_6	1.044	18	stirred at 400 rpm, 27°C	Initial: 2
	TAA	2.000	17	stirred at 250 rpm, 27°C	Final: 8
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27°C.				
	Solution mixture kept at 220°C for 24 hours in a 50 mL Teflon-lined autoclave.				
S4 (TAA into WCl_6)	WCl_6	0.632	18	stirred at 400 rpm, 27°C	Initial: 2
	TAA	1.211	17	stirred at 250 rpm, 27°C	Final: 6
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27°C.				
	Solution mixture kept at 220°C for 20 hours in a 50 mL Teflon-lined autoclave.				
S5 (TAA into WCl_6)	WCl_6	1.566	17	stirred at 280 rpm, 27°C	Initial: 2
	TAA	3.000	18	stirred at 400 rpm, 27°C	Final: 6
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27°C.				
	Solution mixture kept at 220°C for 20 hours in a 50 mL Teflon-lined autoclave.				

After 24 hours, samples were cooled down to room temperature. Then the samples were collected via centrifugation at 7,000 rpm for 7 min after washing with DI water and ethanol before drying at 60˚C for 24 hours. The formed samples were collected in Eppendorfs after crushing and named as ‘S4’and ‘S5’ respectively.

3.3 ZnO-MoS$_2$ COMPOSITE SYNTHESIS

Two synthesis approaches were followed for the synthesis of the ZnO-MoS$_2$ nanocomposite, first or type-I reactions were adding prepared MoS$_2$ in the synthesis of ZnO and the type-II were by the vice-versa method i.e., adding prepared ZnO into the synthesis of MoS$_2$. In total, 15 samples were prepared with different compositions and conditions. Fig. 3.2. gives an outline of the hydrothermal process (type-I) used for ZnO-MoS$_2$ nanocomposite synthesis in NRL lab, DTU, Delhi, India.

In type-I synthesis, prepared MoS$_2$ nanoparticles [43] (named as MS1 and MS2) were added in the synthesis of ZnO nanostructure and the resultant nanomaterial obtained was a nanocomposite of ZnO-MoS$_2$ as can be interpreted by the literature survey [44], [45] and the preliminary XRD results.

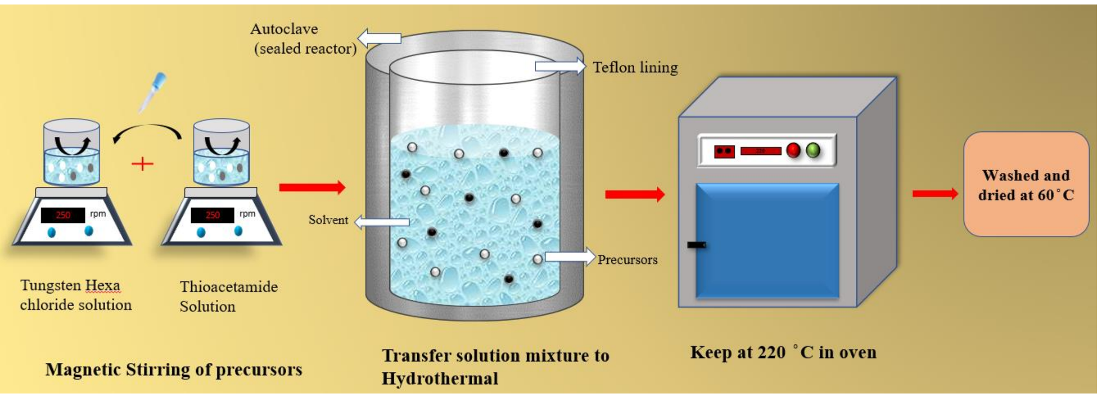


Fig. 3.1 A diagrammatical representation of the general hydrothermal process used for WS$_2$ sample preparation in NRL, DTU, Delhi, India.

We have got the optimized conditions for ZnO nanostructures from our senior, Ms. Nikita Jain. For the synthesis of these ZnO nanoparticles, the two precursors taken were Zinc Acetate ($ZnC_4H_6O_4$) and Sodium Hydroxide (NaOH). These were added to the different amounts of DI water and magnetically stirred until completely dissolved. 11 samples of the nanocomposite were prepared using this approach with varying amounts of precursors, DI water, temperature and stirring conditions. Prepared MoS_2 was added as a liquid solution of varying concentrations (10, 12 and 20 mL) to these solutions of precursors and with weight percentages of 0.5, 1.5, 2, 5 and 10 % with respect to ZnO. In some reactions, MoS_2 solution was ultrasonicated to obtain a homogenous mixture for fast and easy synthesis. The mixture solutions were again magnetically stirred using magnetic beads and then transferred to Teflon-lined autoclaves. The time of reactions was generally kept at 24 hours and varied temperatures ranging from 130 to 220˚C.

After 24 hours, the samples cooled down naturally to room temperature. Then they were collected via centrifugation after washing with DI water and ethanol, 3 times each. Later, the washed samples were kept for drying. In one reaction of 5 wt % MoS_2, the washed and dried sample was even annealed at 300˚C for 5 hours to obtain well pronounced XRD peaks. The powdered form of samples was then collected in an Eppendorf after crushing them and sent for XRD.

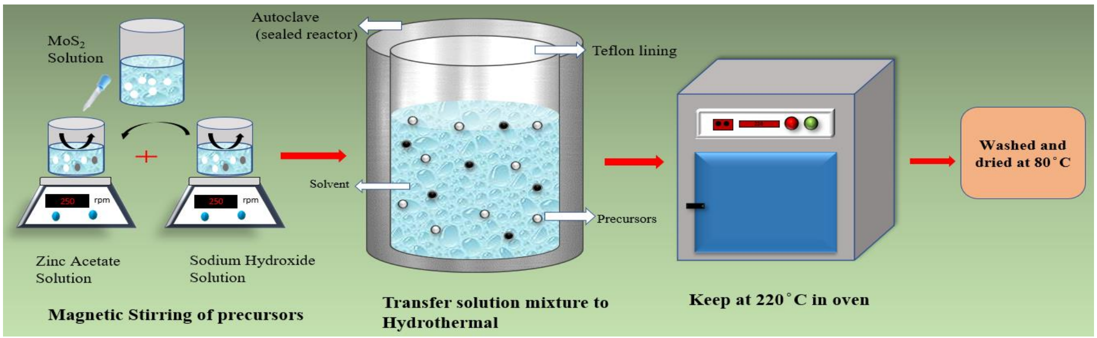


Fig. 3.2. A diagrammatical representation of the general process (type-I) used for sample preparation in NRL, DTU, Delhi, India.

In type-II synthesis, prepared ZnO nanoparticles (sample named as Z1) were added in the synthesis of MoS_2 nanostructures and the resultant nanomaterial obtained was a nanocomposite of ZnO-MoS_2 as can be interpreted by the literature survey and the preliminary XRD results. Following Table 3.2. is the summary of the reaction attempts for the preparation of the synthesis of the composite by this second approach.

Table 3.2: Reaction attempts summary for ZnO-MoS_2 nanocomposite synthesis (type-II)

Sample	Precursor name	Amount (g)	DI water (mL)	Stirring	
1 wt % ZnO in MoS_2 (Rn 1`)	Ammonium Molybdate Tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O)$	2.4718	25	stir at 350 rpm, 30 min	(1)
	Thiourea (CH_4N_2S)	2.1504	25		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.0673	20	Stir for 30 min	(4)
	Add (4) into (1) dropwise and stir at 350-450 rpm for 60 min.				
	Transfer the solution mixture of (1) into 100 mL Teflon-lined autoclave and keep at 220˚C for 24 hours				
6 wt % ZnO in MoS_2 (Rn 2`)	Ammonium Molybdate Tetrahydrate	2.4718	25	stir at 350 rpm, 30 min	(1)
	Thiourea	2.1504	25		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.4041	20	Ultrasonicate for 5 min then stir for ½ hr	(4)
	Add (4) into (1) dropwise and stir at 350-450 rpm for 1 hour.				
	Transfer the solution mixture of (1) into 100 mL Teflon-lined autoclaves and keep at 220˚C for 24 hours				
1 wt % MoS_2 in ZnO (Rn 3`)	Ammonium Molybdate Tetrahydrate	2.4718	11	stir at 350 rpm, 30 min	(1)
	Thiourea	2.1504	12		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.0673	12	Ultrasonicate for 30 min then stir for ½ hr	(4)
	Add (4) into (1) dropwise and stir at 350-450 rpm for 1 hour.				
	Transfer the solution mixture of (1) into 50 mL Teflon-lined autoclave and keep at 220˚C for 24 hours.				
6.4 wt % ZnO in MoS_2 (Rn 4`)	Ammonium Molybdate Tetrahydrate	2.4718	11	stir at 350 rpm, 30 min	(1)
	Thiourea	2.1504	12		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.4310	12	Ultrasonicate for 30 min then stir for ½ hr	(4)
	Transfer the solution mixture of (1) into 50 mL Teflon-lined autoclave and keep at 220˚C for 24 hours.				

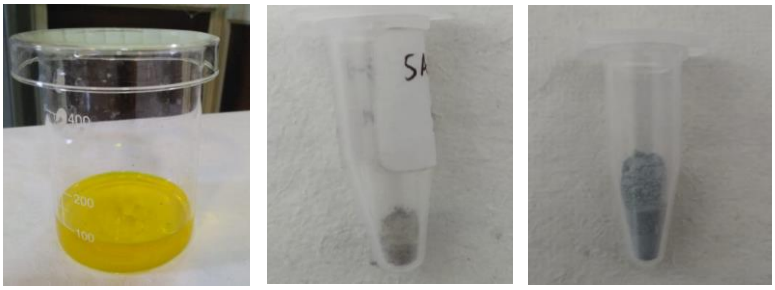
After 24 hours, the samples cooled down naturally to room temperature. Then they were collected via centrifugation at 10,000 rpm for 10 min after washing with DI water and ethanol, 3 times each. The washed samples were kept for drying at 60˚C for 24 hours. The powdered form of samples was collected in an Eppendorf after crushing them and named as ‘Rn1``’, ‘Rn2``’, ‘Rn3``’, Rn4``’ respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. WS_2

In the first three attempts of WS_2 synthesis, no sample was obtained at the bottom of the Teflon as shown in Fig. 4.1. (a) but in the 4th attempt, as shown in Fig. 4.1. (b) and 5th attempt, as shown in Fig. 4.1. (c), impressive amounts of greyish-colored samples were formed. Here, we have included the obtained XRD results of our 4th and 5th reaction attempts of the synthesis of WS_2 nanomaterial. The phases of the resultant nanomaterials obtained in the last 2 reactions were checked for the confirmation of the WS_2 phase as can be interpreted from the preliminary XRD results compiled in the following sections.



(a) (b) (c)

Fig. 4.1. (a) No sample obtained in the first three attempts **(b)** Sample formed in the fourth attempt **(c)** Sample formed in the fifth attempt

4.2. ZnO-MoS_2

Several attempts were made to synthesize the nanocomposite by two different calculations as discussed in chapter 3 with varying weight percentages of MoS_2 or ZnO. The pictorial representation of one of the resulting prepared sample of ZnO-MoS_2 nanocomposite is shown in Fig. 4.2. Here, we are reporting the preliminary XRD results of the prepared MoS_2 sample (MS1 and MS2), prepared ZnO sample (Z1) and all 14 reaction attempts in the preparation of the ZnO-MoS_2 nanocomposite and the UV results of the nanocomposite. The ZnO-MoS_2 phase can be interpreted from the preliminary XRD results compiled in the following sections.

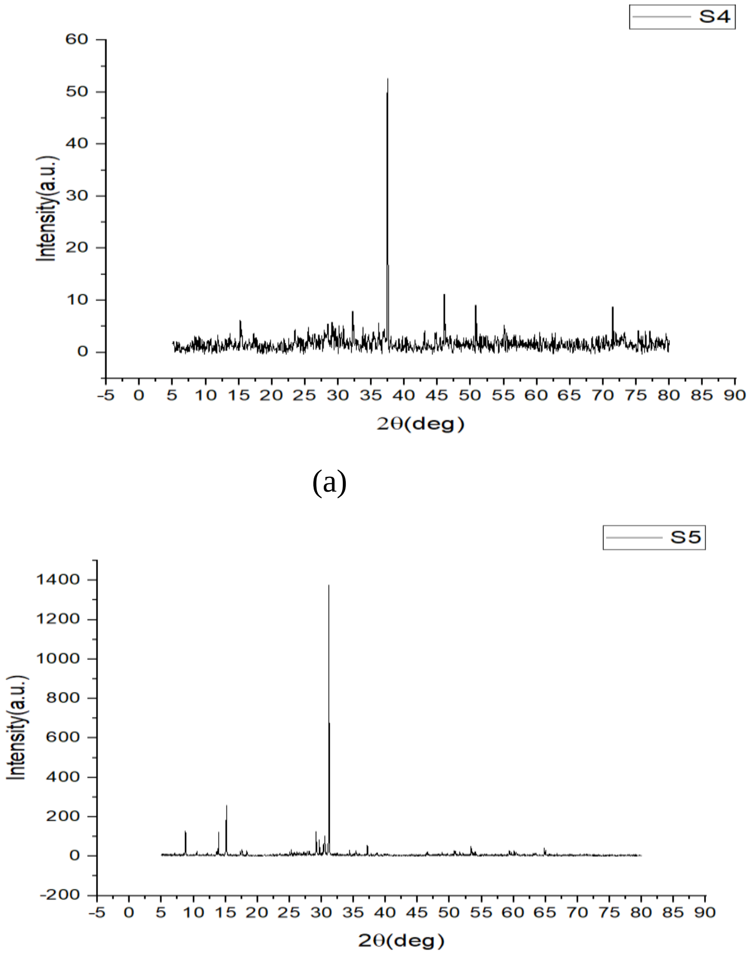
4.3 CHARACTERIZATION

XRD patterns were recorded using Bruker 8D Advance System using CuK{alpha} λ=1.54 Angstrom at 40 kV voltage and 20 mA current with a scan rate of 1 ° per minute to study and verify the phase of the as-prepared samples and UV-vis spectroscopy is done using Carry-500 spectrometer which can be further studied to know the optical properties of the nanomaterial samples. The diffraction patterns for WS_2 are recorded within the 2θ scanning range of -5 to 90 degrees and that of ZnO-MoS_2 nanocomposites is 5 to 80 degrees and the UV-vis spectra are recorded for the liquid composite samples within a range of 200-800 nm.

Fig. 4.2 Pictorial representation of resulting prepared sample of ZnO-MoS_2.

4.3.1 XRD Characterization of WS_2

XRD results of the prepared WS_2 sample numbers 4 (S4) and 5 (S5) corresponding to reaction attempts 4 and 5 (from Table 3.1) are as shown in Fig. 4.3. (a) and Fig. 4.3. (b). The crystal structure of these samples was interpreted using XRD spectra. In the XRD results of sample 4, diffraction peaks are obtained at 2θ angles of 15.05°, 28.87°, 32.12°, 37.36°, 46.20°, 50.80° and 71.26° whereas, for sample 5, the diffraction peaks are more prominent and are obtained at 2θ angles of 8.81°, 13.80°, 15.29°, 29.00°, 29.63°, 30.63°, 31.12°, 37.23°, 53.43°and 64.89°. The diffraction peaks corresponding to these samples were plotted and labelled using OriginPro-2021 software.



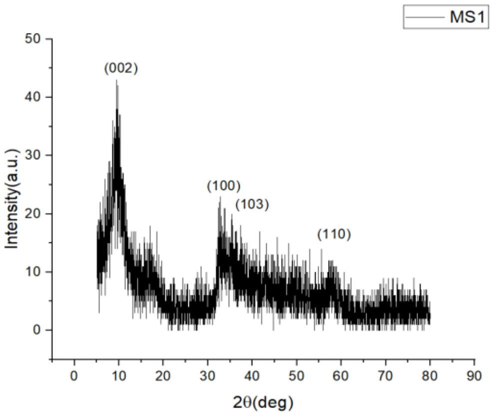
(a)

(b)

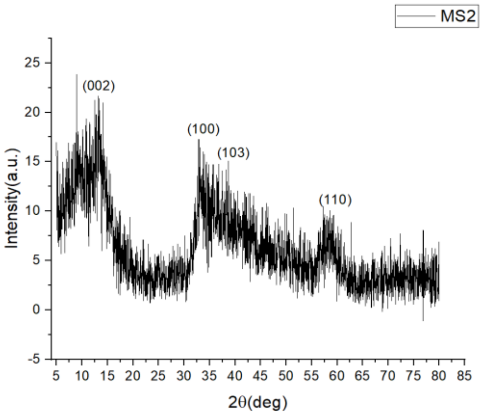
Fig. 4.3. XRD of **(a)** Sample 4 (S4), **(b)** Sample 4 (S5)

4.3.2 XRD Characterization of ZnO-MoS_2

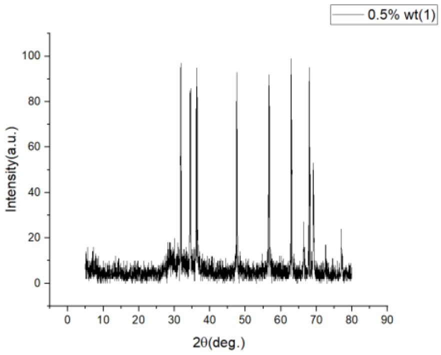
For type-I synthesis, the XRD results of the pre-prepared MoS_2 samples (MS1 and MS2) are as shown in Fig. 4.4 (a) and (b) and that of the ZnO-MoS_2 composites loaded with 0.5%, 1.5%, 2%, 5% and 10% MoS_2 are shown in Fig. 4.4 (c) to Fig. 4.4 (l). The crystal structure of the prepared composite samples is interpreted by these XRD curves. In the diffraction results of pure MoS_2 (Fig. 4.4 (a)), diffraction peaks are obtained at 2θ angles of 13.04˚, 32.20˚, 38.6˚ and 58.6˚ corresponding to the miller planes (002), (100), (103) and (110) respectively which can be interpreted from the literature. The diffraction peaks of ZnO in the composite samples correspond to the 2θ angles of 31.8˚, 34.5˚, 36.2˚, 47.5˚, 56.6˚, 62.8˚, 66.3˚, 68.0˚ and 69.1˚ which can be indexed to the planes of (100), (002), (101), (102), (110), (103), (112), (201) and (202) respectively.



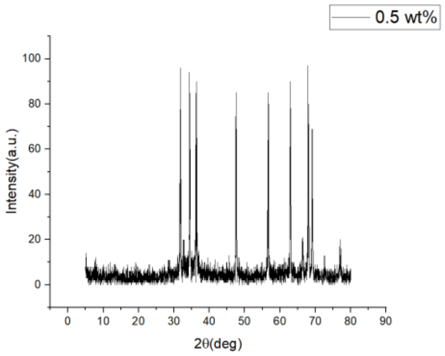
(a)



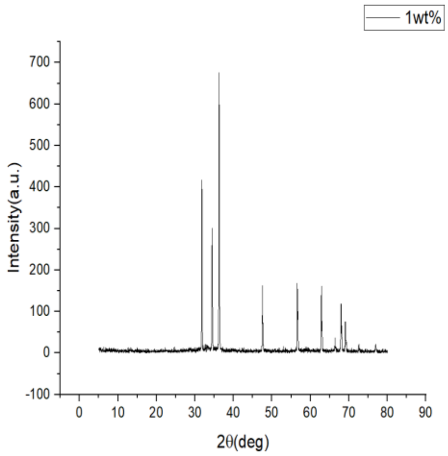
(b)



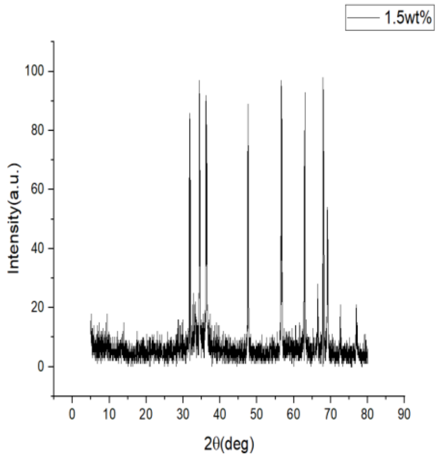
(c)



(d)


1wt%
Intensity(a.u.)
700
600
500
400
300
200
100
0
-100
0 10 20 30 40 50 60 70 80 90
2θ(deg)

(e)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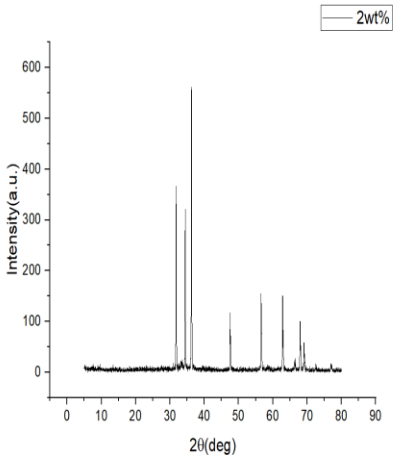
0 10 20 30 40 50 60 70 80 90
2θ(deg)

(f)


2wt%
Intensity(a.u.)
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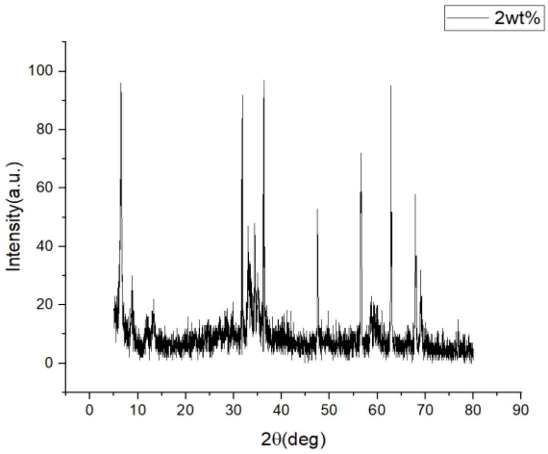
200
100
0
0 10 20 30 40 50 60 70 80 90
2θ(deg)

(g)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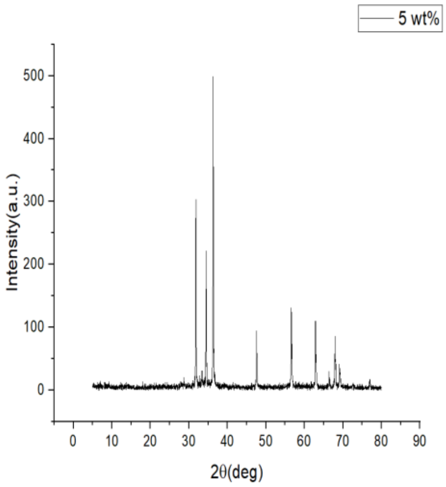
(h)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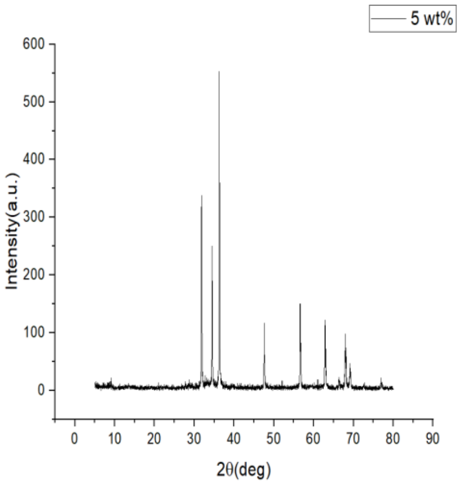
2θ(deg)

(I)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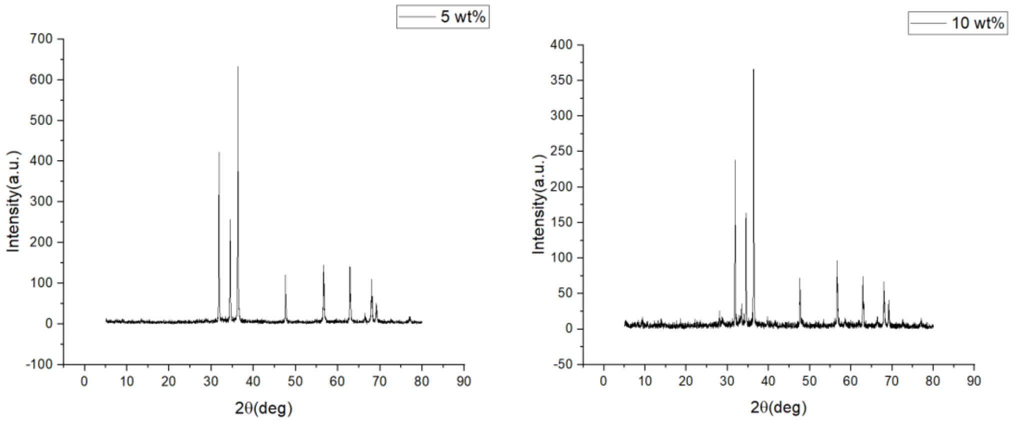
0 10 20 30 40 50 60 70 80 90
2θ(deg)

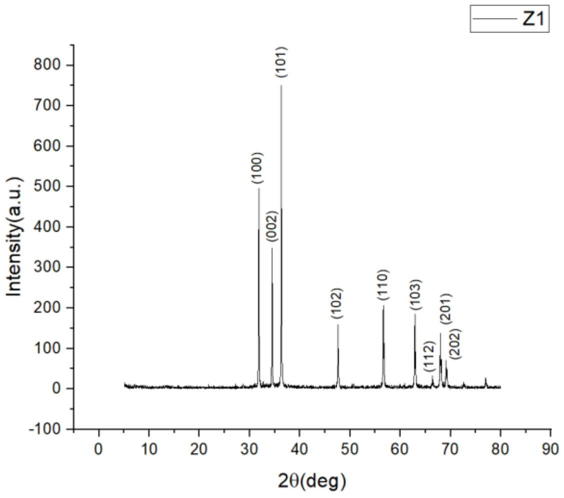
(j)



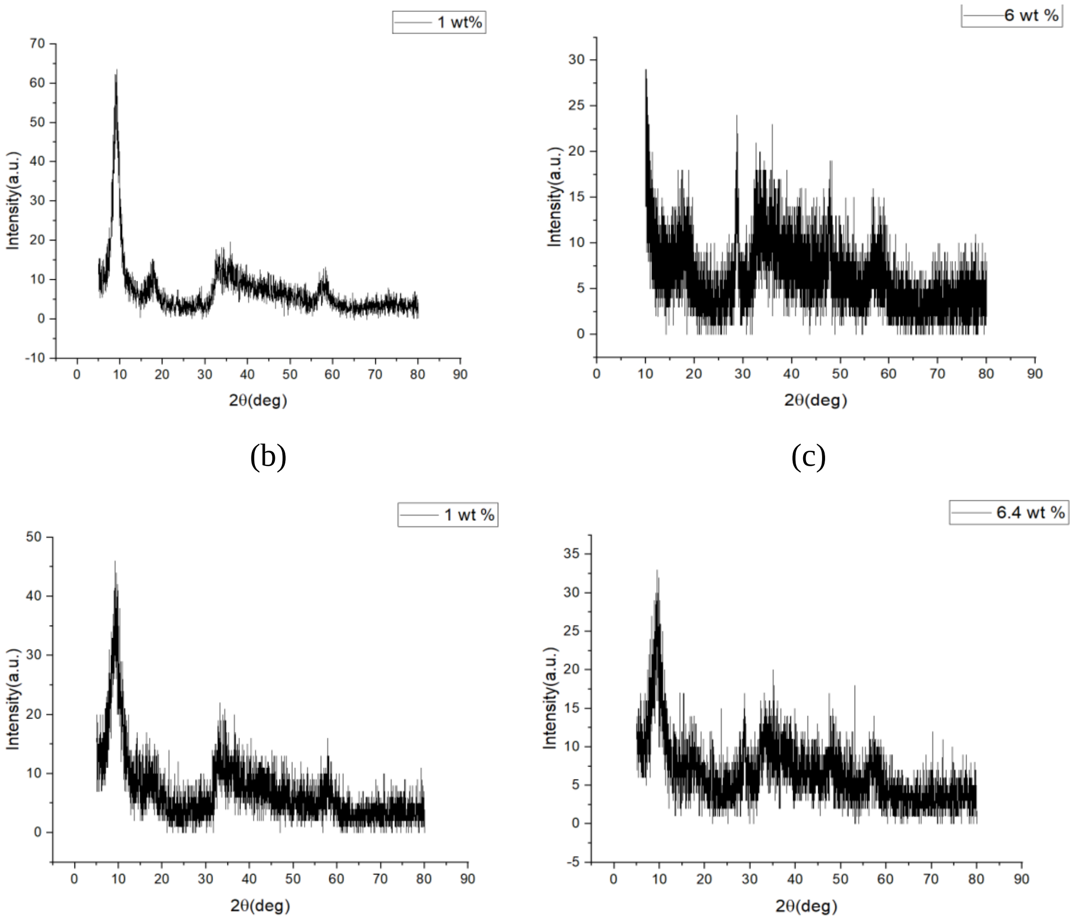
(k) (l)

Fig. 4.4. XRD of **(a)** prepared MoS_2 samples (MS1), **(b)** prepared MoS_2 sample (MS2), **(c)** 0.5 wt % (Rn1), **(d)** 0.5 wt % (Rn2), **(e)** 1 wt % (Rn3), **(f)** 1.5 wt % (Rn4), **(g)** 2 wt % (Rn5), **(h)** 2 wt % (Rn6), **(i)** 5 wt % (Rn7), **(j)** 5 wt % (Rn4), **(k)** 5 wt % (Rn4), **(k)** 5 wt % (Rn4), **(l)** 10 wt % (Rn4) sample.

Now, for type-II reactions, XRD plots of the pre-prepared ZnO samples are as shown in Fig 4.5. (a) and that of all 4 reaction attempts of the ZnO-MoS_2 nanocomposite are as shown in Fig. 4.5 (b), (c), (d) and (e).



(a)



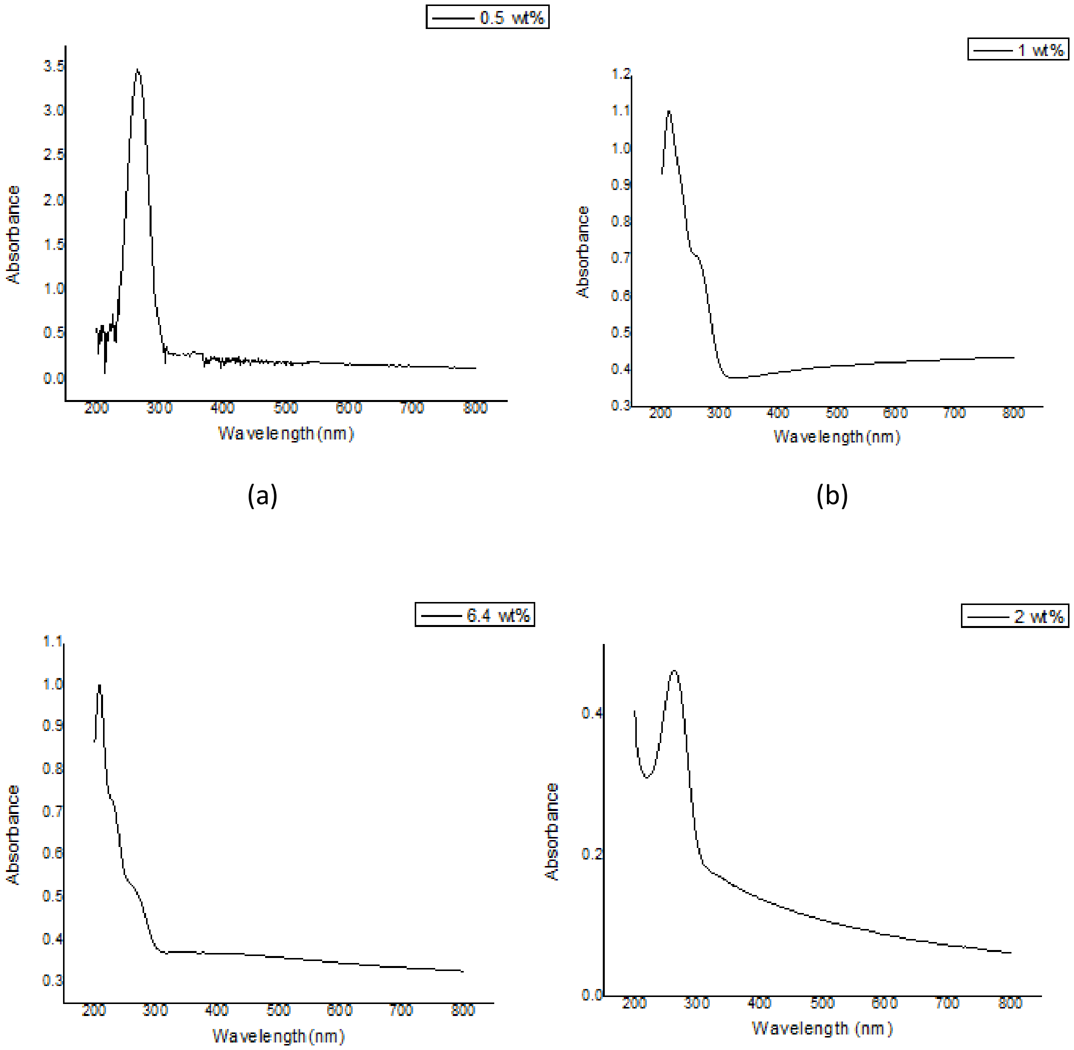
(b) (c)

(d) (e)

Fig. 4.5: XRD results of (a) pre-prepared ZnO nanoparticles (b) Rn 1', (c) Rn 2', (d) Rn 3' and (e) Rn 4'

4.3.3 UV-vis Spectroscopy

The nanoparticles show a broad absorption spectrum due to quantum confinement effects and the absorption peaks shift toward smaller wavelengths (higher energies) as the crystal size of the nanoparticles decreases, while the molar absorption coefficient increases with decreasing size. The peak widths of the nanoparticles also depend on the size distribution of the nanoparticles. The shift of absorption peak from higher to shorter wavelength is called a blueshift. UV–vis spectroscopy is used to determine the concentration, size, purity, and aggregation state of the constituents, and functional groups in molecules. It also provides size- and composition-dependent spectrum for the nanomaterials. The wavelength (λ) of light required for electronic transitions is typically in the ultraviolet (λ = 200–390 nm) and visible region (λ = 390–780 nm) of the electromagnetic radiation spectrum. Uv-vis analysis of a few ZnO-MoS_2 samples was done and their absorbance versus wavelength curves are as shown in the Fig. 4.6 ((a) to (d)). In these UV results of the nanocomposite, the absorption edge of the composite sample was obtained at the range of 250-310 nm as is shown in the figure below.



(a) (b)

(c) (d)

Fig. 4.6. UV-vis spectrum for (a) 0.5 wt% MoS_2 in ZnO, (b) 1 wt% MoS_2 in ZnO, (c) 6.4 wt% MoS_2 in ZnO, (d) 2 wt% ZnO in MoS_2

4.4 CONCLUSION AND DISCUSSIONS

There are many Physical and Chemical synthesis techniques for the preparation of nanoparticles namely Hydrothermal, Solvothermal, Sonochemical, CVD, Sol-gel, and Chemical Exfoliation techniques. Some are Top-Down approaches while others are Bottom-Up approaches. Both types of techniques have their advantages and disadvantages offering a variety of options to the users. Different types of nanomaterials like metal oxides, TMDs, etc. can be prepared by these approaches. Among the various metal oxides, Zinc Oxide (ZnO) is the one which has been explored vastly due to their exceptional properties. But on the other side, TMDs like Molybdenum disulfide (MoS_2), Tungsten Disulphide (WS_2), etc. have also attracted attention due to their remarkable optical and electronic properties. Here, various attempts of preparation of the WS_2 nanocomposite and the ZnO-MoS_2 nanocomposite via facile Hydrothermal method are reported with the preliminary XRD and UV results.

In results of reaction of WS_2 nanocomposite, for the first three attempts, no sample was formed while in other attempts, greyish colored powder was obtained after centrifugation and washing. The suspected reason for the improper phase obtained in the XRD results of the WS_2 samples as shown in the previous section is the manual or incomplete stirring of precursors due to unoptimized conditions.

This material can be used for a variety of applications in which solid lubrication is a famous one. The adhesion between Sulfur layers is relatively weak which results in the sliding of layers over each other.

The ZnO-MoS_2 nanostructure's synthesis using two different approaches and characterization results were also presented here. In first approach, MoS_2 powder was synthesized which was then added in the preparation of ZnO and in the second approach, prepared ZnO nanoparticles were added in the preparation of MoS_2. UV-vis spectroscopy was also done of the as-prepared samples of ZnO-MoS_2 nanocomposite which can be used to further study the sample's optical properties.

From these preliminary XRD results, the phase of both the composites can be interpreted from the literature.

CHAPTER 5

CHEMICAL VAPOUR DEPOSITION

5.1 HISTORICAL BACKGROUND

In the twentieth century, revolutionary advancements were going on in the electronics industry. Silicon (Si) was replacing Germanium (Ge) to be used as a basic semiconductor material for all device fabrications due to its remarkable properties like large bandgap and ease in forming the oxide layer on the surface [46], [47]. Soon, the basic requirements of n-, p- doped Si for Si integrated circuit technology was at peak heights to meet the ever-increasing demand for personal computers [34]. It was in the year 1960 that Theurer successfully fabricated good quality Si films which attracted the attention of various industries towards the manufacturing of silicon semiconductor devices [48]. These advancements have created a tremendous urge for highly pure ultra-thin films in the scientific world.

Though various methods like Electroplating [49], Spin coating [50], [51], Vacuum evaporation [52], Sputtering [53], and others have been explored at times to meet the early requirements of film deposition/coatings, many drawbacks and complications like deposition of multiple films, coating of large surface area, and conformal coverage have been observed with them[54]–[56]. This search takes us to the Chemical Vapor Deposition (CVD) technique which was at an early stage at that time. Since the late 1960s, its usage has gained momentum due to various advantages that it offers and it has emerged as the leading candidate for good quality thin film deposition [57]. It involves the deposition of one or more stable solid films on a heated substrate by a suitable chemical reaction at the surface of the substrate [58].

5.2 VARIANTS OF CVD

Various variants of CVD including Thermal Chemical Vapor Deposition, Plasma Enhanced Chemical Vapor Deposition (PECVD), Metal-Organic Chemical Vapor Deposition (MOCVD), and Atomic Layer Chemical Vapor Deposition (ALCVD) have been introduced at times [59]–[63]. Every variant has some advantages as well as disadvantages over others. Thermal CVD can be considered more of kind of a growth process rather than a deposition process in which the chemical reaction takes place at the surface of the substrate. In thermal CVD, the reaction is initiated by thermal energy provided by various means while in PECVD, the electrical energy is used to initiate homogeneous reactions for the production of chemically active ions and radicals that can participate in the heterogeneous reaction. CVD variants can also be differentiated based on zones. (a) Single zone CVD (b) Multiple zone CVD (two or more zones).

Looking at their significant advantages and future scopes, the Double Zone Thermal CVD System and PECVD systems present in the Nanomaterials Research Laboratory (NRL), Department of Applied Physics of Delhi Technological University (DTU), Delhi have been studied. Here, in this chapter, the detailed role of their various components, technical specifications, and working with labelled diagrams, schematics and relevant flowcharts are discussed.

5.2.1 Double Zone Thermal CVD

Double Zone Thermal CVD technique is a versatile, non-line of sight deposition technique by which uniform thin films can be deposited at a reasonable processing cost. Highly dense and pure materials can be obtained by this method. Though this method is a little complex, uniform and conformal deposition of films is possible with good reproducibility which is the biggest advantage [64]–[66]. Since the inception of novel CVD, its market has skyrocketed. The films deposited by the CVD technique have found their applications in numerous fields like the communication industry, optoelectronics industry, synthesis of high-temperature superconductors, coatings, and many interdisciplinary fields [59], [67]–[70]. One of the key reasons for the popularity of this technique comes from the fact that a variety of materials can be used as precursors in this method. Some of them are metals, metal hydrides, halides, halo-hydrides, and metalorganic compounds, and many more [59], [70]–[75]. A typical laboratory Double Zone Thermal CVD in NRL, DTU, Delhi, India is shown in Fig. 5.1.

5.2.2 Plasma Enhanced CVD

PECVD is one of the numerous variants of CVD used to deposit thin films. Like Double Zone Thermal CVD, it is also a non-line of sight technique that involves a chemical reaction at a low temperature activated by a high-energy plasma stream. The stream is produced using electrical energy which later transfers the energy of its species to the precursors. This initiates the homogeneous reaction to free

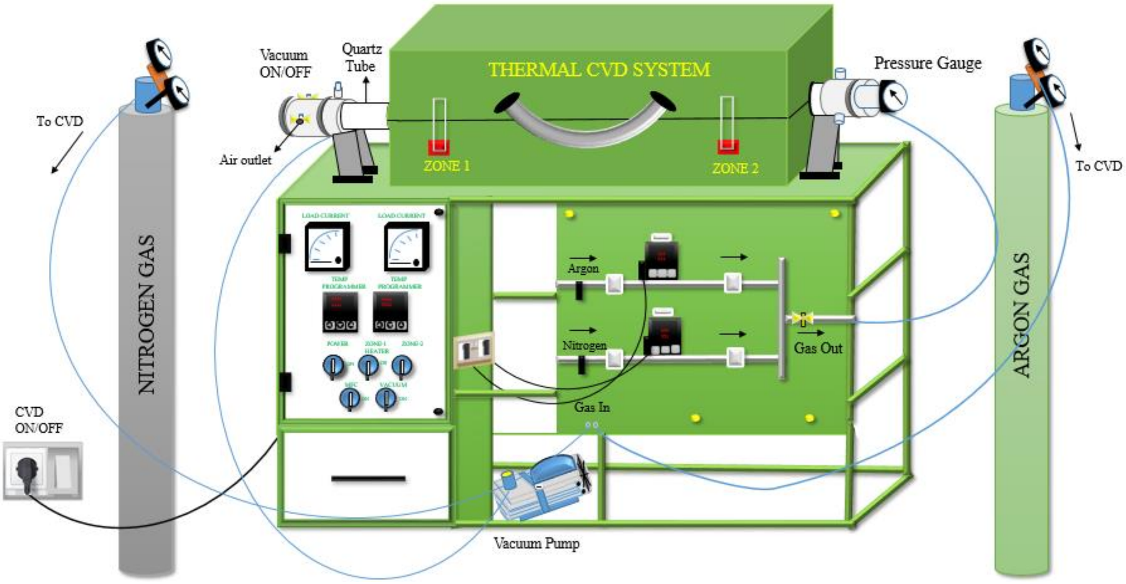


Fig. 5.1. Labelled diagram of typical laboratory Double Zone Thermal Chemical Vapor Deposition (CVD) in NRL, DTU, Delhi, India.

radicals or active ions followed by radical polymerization resulting in the deposition of thin films. It is a widely used technique to fabricate various thin nano-films and modify their properties for diverse applications [76]. A typical laboratory PECVD in NRL, DTU, Delhi, India is shown in Fig.5.2.

5.3 INSTRUMENTATION: IMPLEMENTATION AND FUNCTION

The impetus provided to the phenomenal usage of thermal CVD in diverse areas is due to ease in its installation and simple fabrication process. The most basic requirements for a CVD system are: a gas supplier with a flow controller, some heating mechanism, a reactor chamber, and a temperature controller. In the Double Zone Thermal CVD system in NRL, DTU, Delhi (shown in Fig. 5.1.), there are two independent heating zones with a 31.4-inch chamber size made up of quartz tube that can operate up to 1000℃ which makes it a high-temperature CVD [76]. On one side of the quartz tube, a gauge meter is attached to observe the pressure inside it. It can show the pressure in the range 0 to 1838 mm Hg on the positive side and 0 to -760 mm Hg on the negative side. On the other side, there is a gas outlet valve and a vacuum valve connected to the vacuum pump used for the suction of air inside the

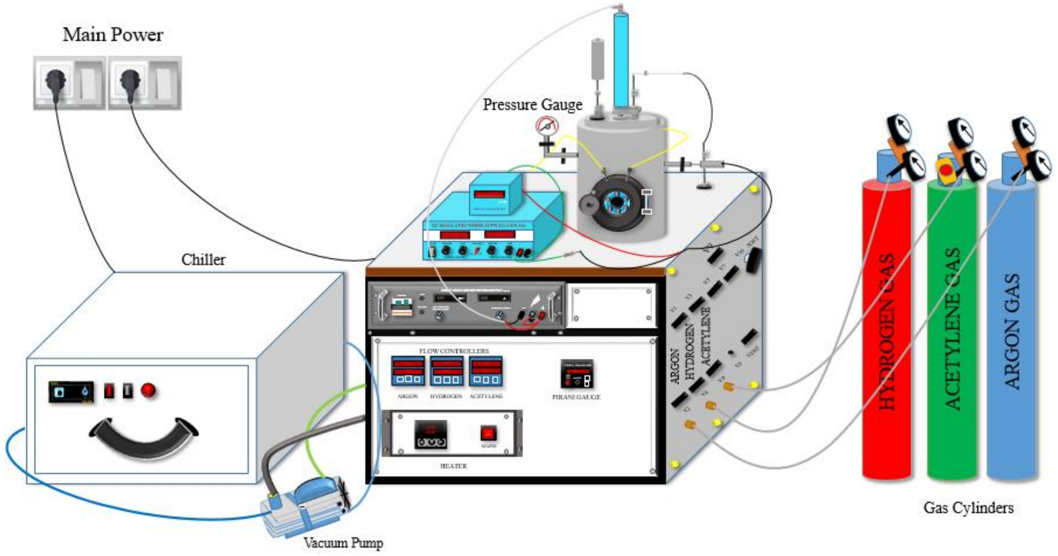


Fig. 5.2. Labelled diagram of PECVD in NRL, DTU, Delhi, India.

tube and creates the desired level of vacuum. There are two load current meters and temperature programmers for both zones respectively. There are two gas cylinders also, containing inert gases, Nitrogen (N_2) and Argon (Ar) respectively. The one filled with N_2 gas has the capacity of 46.7 liters weighing 51.7 kg and the other one filled with Ar has the same capacity weighing 52.2 kg. Complete technical details are presented in Table 5.1. As it is a hot wall reactor, the whole quartz tube is heated uniformly with the precursors and the substrate is placed inside it. Fig. 5.2. shows the PECVD system in NRL, DTU, Delhi. PECVD has three cylinders of gases containing acetylene, hydrogen and argon gas. A chiller and heater are attached to the system for cooling and heating purposes respectively. A vacuum pump is also attached for suction of the air and creating vacuum as per the desired conditions.

5.4 PRINCIPLE

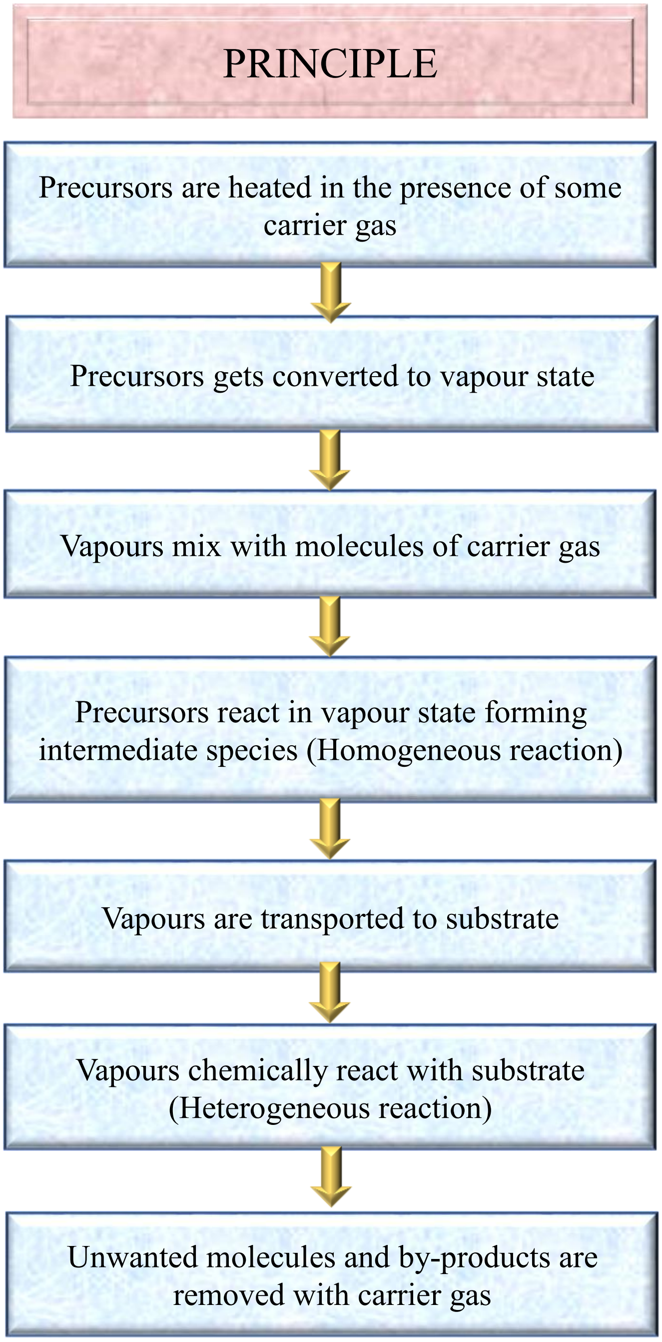
5.4.1 Double Zone Thermal CVD

The basic principle of Thermal CVD is described in the flowchart in Fig. 5.3. Here, volatile precursors are provided thermal energy in the presence of an inert

Table 5.1. Technical details of Double Zone Thermal CVD system

Technical Parameters	**Values**
Zones	2
Chamber Size	31.4 inch
Maximum Temperature	1000℃
Pressure Range (Positive Side)	0 to 1838 mm Hg
Pressure Range (Negative Side)	0 to -760 mm Hg
Volume (Cylinder filled with N_2)	46.7 litres
Volume (Cylinder filled with Ar)	46.7 litres
Weight (Cylinder filled with N_2)	51.7 kg
Weight (Cylinder filled with Ar)	52.2 kg

gas that is used as a carrier gas. At appropriate temperatures, when precursors are in the vapor state, they get mixed with the molecules of inert gas and undergo a homogenous vapor phase reaction. These precursors diffuse to the substrate surface and the gas molecules get adsorbed on the surface of the substrate. The molecules of precursors heterogeneously react with heated substrate forming a thin solid film. After this, the by-products formed, the adsorbed gas molecules and other unwanted



PRINCIPLE

Precursors are heated in the presence of some carrier gas

Precursors gets converted to vapour state

Vapours mix with molecules of carrier gas

Precursors react in vapour state forming intermediate species (Homogeneous reaction)

Vapours are transported to substrate

Vapours chemically react with substrate (Heterogeneous reaction)

Unwanted molecules and by-products are removed with carrier gas

Fig. 5.3. Principle of Thermal CVD

materials are carried out of the reactor by outlet valve with the flow of gas [77]. The principle of Double Zone Thermal CVD is no different from the above principle. Double zone CVD is better to control the evaporation moment of the precursors. Here, the precursors that require different temperatures to evaporate can be placed in different zones. Thus, the precursor-1 with lower evaporation temperature is placed in zone-1. The precursor-2 with a higher evaporation temperature is placed in zone-2. Both the precursors are placed in the center of the respective zones. The substrate is placed downstream at an optimized distance from the precursor-2. Both the precursors and the substrate are placed in boats of appropriate material depending on temperature.

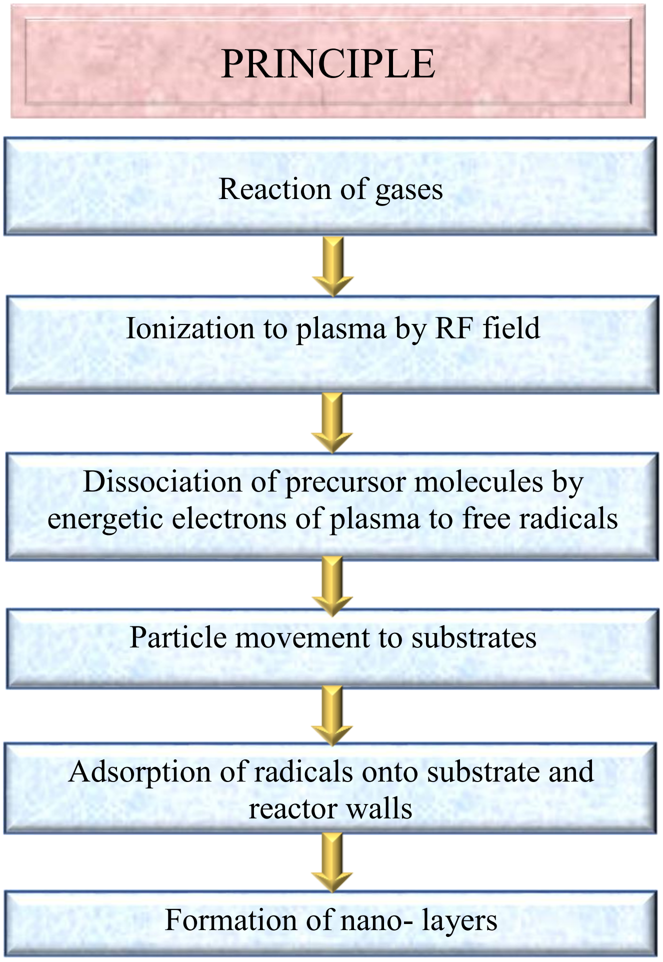


Fig. 5.4. Principle of PECVD

5.4.2 PECVD

The basic principle of the PECVD system is described in Fig. 5.4. The process starts with the reaction of gases followed by the ionization of gases to form the plasma state by DC current. It leads to the dissociation of precursor molecules by energetic electrons of plasma to free radicals which results in the particle movement to the substrates. Finally, the radicals are adsorbed onto the substrate and the reactor walls. Thus, the nano-layers are formed.

5.5 WORKING OF DOUBLE ZONE THERMAL CVD

The working of the Double Zone Thermal CVD system is shown in Fig. 5.5. Here, ‘A’ denotes the flow of inert gas from cylinders through the gas tubes controlled by flow controllers. ‘B’ denotes the flow of gas into the quartz tube in the direction shown. ‘C’ & ‘E’ denotes the heating of volatile precursors by heating elements attached to the CVD. ‘D’ & ‘F’ denotes the conversion of precursors from solid form to vapor form. ‘G’ denotes the diffusion of precursors in the vapor phase to the substrate’s surface. ‘H’ denotes the heterogeneous reaction at the substrate’s surface and the formation of a thin solid film. ‘I’ denotes the removal of by-products and unwanted materials. The complete procedure of depositing the films on the system present in the lab is shown in Fig. 5.6. Initially, the precursors have to be placed inside the boats and then the boats are positioned at the center of the respective zones. In the

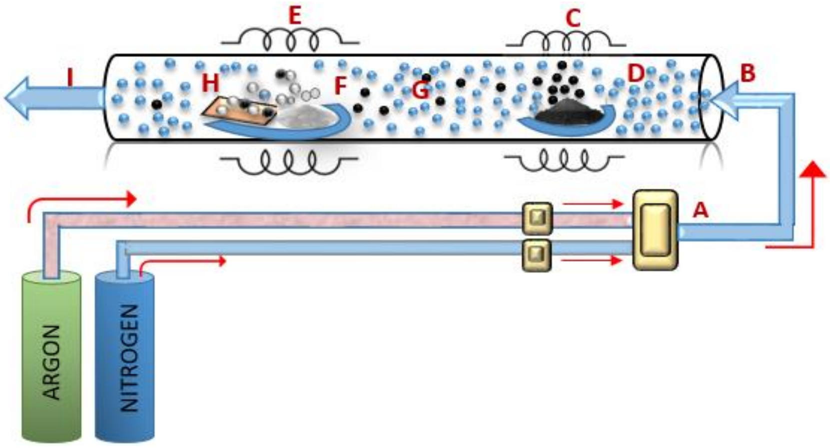


Fig. 5.5. Schematic diagram of Double Zone Thermal CVD

second zone, at some distance from the precursors downstream, the substrate has to be placed. Then, CVD has to be switched ON by turning the power ON knob present on the system. After that, the vacuum inlet valve has to be opened and the vacuum knob has to be turned ON. Then, the pressure gauge has to be checked which should

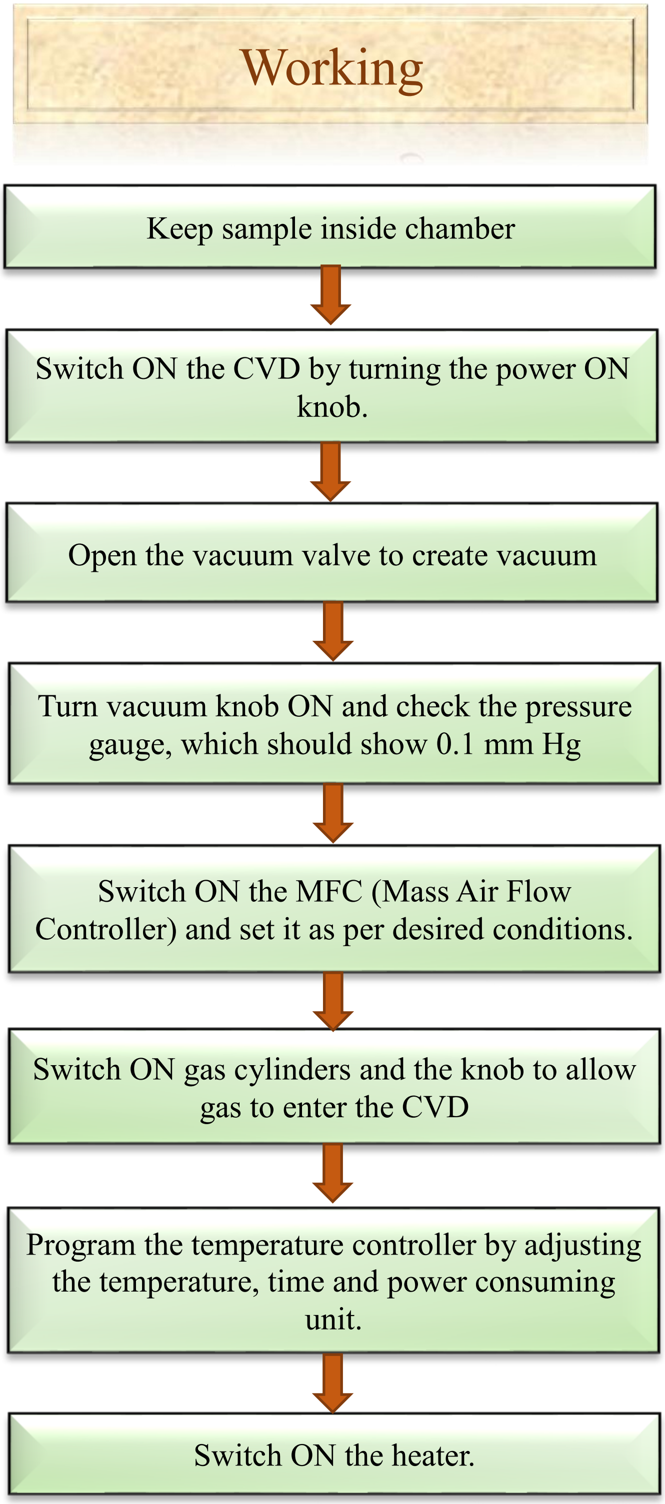


Fig. 5.6. Flow chart of working of Double Zone Thermal CVD system at NRL, DTU

have been showing the reading of 0.1 mm Hg. After checking that, the mass air-flow controller (MFC) has been switched ON and has to be set as per desired conditions. Then, knobs of gas cylinders have to be turned on to allow the gas to enter CVD.

After all the initial steps, finally, temperature controllers have to be programmed to set the temperature, time, and power-consuming unit of both zones. To run the temperature-controlled program, the 'Set' button has to be pressed seven times. After setting the temperature, time, and power consumption unit, the up button has to be pressed to run the program. After looking for all the initial check-points and taking all the precautionary measures, the heater has to be switched on and it starts functioning. The program can be shut off by pressing the "Set" and "Down" buttons simultaneously.

5.6 DIFFERENCES BETWEEN THERMAL CVD AND PECVD

In conventional CVD, the temperature ranging from 500 to 1000 ° C is taken to thermally decompose the precursor gases. Whereas, in PECVD, much lower temperatures are considered. PECVD technique has some limitations which are listed here:

(a) It requires a sophisticated reactor to contain the plasma.

(b) It is difficult to deposit high purity films using PECVD. The reason could be the incomplete desorption of by-products and unreacted precursors at low temperatures.

(c) Incorporation of impurities like toxic, explosive gases in the plasma stream which can be detrimental for many applications.

(d) High ion energy plasma (< 20eVs) used in PECVD can damage fragile substrates because of ion bombardment, (e) the selection of an appropriate monomer is a challenge.

(f) Suitable inlet instruments are needed to be installed separately.

(g) Films formed may comprise compressive and residual stresses because of low-frequency requirements in PECVD.

(h) If superlattice structures are synthesized using PECVD, it could be time-consuming.

(i) Instability against humidity and aging are two more disadvantages.

(j) Costly parts of equipment and machinery that are generally not desirable.

5.7 PRECURSOR SELECTION

As stated above, one of the key reasons for the popularity of CVD is the variety of precursors used in the technique. The precursors can be inorganic compounds like halides, hydrides, halo-hydrides of metals, and metalloids. The precursors used can also be organic compounds like alkoxides, acetylacetonates, alkyl, aryl-derivatives of metal, carbonyls, arenes, etc. as is shown in the classification in Fig. 5.7.

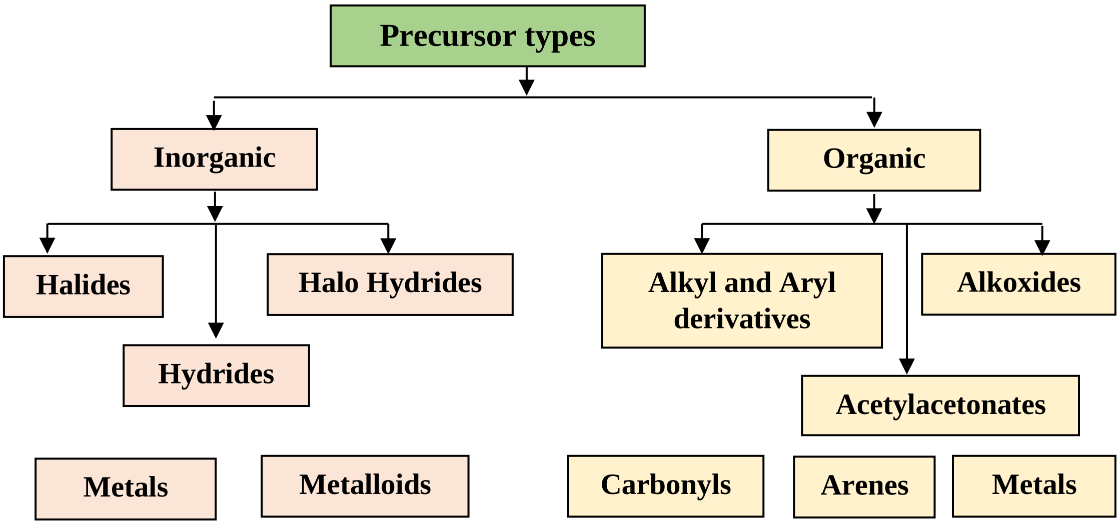


Fig. 5.7. Classification of Precursors used in CVD

Though a large no. of materials can be used as the precursors in this technique, some conditions that are applied to the materials to be used as a precursor are as follows:

(a) At room temperature, the precursor should be stable.

(b) It should have a low evaporation temperature such that it has sufficient volatility.

(c) Its reaction temperature should be below the melting point of the substrate.

(d) It should be available in an adequate amount in pure form at a low cost.

(e) It should be non-hazardous [34], [35], [58].

Above stated conditions are applicable on all the precursors irrespective of the variant of CVD, while some more conditions may vary depending upon the variant of CVD in which they will be used.

5.8 PRECAUTIONARY MEASURES

While operating any device, there are always some safety guidelines that must be followed. Failure in doing so may cause trouble to the user and damage to the instrument. Unlike any other device, while operating a double zone thermal CVD system too, there are some safety precautionary measures that must be followed for the safety of the user and the long life of the CVD system. These are listed here:

(a) CVD should not be operated at power-consuming units greater than 60 percent.

(b) The heater should be switched ON only after the last step described in the working procedure. It shouldn’t be switched on in between.

(c) The pressure inside the chamber should be ensured at 0 psi or 0 mmHg. If it increases, the outlet valve should be opened otherwise the quartz tube may get cracked.

(d) If we do not create a vacuum inside the quartz tube in the procedure, the outlet valve should be open so that the moisture doesn’t get collected inside the tube. Moisture developed inside the tube might break the quartz tube.

(e) The value of the mass airflow controller should always be set to less than 500 scm.

(f) The main valves of the cylinder should be shut off while not in use.

Some precautions that need to be followed while operating the PECVD system are listed as follows:

(a) UPS should always be kept on.

(b) After starting the rotary pump, the user should open the SOFT valve first and only after a few min of suction ROUGHING valve should be open.

(c) Valves should be operated softly.

(d) V11 valve should be open before injecting gases into the process chamber and it should be closed before opening the VENT valve.

(e) Acetone should be avoided for cleaning purposes, especially for o-rings.

Apart from these instrumental precautions, there are some other rules too that should be followed thumb rule. Especially, while handling hazardous chemicals, extra care needs to be taken to avoid accidents. Some of them are listed here:

(a) Good ventilation should be ensured while handling the hazardous chemicals or the instrument.

(b) Enough equipment should be arranged for the protection of the user’s safety like a face shield, glasses for eyes and others.

(c) Fire extinguishers should be installed at various places to ensure people’s safety.

(d) Arrangement of first aid treatment should have been ensured in case of any emergency [35], [58].

5.9 CONCLUSION

CVD technique finds potential applications in the deposition of thin films offering many advantages like conformal coverage and coating over the large surface area. There are numerous variants of CVD including Thermal CVD, PECVD, MOCVD, ALD, and others. Two of the variants of CVD i.e., Double Zone Thermal CVD and PECVD were studied and it is concluded that both have their own advantages and disadvantages. However, achieving control over ultimate film properties like thickness and film composition is a challenge in PECVD which is not the case with the thermal CVD system. Furthermore, these systems can be used to synthesize various types of materials ranging from pure-dense materials to thin-nano films for many industries. They find applications in areas like microelectronics (electrical insulation and conductive films, diffusion masks, capacitors, etc.); optoelectronics; protective, decorative, optical coatings (photovoltaics and photonics e.g., notch filters and anti-reflective coatings); synthesis of Transition Metal Dichalcogenides, Carbon films, Graphene-based polymeric nanocomposites, etc.; fabrication of integrated circuits, solar cells, transistors, and some others like food packaging, biosensors, device fabrication and various biomedical applications (immobilization of biomolecules, degradation of biopolymers, etc.).

CHAPTER 6

FUTURE APPLICATION - SENSING

After synthesizing these nanostructures successfully, they can be used to explore the incredible properties and for a variety of applications. We aimed to use the nanostructures for the application in Gas-Sensing, which couldn’t be done due to the COVID-19 pandemic. But, it can certainly be achieved in the future. We have studied two types of Gas-Sensing which will be discussed in the current chapter.

6.1 SENSORS

Sensors, similar to human senses in their function, are devices that can sense a signal, be it mechanical or chemical or optical and then converts it into another signal that is electrical in nature. This output signal is received and studied using systems of devices like computers.

The two main parts of a sensor are An active sensing part that acts as a translator for the input signal to convert it into an intermediate signal and the transducer part that converts that intermediate signal into the final output signal.

6.1.1 Working of Sensors

The above-mentioned parts consist of the working process for the sensors. Fig. 6.1 describes the same in the form of a flowchart.

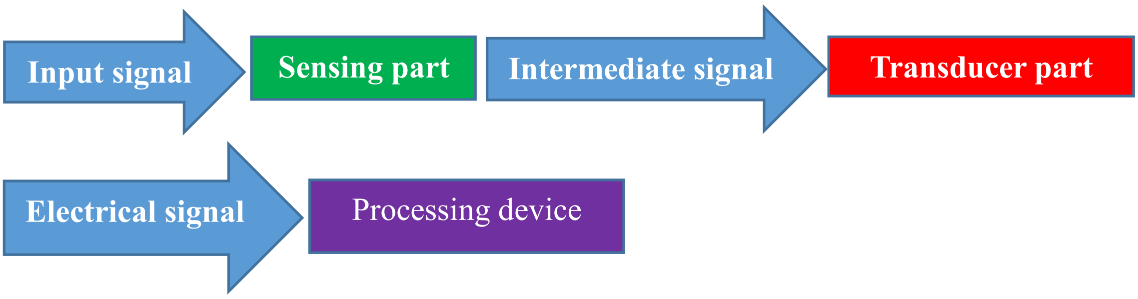


Fig. 6.1: Flowchart of working of sensors

6.1.2 Types of Sensors

There are many types of sensors. Some of them are named as follows:

1. Gas sensor
2. Temperature sensor
3. Bio sensor
4. Chemical sensor
5. Nano sensor
6. Light sensor
7. Touch sensor
8. IR sensor
9. Humidity sensor

6.1.3 Factors influencing the performance of sensors

Many factors affect a sensor’s performance like:

(a) Morphology of the material of the sensor - if the morphology is not developed appropriately then it may cause functioning issues in some particular sensors like gas sensors and decrease their sensitivity.

(b) Its structure – similar sensitivity issues could be faced as that of morphological ones.

(c) Surface area – they must have huge surface areas as they function at low ppb so high surface areas are required for maximum adsorption of analytes to obtain quick and strong sensitivity.

6.2 ELECTROCHEMICAL-BIO SENSORS

Electrochemical-bio sensors are an important class of Bio-sensors that converts biological information into an electric signal with the help of an electrochemical transducer. That output signal is then processed using a detecting device. These are used to detect a variety of biological materials like enzymes, ligands, tissues, etc. Generally, enzymes are used as bioreceptors in electrochemical biosensing because of their biocatalytic and binding nature [36]. Some main components of Electrochemical Bio Sensors are:

1. Bioreceptors – enzymes, antibodies, nucleic acids, etc.
2. Analytes – biological samples e.g., blood, saliva, food samples, etc.
3. Electrolytes – salts, acids or bases in aqueous format room temperature acts as electrolytes.
4. Transducers – to integrate these biochemical materials.
5. Computer software – to detect and process the converted output electrical signal
6. Electrodes – provide surfaces for the chemical reactions to occur. An electrochemical bio sensor’s sensing ability majorly depends upon the material and dimensions of the electrodes used.

Electrodes are used at three different places in the mechanism : (a) as a reference electrode (Ag/AgCl) to maintain the desired potential and is kept near the reaction site. (b) as a working/redox electrode that acts as the transducer and (c) as an auxiliary electrode to connect the working electrode to the analytic solution. Generally, depending on the requirement of analyte solution, metals like gold, platinum, carbon and silicon are used as electrodes as they possess properties like conductivity and stability.

6.2.1 Working of Electrochemical-bio Sensors

The above components follow the following process for the working of the electrochemical sensors:

Step 1: First, selective binding of the bioreceptor and the analyte takes place. Only the target analyte attaches to the surface of the bioreceptor layer.

Step 2: A specific biological event occurs at the interface and an intermediate signal is formed which is then measured in an electrochemical transducer, amplified and converted in the form of an electronic signal.

Step 3: The amplified output signal is fed into a detecting device like a computer.

Step 4: The computer software converts the electronic signal into a readable notation that is interpreted easily.

Step 5: This is then presented through the user interface to the operator.

This is the complete working mechanism of an electrochemical biosensor as depicted in Fig. 6.2 below:

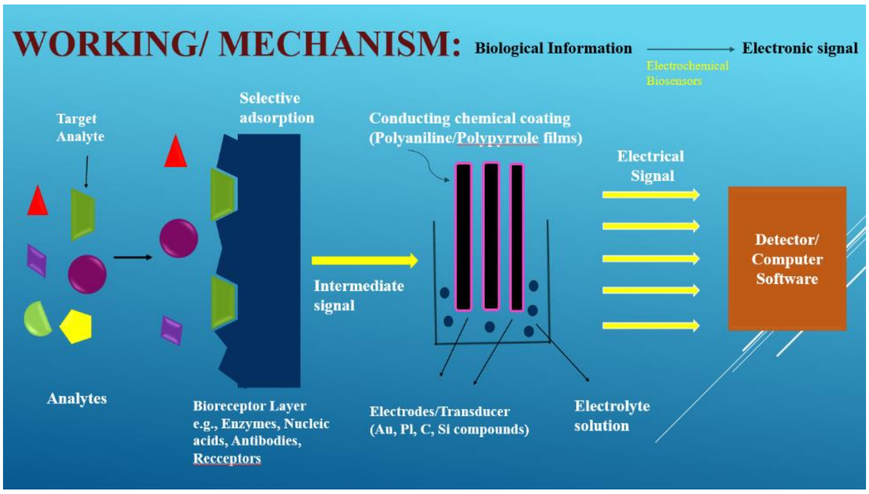


Fig. 6.2: Working of the electrochemical-bio sensor

6.2.2 Advantages of Electrochemical Biosensors:

- They are small and compact in size and mechanically robust.
- These are simple and cheap electronic gadgets are used for their production.
- They have a user-friendly interface.
- They are easy in operating and have conventional processing.
- They have a very good resolution.
- They have negligible external heating.
- They have very low power requirements.

6.2.3 Disadvantages of Electrochemical Biosensors:

- They have a very narrow temperature range.
- They have a short shelf life.

6.3 CONDUCTOMETRIC GAS SENSING

Chemiresistor is a material whose internal resistance is modulated by the change in chemical composition in its surroundings. Here, the carrier concentration at the surface changes on the interaction between material and analyte. The sensing material acts as a bridge covering the fine gap between electrodes as shown in fig. 6.3. and it controls the conductance. It is generally made up of metal oxide and is thus also known as a metal oxide gas sensor. The metal oxide gas sensors have many

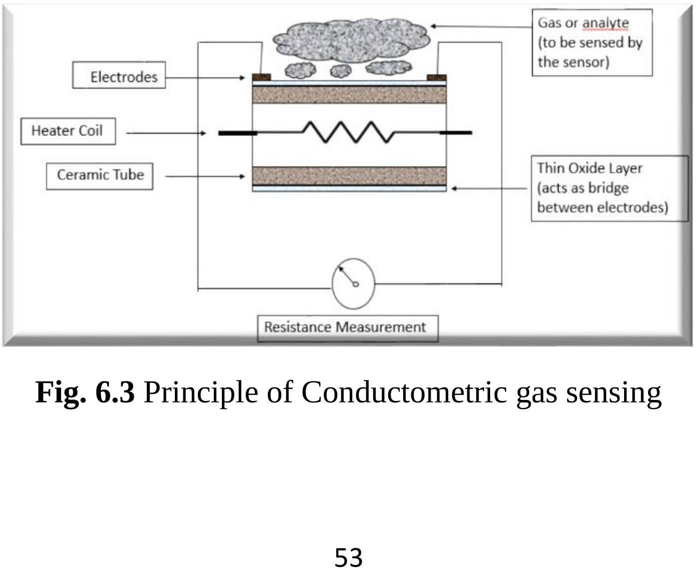


Fig. 6.3 Principle of Conductometric gas sensing

advantages over other sensors. They are highly selective, sensitive, compact in size and their fabrication is quite simple. A simple dc circuit can be used as a resistance measuring device. It can also be a simple Op-Amp circuit that is used as a voltage-current converter.

Initially, a film of metal oxide is deposited on a substrate, often silica, by any of the myriad techniques present. It can be done either by any of the physical methods like evaporation, sputtering, etc. or chemical methods like sol-gel method, solvothermal method, etc. The substrate should be heat stable and electrical insulator. There are two physical interactions in the process of gas sensing, the gas-solid interaction which changes the physical properties of the surface, and transduction which modifies the resistance.

The material is heated in the presence of ambient oxygen and the molecules are adsorbed at the surface and active oxygen species are formed like O^{2-}, O^{-}, etc. This results in the trapping of electrons by the molecules and thus forming a potential barrier.

It is heated till saturation. The temperature is required to overcome the activation energy and change the resistivity. Some apparatus include microheaters to improve the sensing response.

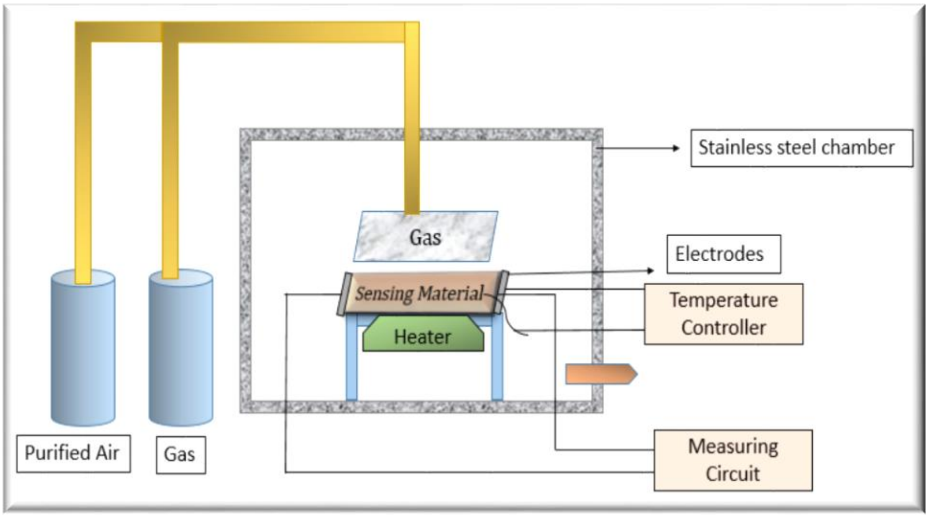


Fig. 6.4 Schematic Diagram of Conductometric gas sensing

When it is placed in a gaseous environment to detect or sense as shown in Fig. 6.4, it interacts with the gas present there and its molecules are adsorbed at the surface. These molecules form a bond with the adsorbed oxygen molecules and the trapped electrons are made free. This decreases the potential barrier and the carrier concentration increases resulting in reduced resistance. The change in resistance is measured which gives an idea of the presence of the analyte and its concentration.

Oxidizing and reducing gases, both can be detected using these sensors. The difference is that in the presence of oxidizing gases, electron depletion is increased in the presence of the analyte, which increases the resistance instead of reducing it. In the presence of reducing gases, the resistance of the material decreases with an increase in the concentration of the analyte.

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DECLARATION

We/I hereby declare that the work which is presented in the Dissertation-II Project entitled **“Hydrothermal Synthesis of TMD Nanostructures along with Elucidation of Double Zone Thermal CVD and PECVD”** in the fulfilment of the requirement for the award of the Degree of **Masters in Science** and submitted to the Department of **Applied Physics**, Delhi Technological University, Delhi is an authentic record of my/our own, carried out during a period from August 2020 to May 2021, under the supervision of **Dr. Nitin K. Puri**.

The matter presented in this thesis has not been submitted by us/me for the award of any other degree of this or any other Institute/University. The work has been published /accepted/communicated in SCI/SCI expanded /SSCl/Scopus indexed journal OR peer reviewed Scopus indexed conference with the following details:

Title of the Paper 1: Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage.

Author names (in sequence as per research paper): Shreya, Anukool Yadav, Ritika Khatri, Nikita Jain, Anurag Bhandari and Nitin K. Puri.

Name of Conference/ Journal: 6th International Conference on Advanced Production and Industrial Engineering (ICAPIE) – 2021.

Conference Dates with Venue (if applicable): June 18-19, 2021.

Have you registered for the conference? (Yes/No): Yes

Status of Paper (Accepted/Published/Communicated): Accepted

Date of paper communication: 15 March 2021

Date of paper acceptance: 12 May 2021

Date of paper publication: October 2021

Title of Paper 2: Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials.

Author’s Names (in sequence as per research paper): Anukool Yadav, Shreya and Nitin K. Puri.

Name of Conference/Journal: 6th International Conference on Advanced Production and Industrial Engineering (ICAPIE) – 2021.

Conference Dates with Venue (if applicable): June 18-19, 2021.

Have you registered for the conference? (Yes/No): Yes

Status of Paper (Accepted/Published/Communicated): Accepted

Date of paper communication: 25 April 2021

Date of paper acceptance: 13 May 2021

Date of paper publication: October 2021

Shreya Anukool.

SHREYA (2K19/MSCPHY/25) ANUKOOL YADAV (2K19/MSCPHY/10)

SUPERVISOR CERTIFICATE

To the best of my knowledge, the above work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere. I further certify that the publication and indexing information given by the student(s) is **correct.**

Place: Delhi **(SUPERVISOR SIGN)**

Date: 31 May 2021

NOTE: PLEASE ENCLOSE RESEARCH PAPER ACCEPTANCE/ PUBLICATION/ COMMUNICATION PROOF ALONG WITH SCOPUS INDEXING PROOF (https://icapie.com/).

LIST OF CONFERENCES AND PUBLICATIONS

CONFERENCE PARTICIPATION: POSTER PRESENTED

Title of Poster: Synthesis of Nanocomposite of ZnO-MoS_2 via Chemical Route and to study its properties.

Name of Conference: International Conference on Advanced Functional Materials and Devices (AFMD-2021)

Status: Poster Presentation : “Participation Award” and “Best Poster of the Day Award” received

Presenting Author: Anukool Yadav

Date of Conference: 3rd - 5th March, 2021

ACCEPTED PAPERS :

1. Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage

Status of Paper: Accepted in Conference

Author’s Names (in sequence as per research paper): Shreya, Anukool Yadav, Ritika Khatri, Nikita Jain, Anurag Bhandari, Nitin K. Puri

Name of Conference: 6th International Conference on Advanced Production and Industrial Engineering (ICAPIE)- 2021

Conference Index: Scopus

Status of Paper: Accepted in Conference

Date of Communication: 15th March, 2021

Date of Acceptance: 12th May, 2021

Date of Conference: 18-19 June, 2021

Date of Publication: October, 2021

2. Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials.

Author’s Names (in sequence as per research paper): Anukool Yadav, Shreya, Nitin K. Puri

Name of Conference: 6th International Conference on Advanced Production and Industrial Engineering (ICAPIE) – 2021

Conference Index: Scopus

Status of Paper: Accepted in Conference

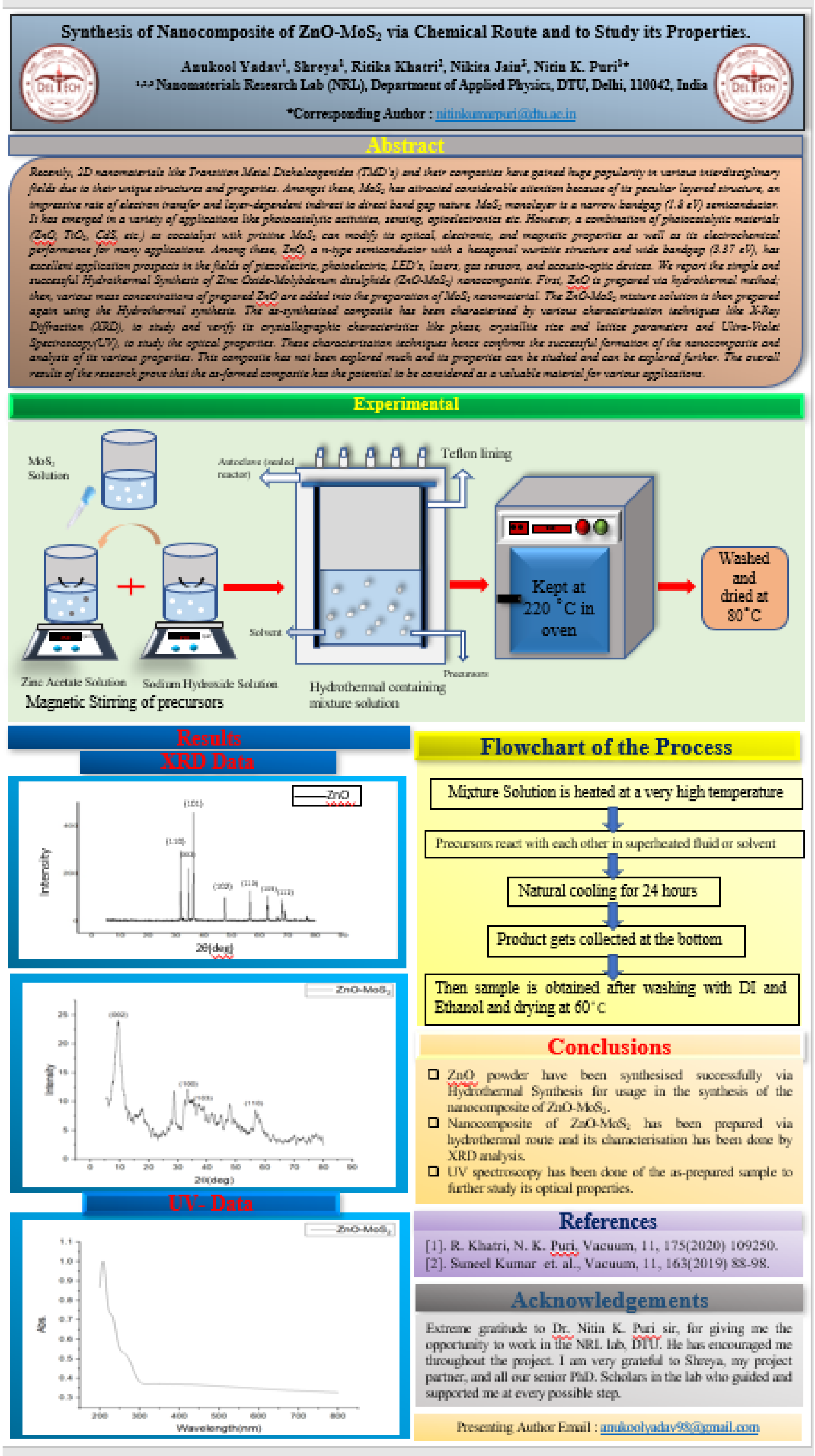
Date of Communication: 25th April, 2021

Date of Acceptance: 13th May, 2021

Date of Conference: 18-19 June, 2021

Date of Publication: October, 2021

AFMD-2021 POSTER



Synthesis of Nanocomposite of ZnO-MoS$_2$ via Chemical Route and to Study its Properties.

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Abstract

Recently, 2D nanomaterials like Transition Metal Dichalcogenides (TMD's) and their composites have gained huge popularity in various interdisciplinary fields due to their unique structures and properties. Amongst these, MoS$_2$ has attracted considerable attention because of its peculiar layered structure, an impressive rate of electron transfer and layer-dependent indirect to direct band gap nature. MoS$_2$ monolayer is a narrow bandgap (1.8 eV) semiconductor. It has emerged in a variety of applications like photocatalytic activities, sensing, optoelectronics etc. However, a combination of photocatalytic materials (ZnO, TiO$_2$, CdS, etc.) as cocatalyst with pristine MoS$_2$ can modify its optical, electronic, and magnetic properties as well as its electrochemical performance for many applications. Among these, ZnO, a n-type semiconductor with a hexagonal wurtzite structure and wide bandgap (3.37 eV), has excellent application prospects in the fields of piezoelectric, photoelectric, LED's, lasers, gas sensors, and acousto-optic devices. We report the simple and successful Hydrothermal Synthesis of Zinc Oxide-Molybdenum disulphide (ZnO-MoS$_2$) nanocomposite. First, ZnO is prepared via hydrothermal method; then, various mass concentrations of prepared ZnO are added into the preparation of MoS$_2$ nanomaterial. The ZnO-MoS$_2$ mixture solution is then prepared again using the Hydrothermal synthesis. The as-synthesised composite has been characterised by various characterisation techniques like X-Ray Diffraction (XRD), to study and verify its crystallographic characteristics like phase, crystallite size and lattice parameters and Ultra-Violet Spectroscopy(UV), to study the optical properties. These characterisation techniques hence confirms the successful formation of the nanocomposite and analysis of its various properties. This composite has not been explored much and its properties can be studied and can be explored further. The overall results of the research prove that the as-formed composite has the potential to be considered as a valuable material for various applications.

Experimental

Results

XRD Data

UV- Data

Flowchart of the Process

Mixture Solution is heated at a very high temperature

Precursors react with each other in superheated fluid or solvent

Natural cooling for 24 hours

Product gets collected at the bottom

Then sample is obtained after washing with DI and Ethanol and drying at 60°C

Conclusions

- ☐ ZnO powder have been synthesised successfully via Hydrothermal Synthesis for usage in the synthesis of the nanocomposite of ZnO-MoS$_2$.
- ☐ Nanocomposite of ZnO-MoS$_2$ has been prepared via hydrothermal route and its characterisation has been done by XRD analysis.
- ☐ UV spectroscopy has been done of the as-prepared sample to further study its optical properties.

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[1]. R. Khatri, N. K. Puri, Vacuum, 11, 175(2020) 109250.
[2]. Suneel Kumar et. al., Vacuum, 11, 163(2019) 88-98.

Acknowledgements

Extreme gratitude to Dr. Nitin K. Puri sir, for giving me the opportunity to work in the NRL lab, DTU. He has encouraged me throughout the project. I am very grateful to Shreya, my project partner, and all our senior PhD. Scholars in the lab who guided and supported me at every possible step.

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AFMD-2021 PARTICIPATION CERTIFICATE

ATMA RAM SANATAN DHARMA COLLEGE

(University of Delhi)

Accredited Grade 'A' By NAAC

All India 13th Rank in NIRF (MHRD)

Certificate No: ARSD/AFMD/009

International Conference on

"Advanced Functional Materials & Devices" (AFMD-2021)

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Department of Physics & IQAC, ARSD College

This is to certify that Prof./Dr./Mr./Ms. **ANUKOOL YADAV** from **NANOMATERIALS RESEARCH LAB, DELHI TECHNOLOGICAL UNIVERSITY** has **presented** his/her research work as **Poster Presentation** in ***International Conference on "Advanced Functional Materials and Devices" (AFMD-2021)*** organised by Department of Physics & IQAC, ARSD College, University of Delhi during 03-05th March 2021 via online mode.

V. Tuli

(DR. VINITA TULI)
CONVENER

(PROF. GYANTOSH KUMAR JHA)
PRINCIPAL

AFMD-2021, BEST POSTER OF THE DAY CERTIFICATE

ATMA RAM SANATAN DHARMA COLLEGE

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Accredited Grade 'A' By NAAC

All India 13th Rank in NIRF (MHRD)

Certificate No: AFMD/ARSD/B07

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AWARD OF EXCELLENCE

This certificate is awarded to Dr./Mr./Ms **ANUKOOL YADAV** from **NANOMATERIALS RESEARCH LAB, DELHI TECHNOLOGICAL UNIVERSITY** in appreciation for his/her Best Poster Presentation (PP-27) entitled Synthesis of Nanocomposite of ZnO-MoS2 via Chemical Route and to Study its Properties. in *International Conference on "Advanced Functional Materials and Devices" (AFMD-2021)* organised by Department of Physics & IQAC, ARSD College, University of Delhi during 3-5th March 2021 via online mode.

V. Tuli

(DR. VINITA TULI)
CONVENER

(PROF. GYANTOSH KUMAR JHA)
PRINCIPAL

RESEARCH PAPER ACCEPTANCE PROOFS (ICAPIE-2021)

Paper 1: Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage

Certificate

Dear Author(s): Shreya, Anukool Yadav, Ritika Khatri, Nikita Jain, Anurag Bhandari and Nitin K. Puri

Paper ID: 168

Paper Title: Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage

This is to enlighten you that the above manuscript has been appraised by the editors of LNME and is accepted for the **6th International Conference on Advanced Production and Industrial Engineering (ICAPIE)- 2021 to be held during June 18-19, 2021**. The paper is recommended for publication in **Lecture Notes in Mechanical Engineering (Scopus Indexed publication of Springer Nature), ISSN: 2195-4356**. The manuscript has been submitted to Springer in May 2021 and will be online during October 2021.

Finally, the team of CAPIER DTU and ICAPIE-2021 would like to extend congratulations to you.

Prof. Ranganath M Singari
(Conference Chair, ICAPIE-2021)

Dr. Harish Kumar
(Convener, ICAPIE-2021)

Paper 2: Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials.

Certificate

Dear Author(s): Anukool Yadav, Shreya and Nitin K. Puri

Paper ID: 395

Paper Title: Preliminary Observations of Synthesized WS2 and Various Synthesis Techniques for Preparation of Nanomaterials.

This is to enlighten you that the above manuscript has been appraised by the editors of LNME and is accepted for the **6th International Conference on Advanced Production and Industrial Engineering (ICAPIE)- 2021 to be held during June 18-19, 2021**. The paper is recommended for publication in **Lecture Notes in Mechanical Engineering (Scopus Indexed publication of Springer Nature), ISSN: 2195-4356**. The manuscript has been submitted to Springer in May 2021 and will be online during October 2021.

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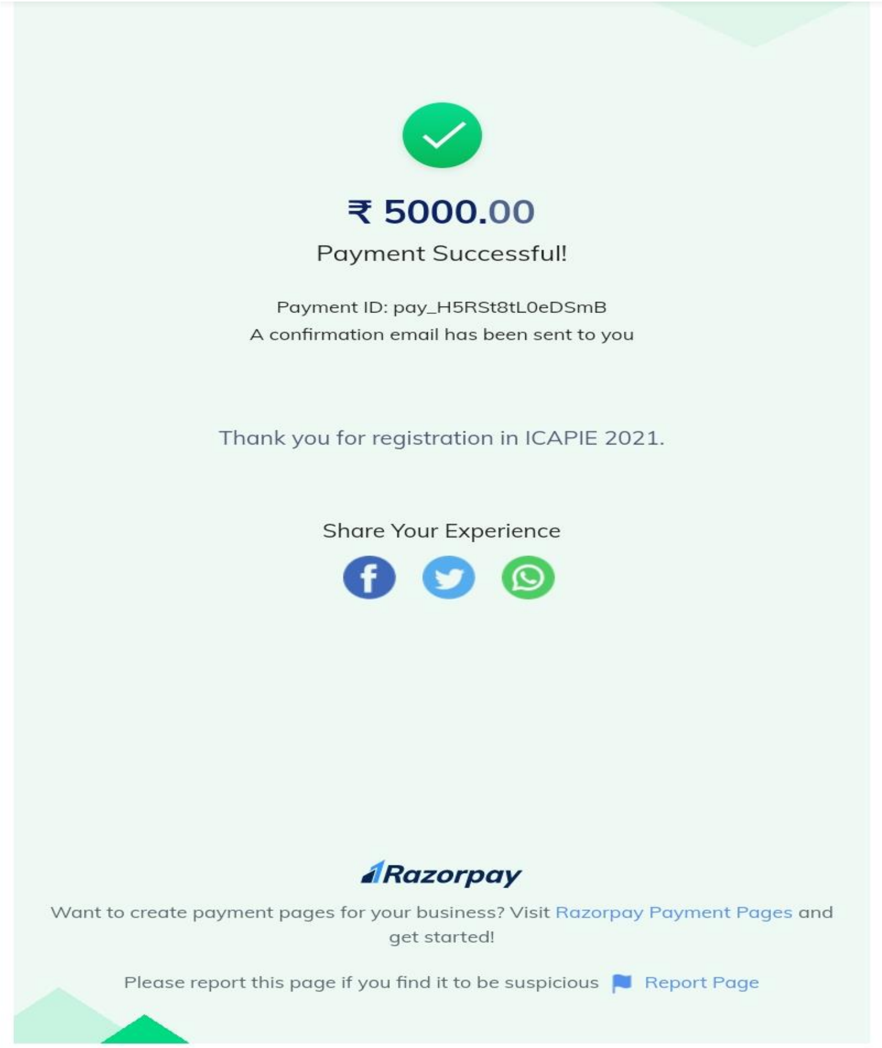

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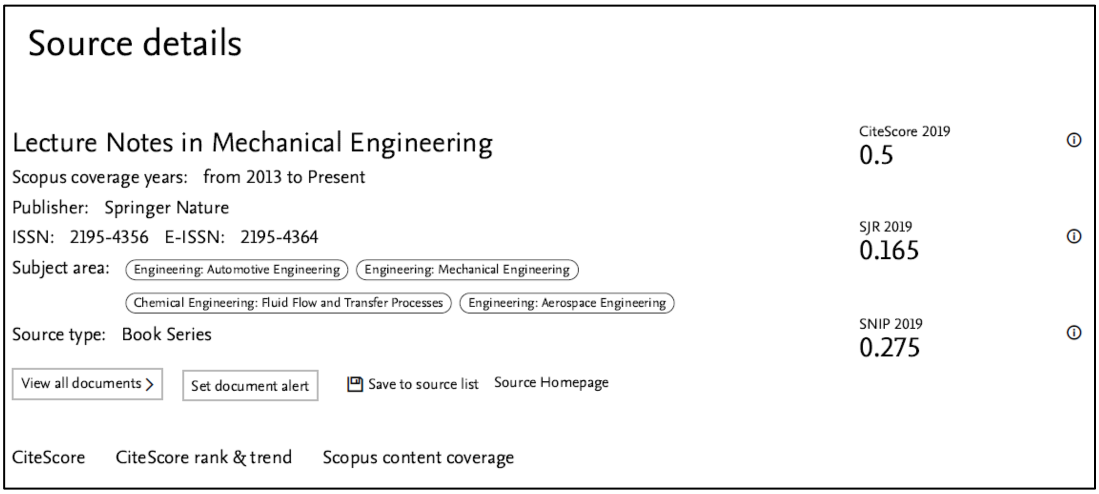

Source details

Lecture Notes in Mechanical Engineering

Scopus coverage years: from 2013 to Present

Publisher: Springer Nature

ISSN: 2195-4356 E-ISSN: 2195-4364

Subject area: Engineering: Automotive Engineering, Engineering: Mechanical Engineering, Chemical Engineering: Fluid Flow and Transfer Processes, Engineering: Aerospace Engineering

Source type: Book Series

CiteScore 2019: 0.5

SJR 2019: 0.165

SNIP 2019: 0.275

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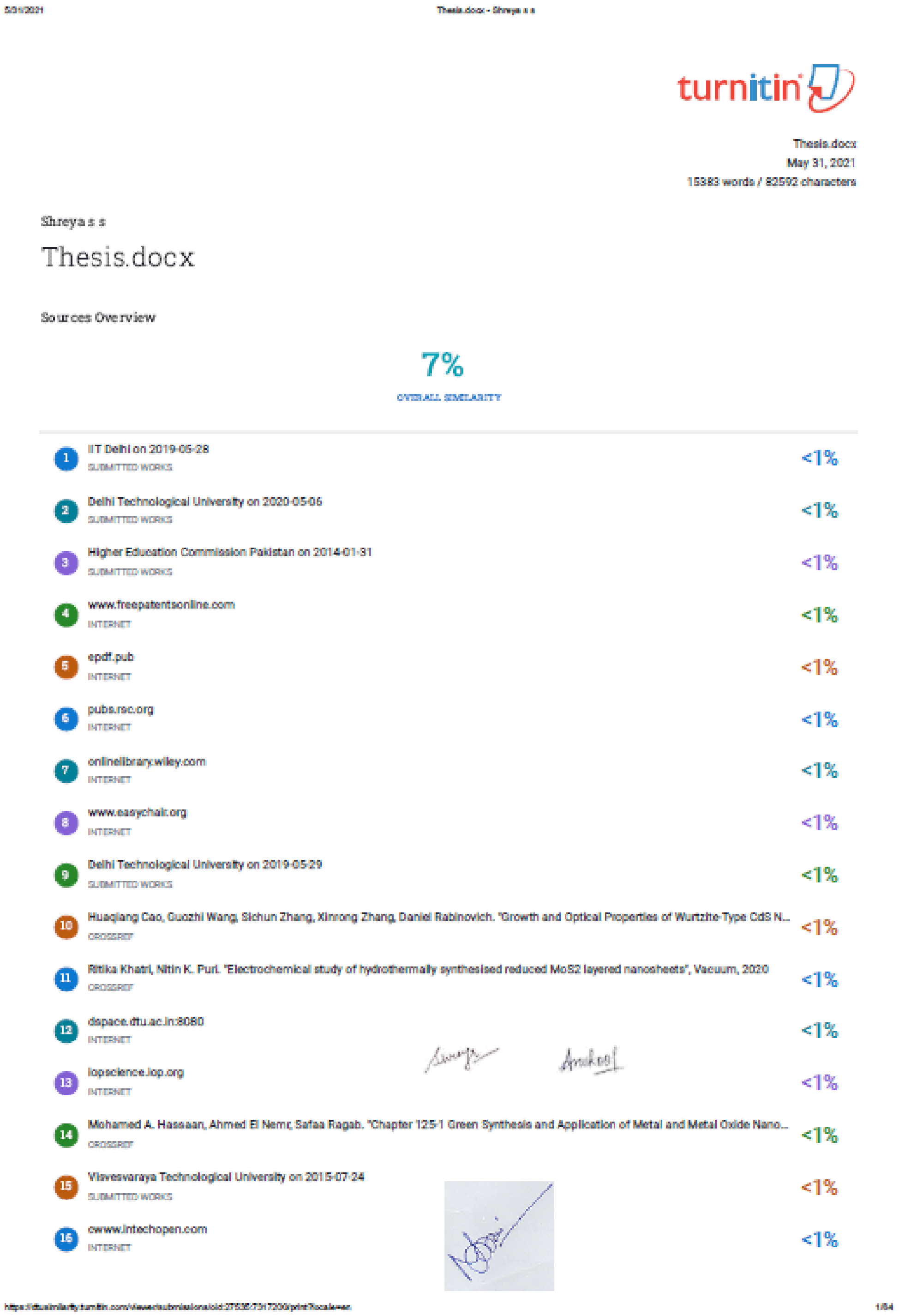

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HYDROTHERMAL SYNTHESIS OF TMD NANOSTRUCTURES ALONG WITH ELUCIDATION OF DOUBLE ZONE THERMAL CVD AND PECVD.

A DISSERTATION

SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE
OF

MASTER OF SCIENCE
IN
PHYSICS

Submitted by:

SHREYA & ANUKOOL YADAV
2K19/MSCPHY/25 & 2K19/MSCPHY/10

Under the supervision of

Dr. NITIN K. PURI

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MAY, 2021

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CANDIDATE'S DECLARATION

We, Shreya & Anukool Yadav, 2K19/MSCPHY/25 & 2K19/MSCPHY/10, students of **M.Sc. Physics**, hereby declare that the project Dissertation titled "Hydrothermal Synthesis of TMD Nanostructures along with Elucidation of Double Zone Thermal CVD and PECVD", performed under the supervision of **Dr. Nitin K. Puri** and submitted by us to the Department of **Applied Physics**, Delhi Technological University, Delhi in the fulfillment of the requirement for the award of the degree of Master of Science, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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CERTIFICATE

I hereby certify that the Project Dissertation titled "Hydrothermal Synthesis of TMD Nanostructures along with Elucidation of Double Zone Thermal CVD and PECVD" which is submitted by Shreya & Anukool Yadav, 2K19/MSCPHY/25 & 2K19/MSCPHY/10, 2 Department of Applied Physics, Delhi Technological University, Delhi in the fulfillment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision. To the best of my knowledge **this work has not been submitted in part or full** for any Degree or Diploma to this University or elsewhere.

Place: Delhi, India

Date: 31st May 2021

Dr. Nitin K. Puri

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ACKNOWLEDGEMENT

The (51) first and foremost, we would like to express our gratitude to the person whom we are most grateful for, our supervisor of this thesis, Dr. Nitin K. Puri. We are indebted to him for providing us this incredible opportunity to work under his guidance. He has always managed to take time out of his busy schedule to discuss the status of dissertation work and gave positive valuable suggestions to work better. Working under his supervision was truly an unprecedented and incredible experience.

Furthermore, we extend our heartfelt thanks to the Research Scholars of our lab, Ms. Ritika Khatri, Ms. Nikita Jain, and Mr. Anurag Bhandari who guided us at every single step during the whole period of dissertation work. They have always made themselves available for us, whenever we have faced any issue and helped us in every possible way. Working with them was indeed a fun learning experience.

The list couldn't be completed without thanking our parents for their constant support and unconditional love. We highly acknowledge their presence and can't thank them enough using words. Furthermore, we want to thank our friends, Ujjawal, Sharad, Vinay and many others for their presence and support in the times of low motivation.

Shreya

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ANUKOOL YADAV

ABSTRACT

The scientific world has always been in hunt of opportunities that have the potential to impact not only academia but the industrial world too. It is the result of the quest to explore new technological advances that a new scientific tool in the form of nanotechnology has emerged. It is the science to unravel the properties of the atomic world and to use those properties for revolutionary changes. An example of revolutionary change is the small size of transistors that have influenced the size of computers and thus our lives greatly. The fascinating microscopic world has lots of hidden features in it. Demystifying those features and exploring the unprecedented properties of that world has created new avenues in diverse fields. Before learning the properties of different materials, synthesizing them is a major task. As the future is more about making things smaller and tinier for various applications, the hunt for better methods is always a hot topic of research. Different approaches are used for the synthesis depending upon the factors like the type of precursors, structure, composition and morphology of the product required, and others. Each technique offers a wide range of advantages and disadvantages, thus, learning about them and their usage in some specific conditions is mandatory in this field. In the present work, numerous synthesis techniques viz. Hydrothermal/Solvothermal, Sonochemical, Chemical Vapour Deposition, Sol-Gel, and Chemical Exfoliation are discussed. Their mechanism is briefly discussed along with advantages and disadvantages.

Furthermore, to explore the properties of nanostructures, different attempts of synthesis have been made and reported briefly here. Initially, attempts have been made to synthesize WS_2 nanostructures via Hydrothermal Synthesis at varied conditions. Their observations and results have been discussed and implications have been drawn from the results. After that, to study more about the TMDs and the heterojunctions, attempts have been made to synthesize the nanostructures of ZnO/MoS_2 composite via the Hydrothermal Synthesis. Two approaches have been used here. In one approach, prepared ZnO nanostructures have been put into the procedure of preparation of MoS_2 nanostructures while in the other approach, prepared MoS_2 nanostructures have been put into the procedure of preparation of ZnO. The results of both the approaches and conclusions drawn from them are discussed in further chapters. Eventually, two variants of another technique CVD that are Double Zone Thermal CVD and PECVD present in NRL, DTU, Delhi have been explored and studied. Both the deposition variants i.e., Double Zone Thermal CVD and PECVD offer a wide range of advantages like the uniformity of thin films along with easy accessibility over a wide range of precursors for nanomaterial synthesis. Thus, the principle, working and technical details as well as the advantages and disadvantages associated with the above-mentioned systems are also discussed in the present work.

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CHAPTER 1

INTRODUCTION

Nature has enormous surprises folded within and human beings have always tried to unfold them by delving into diverse disciplines to fulfill their quest. One of the numerous surprises is a world, which is truly alien and fascinating to humanity. If you started guessing that this world is on some other planet or deep into the ocean and entire series of science fiction movies started reeling into your mind, then sorry to say that you are wrong. This world is not elsewhere but in the depth of every single thing. This is the microscopic world that has captivated everyone's attention and it is none like ours. It has weird properties and phenomena happening there on a smaller scale. This weird world has infinite potential. It harnesses the power of materials to build gadgets of paramount importance by taking the advantage of elements' intrinsic properties [1].

Nanotechnology is all about the exploration of this enigmatic microscopic world and the potential that it holds to transform the world by unprecedented technological advances. The heart of this science lies in manipulating matter precisely at the atomic scale. It had emerged as a branch of physics initially but now has become the center of various disciplines. It holds the power of transforming our world. [2]. This chapter sheds light on the historical background of this science followed by the fundamental concepts needed to understand it. Furthermore, the applications and implications of this technology in diverse fields have been discussed.

1.1 CLASSIFICATION OF NANOMATERIALS

Nanomaterials are materials in which one or more dimensions are in the nanoscale range. These can be classified into four categories that will be discussed in further sections. To understand the need of exploring different categories, let us go to the example of transistors. We see today, that the electronics world is getting faster and faster by going smaller. Today, billions of transistors can be squeezed in a tiny silicon chip which was beyond imagination, just a few years ago [3]. But, as man's quest is never-ending, scientists try to fit the maximum number of transistors into a small area. This certainly decreases the gap between transistors and after a certain limit, the transistors are so close that they start affecting each other's working. Thus, the need to reduce the surface area of the transistors was felt. These transistors are layered shaped and thus the solution of the above problem appeared in the form of 1-D transistors i.e. nanorods. These vertical transistors have less surface area [4], [5] and thus an opportunity for scientists to squeeze more transistors into a smaller area and making the electronics world even faster.

1.1.1 0-D Nanomaterials

0-dimensional materials (as shown in Fig. 1.1) are the materials in which all three dimensions are confined in the nanoscale range. Quantum dots are 0-D nanostructures that are sometimes referred to as 'artificial atoms' as they can behave like naturally occurring atoms. They are tiny semiconductor particles, just a few nm in size. Because of the quantum phenomena occurring at a small scale, quantum dots have optical and electric properties that differ from larger particles [6]. They have applications in diverse fields. [7]–[9]. However, the process of creating quantum dots

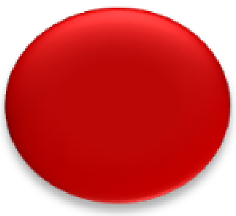

Fig. 1.1 Diagrammatical Representation of 0-D nanomaterials

generates a huge amount of waste and we find ourselves revisiting the environmental concerns [10]. Amazingly though, a low-cost method has been designed to make quantum dots using green leaf extracts, which is an economical method and non-toxic by-products [11].

Some examples of 0-D materials include Fullerene (C-60), Graphene quantum dots, carbon quantum dots, and others.

1.1.2 1-D Nanomaterials

1-dimensional nanomaterials (as shown in Fig. 1.2) 3 are the materials in which two dimensions are confined in the nanoscale range, while the third dimension is significantly large. Nanowires and nanorods are some 1-D nanostructures. Due to quantum confinement effects, electrons and photons can only propagate through the length in nanowires and nanotubes [12]. This makes them very interesting for nano-electronics and optical applications [13], [14]. These are the smallest structures that can effectively transport electrical carriers. The ratio of surface area to volume in this category of nanomaterials is quite high. This makes them potential candidates.

In nanowires, multi-segment materials can be easily grown which is very difficult in any other kind of materials. Thus, they can be used as the junctions in the nanosystems and this is the biggest advantage of 1-D nanostructures [14]. Nanowires can be made up of metals, semiconductors, oxides, and multi-segments. Carbon nanotubes are the most famous 1-D nanostructures.

Fig. 1.2 Diagrammatical Representation of 1D nanomaterials

1.1.3 2-D Nanomaterials

2-D nanomaterials (as shown in Fig. 1.3) are materials in which two dimensions are relatively large while the third dimension is in the nanoscale range. They have a thickness of just a few atoms. These structures are like thin sheets and are called nanosheets. They include nanofilms, nanolayers, nanocoatings, etc. They are intrinsically thin in a physical sense and that has advantages for electronics and shows quantum confinement behavior. A well-known example of nanosheets is graphene [15]. Beyond Graphene, other 2D materials are Transition Metal Dichalcogenides, Hexagonal Boron Nitride, 2-D Oxides.

2-D nanomaterials form artificial materials when assembled into vertical stacks, called van der Waals heterostructure. The properties of individual layers of these heterostructures can be combined by controlling the sheet order. Using this, electroluminescent devices can be constructed for numerous applications[16]. Modern flexible electronic devices can be build using these van der Waal heterostructures.

1.1.4 3-D Nanomaterials

3D nanomaterials (as shown in Fig. 1.4) are bulk materials having all the dimensions relatively large and no dimension in nanoscale range and thus rightly called equiaxed nanomaterials. Thus, all three dimensions are more than 100 nm in size. These materials can be formed by a cluster of different other types of nanomaterials like

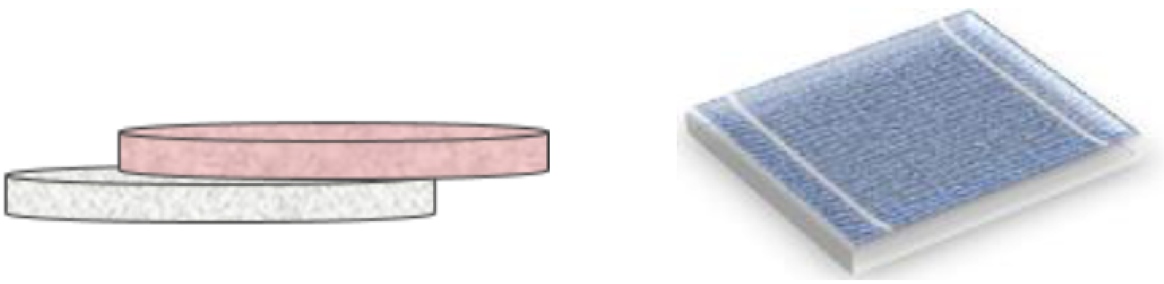

Fig. 1.3 Diagrammatical Representation of 2D nanomaterials

multi-nanolayers, a bunch of nanowires, or dispersed 0-D nanoparticles. Examples of these types of nanomaterials include DNA, viruses, etc.

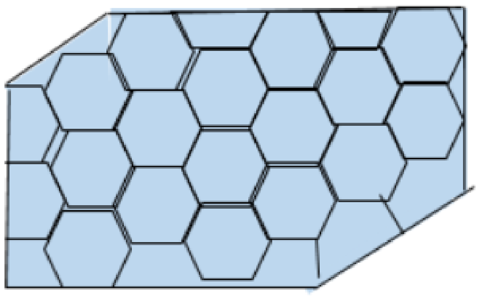

Fig. 1.4 Diagrammatical Representation of 3-D nanomaterials

1.2 SCIENTIFIC BACKGROUND

As discussed in the previous section, TMDs are vastly explored two-dimensional nanomaterials due to their exceptional properties that will be discussed in the coming sections. However, it is essential to know at the point that how these materials came into the picture. Thus, in this section, the properties, importance, and historical background will be discussed.

1.2.1 Graphene

Before learning about TMDs, there is a dire need to know about the most famous and first-ever two-dimensional material, Graphene. Monolayer Graphite is known as Graphene and it is the strongest of the materials ever known [17]. Approximately, it is hundreds of times stronger than steel yet flexible. It is an excellent conductor and conducts electricity better than copper. In previous times, it was believed that 2-D nanomaterials are not stable and thus, can't be produced. But, it was in 2004, when graphene was synthesized successfully and left the scientists' community awestruck. Since then, it has been exploited to find applications in diverse fields. And rightly, it has changed the scenario of the electronics industry which further put the world in a digital race.

However, the zero band gap in Graphene created a gigantic issue while learning its usage in some applications like switches and others. This limitation of graphene baffled scientists and they tried to find a solution to the above problem. Two different solutions were suggested to overcome this limitation. One was to increase its bandgap by various means while the other one was to find new analogous materials with higher bandgap showing semiconducting behavior. The efforts were made to increase the bandgap of graphene layers but changing its bandgap changed its properties as well, which didn't solve the problem [18], [19].

Thus, the second solution, which was to find the analogous materials, was implemented, and eventually, TMDs came into the picture as analogous materials with semiconducting character. After that, research has been started to learn about their applications in different fields including sensing, electronics, optical, and others.

⑥ 1.2.2 Transition Metal Dichalcogenides

TMDs or Transition Metal Dichalcogenides are materials that have thickness relatable to Graphene along with exceptional semiconductor properties.

TMD layers consist of metal atoms, such as Molybdenum or Tungsten and this layer is stuck ㊼ between two layers of chalcogen atoms like Sulfur, Selenium, etc. The adjacent layers are bound together very weakly and thus layers can slide over each other. This is the reason, why these materials are widely used for solid lubrication. They have hexagonal structures, which resemble graphene.

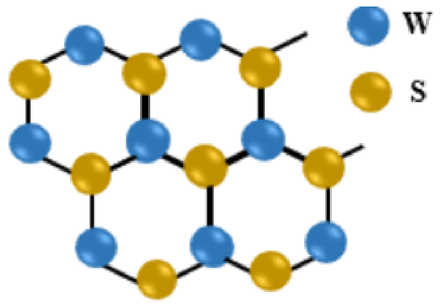

Fig. 1.5 Schematic hexagonal structure of WS_2

TMD monolayers have direct bandgap [20], [21]. While for multilayer TMD, like bilayer or trilayer, the bandgap is indirect. Thus, there is a need to separate monolayers from bulk. To do this, there are numerous techniques that will be further discussed in Chapter 2.

Two of the TMD materials, Tungsten Disulfide (as shown in Fig. 1.5) and Molybdenum Disulfide are studied for the completion of this thesis work. The synthesis mechanism, properties, and results of the synthesized nanostructures of both materials will be discussed in further chapters.

1.3 APPLICATIONS

These discoveries in the field of nanotechnology have a very promising future where the arrangement of atoms in the desired way can show some amazing results. There are a large number of pieces of evidence that show how the world's smallest materials are changing our lives including the nano-machines that defeat the cancer cells, tiny computer chips, a few inches long high definition cameras, and others. There is no limit to the extent, to which nanotechnology can change the world by technological advances. It holds numerous mysteries and infinite possibilities within. Advances have been made in diverse fields including mechanical, medical, chemical, computing, and others. There are several applications of nanotechnology in diverse fields. Few of the applications are discussed here.

1.3.1 Nano-medicine

The idea of subatomic disease-fighting machines has been in science fiction for decades. So, this idea is not a new one but would have come a lot closer to experimentally making this idea a reality in the past decade. This sounds like a new perfect solution to many modern problems. But let's just explore how, when, and where science fiction meets facts and what challenges may lie ahead. Nanotechnology is already heavily incorporated into medical tools. Nano-medicine is a very important application of nanotechnology in medicine. It’s used for disease prevention, diagnosis, and treatment.

Nano-medicine is the era of the nanobot. Nanorobots are tiny packages that complete tasks at the desired locations inside the human body in an automated way. Currently, water-soluble drugs are widely used in the medical field for all kinds of treatments, but, they are far from a perfect solution and present numerous difficulties in the treatment. Through these nano-bots, scientists can directly have access to a specific area of the body and can provide better and fast treatment by releasing drugs at the desired location directly. They also hold the potential to replace the pacemakers completely by treating the heart cell directly. They are super durable and can theoretically operate for years without any damage [24].

Another technological advancement is a high-definition camera that is just a few inches long in size, encapsulated like a capsule. It has quite a bright future in the field of medicine. It can be directly engulfed like a drug capsule and provide high pixel images. With the help of those images, scientists can directly look for the problem in the body and can more precisely work upon them. They can be more advanced in the future, where instead of taking images within a time interval, they can make long videos of 360 degrees and can give a better overview of the internal system and specific issues. Though it seems some part of science fiction, hopefully, going to be a stunning reality soon.

1.3.2 Nano-electronics

The crazy advances in electronics have left everyone awestruck. A tiny wafer contains an unbelievable number of sophisticated machines made up of different materials like Gallium, Germanium, Arsenic, and many others. The trend and advances of new tinier gadgets have captivated everyone’s attention from the scientific as well as the non-scientific world. Today, a gigantic amount of information can be stored in a microchip, just a few inches long consisting of billions of transistors in an area of only a few microns. The storage of the same data would have taken an entire building, long years back. Semiconductors, a strange class of elements holds large credit for this evolution. The race to miniaturize began 500 years ago. Since then, miniaturization started another era of the electronic revolution and has changed our lives completely [25]–[27].

CHAPTER 2

SYNTHESIS TECHNIQUES

All the technological advancements of the future that seem impossible right now can indeed become a reality by the discoveries of today. These discoveries in the field of nanotechnology have a very promising future where the arrangement of atoms in the desired way can show some amazing results. Synthesis of these nanomaterials is in itself a huge topic of research where the change in a single parameter like temperature can also make a difference in the structure and morphology of the product [28]. There are various synthesis techniques with different working principles which give very different products at specific conditions. The hunt for new tiny gadgets creates a need for new and better synthesis techniques to get products of high purity and controlled dimensions.

There are two different 20 types of approaches: (i) Top-Down Approach, (ii) Bottom-Up Approach. Both of these approaches have different principles, advantages disadvantages, and methodology. All the synthesis techniques, whether physical or chemical, fall under either of these categories. In this chapter, we will shed light on these two approaches. Furthermore, various synthesis techniques are discussed here mentioning their principle.

57 2.1 TOP-DOWN APPROACH

It involves miniaturization. In this approach, synthesis is usually started with large bulkier material, and then its size is reduced to the desired level using various techniques like cutting, etching, etc. Generally, the starting material in this approach is in solid form. The flowchart depicting the process is shown in Fig. 2.1.

The advantages of this approach can be summarized as:

(i) Large-scale production of nanomaterials is easily possible.
(ii) Chemical purification is not required in this approach.

Along with advantages, there are several disadvantages also while using this approach. Some of them are:

(i) An only a limited number of structures can be formed by this approach.
(ii) Control over deposition parameters here is very difficult.
(iii) It is much costlier than the bottom-up approach.

Some examples of the Top-Down Approach are the Solid State Reaction Method, Lithography Techniques, Liquid Phase Exfoliation Method, and others.

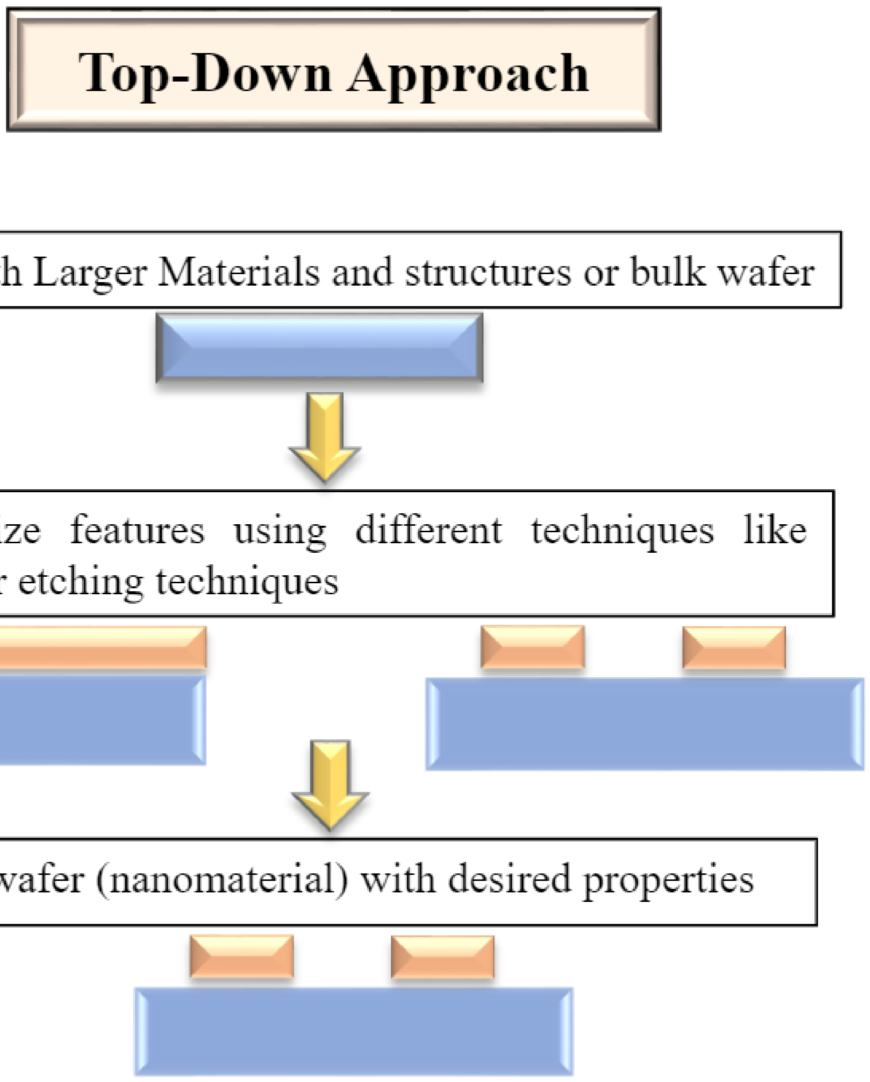

Fig. 2.1 Flowchart depicting Top-Down approach

2.2 BOTTOM-UP APPROACH

In this approach, synthesis takes place by atom-by-atom deposition of nanomaterials or layers of nanomaterials on the desired substrate. In this approach, the starting material or precursor is generally in the liquid or gaseous phase. Here, we start with tiny structures, and their controlled deposition results in the desired structure. The flowchart depicting the process can be shown in Fig. 2.2.

There are numerous advantages of synthesizing the nanomaterials using this approach which can be summarized as follows:

(i) Fewer defects are introduced while the material is synthesized using this approach

(ii) The structures obtained are more homogeneous

(iii) The parameters involved in the deposition can be well controlled

(iv) It is more economical and produces less waste.

However, like any other technique, it has some disadvantages too, which are:

(i) Large scale production is difficult if we use this approach

(ii) Chemical purification of nanoparticles is required to remove any contamination introduced during synthesis.

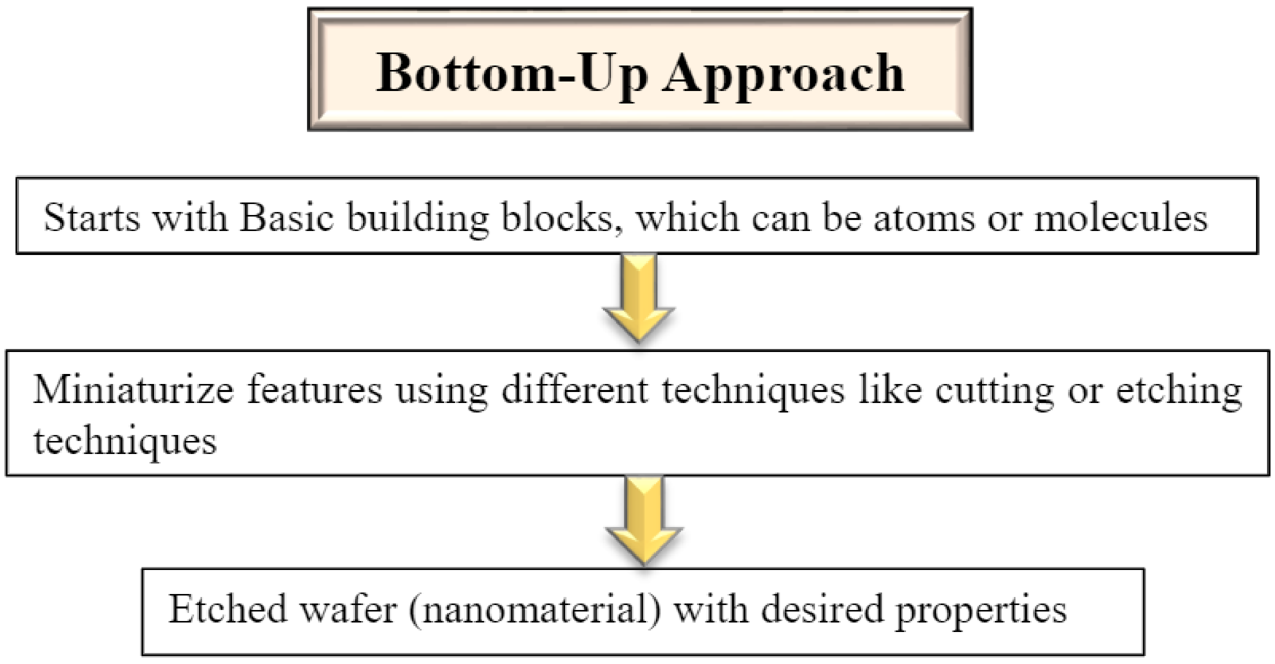

Fig. 2.2 Flowchart depicting Bottom-Up approach

2.3 HYDROTHERMAL/SOLVOTHERMAL SYNTHESIS

These are two promising inorganic synthesis methods that involve the synthesis via chemical reaction as shown in Fig. 2.3. (a). These are the green processes as the reaction takes place in a sealed reactor known as Autoclave shown in Fig. 2.3. (b). The autoclave is generally made up of metal and is employed with Teflon or alloy lining to protect it from highly corrosive solvent.

These processes offer numerous advantages over other techniques apart from being the green processes:

(i) These are relatively low-cost processes
(ii) It is an environment-friendly process as it takes place inside a sealed reactor
(iii) High purity products are formed in this reaction [29].

In the hydrothermal method, the solvent used is water while the solvothermal process uses aqueous and non-aqueous organic solvents like ethylene diamine, ethanol, diethylenetriamine [30], [31], polyethylene glycol [32], etc.

Furthermore, the solvothermal process has some additional advantages over the hydrothermal process:

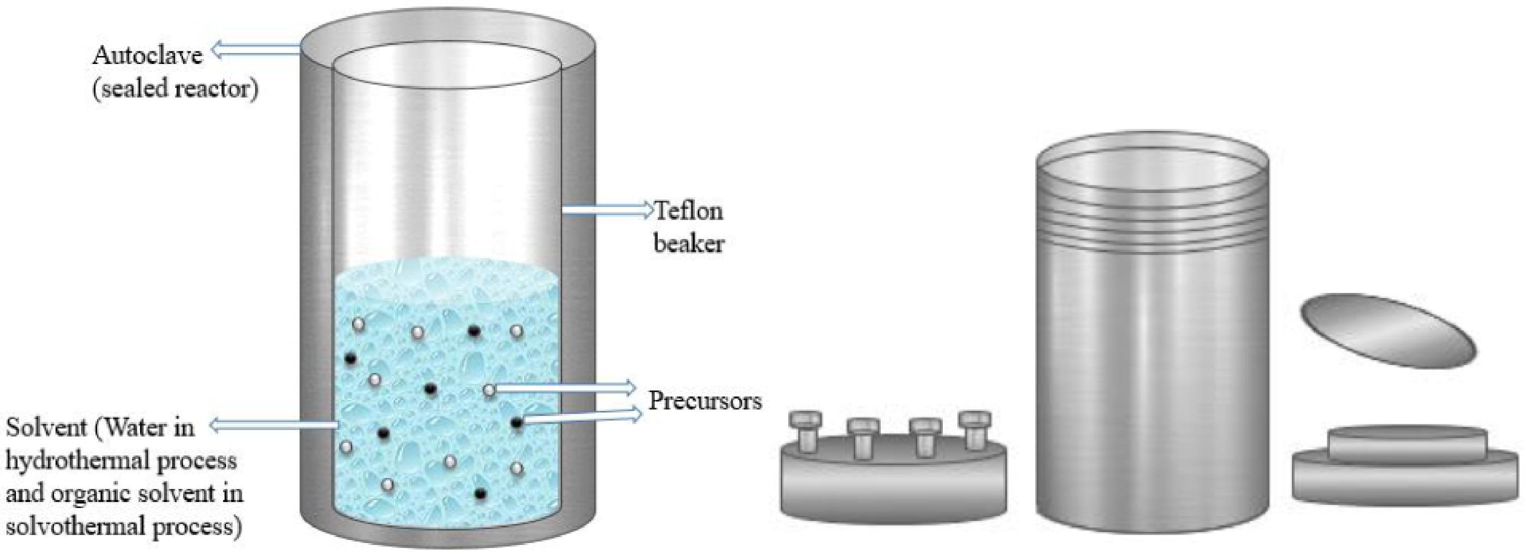

Fig.2.3. (a). A diagrammatical representation of Hydrothermal/Solvothermal Synthesis. **(b).** A diagrammatical representation of an autoclave in Nanomaterials Research Laboratory (NRL), DTU, Delhi, India.

(i) It requires relatively low temperature and pressure
(ii) Precursors which are sensitive to water can be used in this process
(iii) The crystallinity of products formed is very well controlled in this process.

2.4 SONOCHEMICAL SYNTHESIS

This is a method which neither requires high temperature and pressure nor long reaction times. In this process, the precursors are mixed and put together in solution form and then the sonochemical treatment is given. It involves passing ultrasonic waves through the solution using an ultrasonicator as shown in Fig. 2.4. In this way, the hotspots are generated which can achieve very high pressure and temperature. The hotspots are the places where the reaction takes place at sufficiently high temperature and pressure conditions and the products are formed [33]. It is a powerful tool for the synthesis or modification of nanomaterials where even a little variation in the reaction conditions can lead us to the change in morphologies and compositions of the product formed.

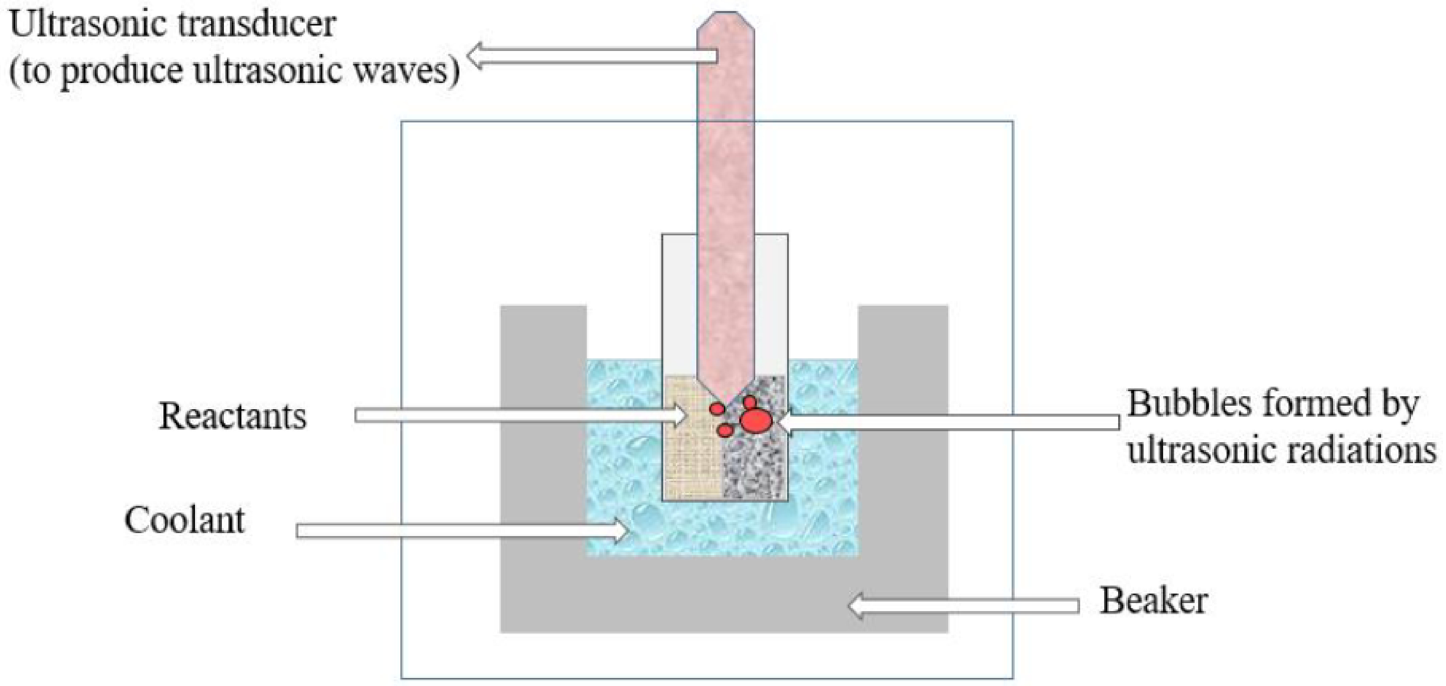

Fig.2.4. A diagrammatical representation of Sonochemical Synthesis.

2.5 CHEMICAL VAPOUR DEPOSITION

It is a vacuum deposition method that involves a chemical reaction inside a vacuum chamber. It is used for the production of various materials like alloys, carbides, oxides, nanoparticles, etc. Layers of materials are deposited on a solid surface called substrate below atmospheric pressure i.e., vacuum. There are many types of CVD's namely Thermal CVD, Metal-Organic CVD (MOCVD), Plasma Enhanced CVD (PECVD), Atomic Layer CVD (ALCVD) [34], [35], etc. The technical details and working of the above two instruments are reported in detail in one of our publications, *"Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage"*, accepted in 'Lecture Notes in Mechanical Engineering'. This bottom-up approach involves the deposition of one or more stable solid films on a substrate at high temperatures by a suitable chemical reaction. A detailed discussion on the same technique is presented further in Chapter 5.

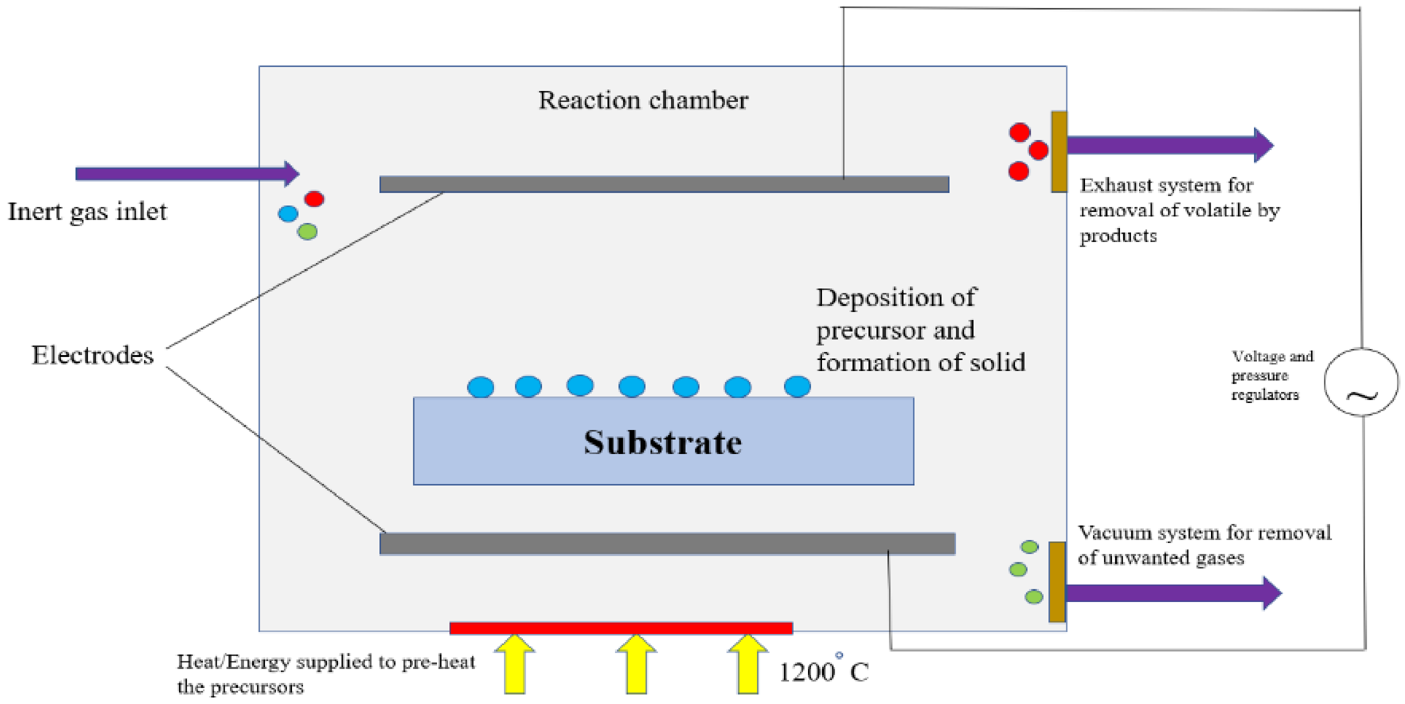

Fig. 2.5. A diagrammatical representation of Chemical Vapour Deposition.

2.6 SOL-GEL SYNTHESIS

This method falls under the bottom-up approach of nanomaterials synthesis in which we start with small atoms and molecules and build up solid nanostructures. It is an inexpensive, wet-chemical technique, used to synthesize ceramic thin films, fibers, and powders at low temperatures, generally nanotubes of silica and TiO_2 [36].

This method was first studied and explained by a chemist named J.J. Ebelmen on silica gels in the mid-19th century (around 150 years ago). The Sol-gel method, as is evident from the name, involves two materials i.e., 'sols' (solid particles suspended in liquid) and 'gels' (porous network of particles having liquid between the pores). First, sols are formed inside a liquid which is then connected after some process to form a network of gels. The liquid then gets evaporated and we are left with the powder or thin-film formation [37].

The basic process of this technique (as shown in Fig. 2.6) involves the conversion of solvent-dissolved precursors into colloids (1-1000 nm in size) via some basic reactions like hydrolysis, polycondensation, or polyesterification. Precursor particles used as initial materials can be metal salts like metal alkoxides or metal chlorides. Catalysts are also used in some reactions to increase the rate of hydrolysis. If the environment has an acidic catalyst, then hydrolysis is slow which causes the formation of linear molecules and if it is basic, then the process is fast, and heavily-branched polymeric chains are obtained. The next step is gelation or precipitation that is connecting the colloids formed to obtain a 3-D, highly viscous, bigger cluster of

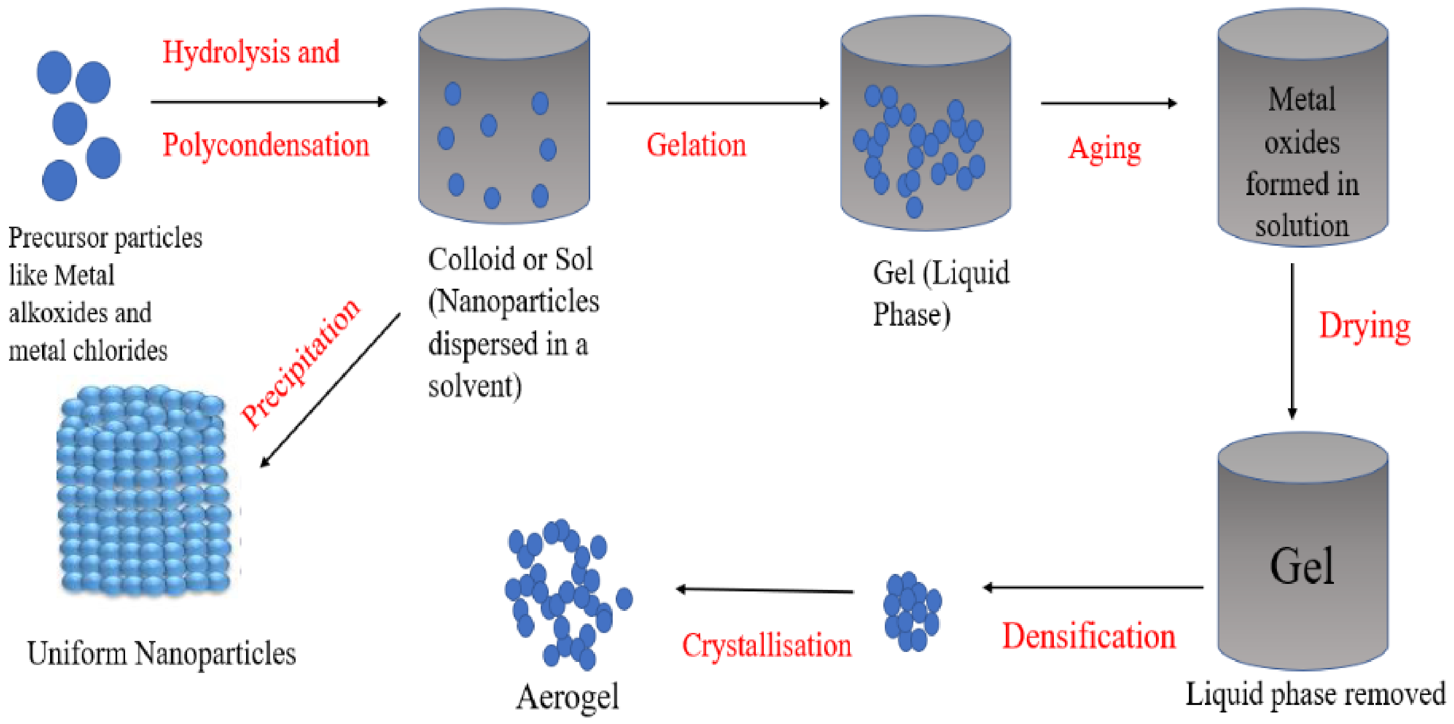

Fig. 2.6. A diagrammatical representation of Sol-Gel Synthesis.

nanoparticles i.e., gel. Gelation majorly depends upon the physical conditions of the network like size and cross-linking of the structures. Aging or syneresis of the gel is done next for many hours or days, where the gel continuously thickens, transforms, and gains enough strength to prevent cracking. Now, extra liquid is extracted out via drying followed by further densification. Under supercritical drying conditions, the highly porous structures may even form aerogels. The last step is the crystallization of the network structures after which the desired nanoparticles are obtained [38].

There are several advantages of the process, which may be summarized as follows:

(i) This method requires less energy consumption leading to less pollution (extensively used in nuclear fuel preparations) and is generally used to generate highly pure and highly dense ceramic and glass materials.
(ii) In this synthesis method, we can obtain desired products even at low temperatures as the reaction rates decrease since the precursors are generally dissolved at atomic scales leading to lowering of the reaction temperatures [39].
(iii) Uniform and small-sized nanoparticles can be obtained with good control over the material's composition.
(iv) We can coat over large and complex surfaces easily.
(v) This method can protect the materials from corrosion as a thick coating can be developed.
(vi) It is an efficient, simple, and cost-effective method of high-quality nanoparticle synthesis.

Along with advantages, there are some disadvantages too, associated with the technique which are as follows:

(i) The raw materials or the precursors are sometimes costly.

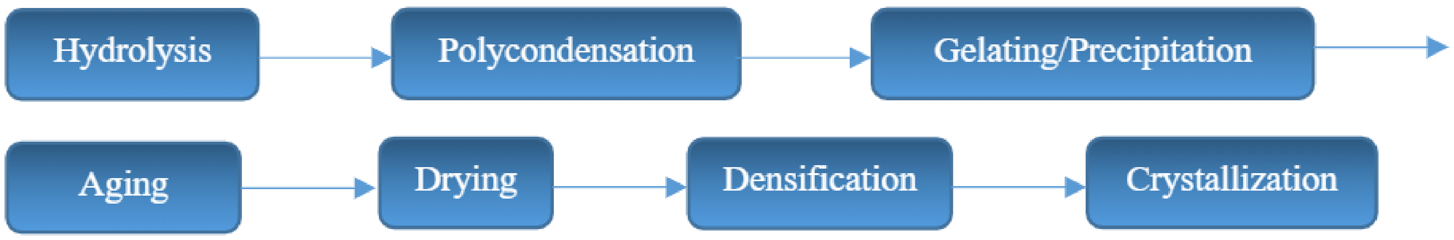

Fig. 2.7. A flowchart of the steps of Sol-gel synthesis

(ii) The synthesis is time taking, compared to other synthesis techniques.
(iii) It uses some toxic organic solutions.
(iv) Impurities may persist in the form of hydroxyl or carbon groups.

2.7 CHEMICAL EXFOLIATION METHOD

In general, exfoliation falls under the category of the top-down approach of nanoparticle synthesis which is done to form layered graphene structures from graphite molecules. Exfoliation can be of major two types: Mechanical exfoliation and Chemical exfoliation. Mechanical exfoliation is a low-cost technique that can be done at room temperatures but the scaling is very poor so generally chemical exfoliation is preferred [40].

In chemical exfoliation synthesis, reduction of interlayer forces takes place followed by the formation of intercalated compounds. After this, the material is exfoliated in the presence of oxygen by rapid heating. This synthesis mechanism (as shown in Fig. 2.8) produces a large amount of graphene at low temperatures [41]. Exfoliation is a phase transition, which takes place when there is a layer to solvent molecule charge transfer and a minimum mixing enthalpy at well-defined elevated temperatures.

The process starts with the reduction of interlayer forces of graphite sheets by overcoming inter-planar Vander-wall forces using energetic ultrasound vibrations followed by dispersion and exfoliation. Graphite molecules are dispersed in a liquid that acts as a solvent and has similar values of surface energy as that of graphite. Then,

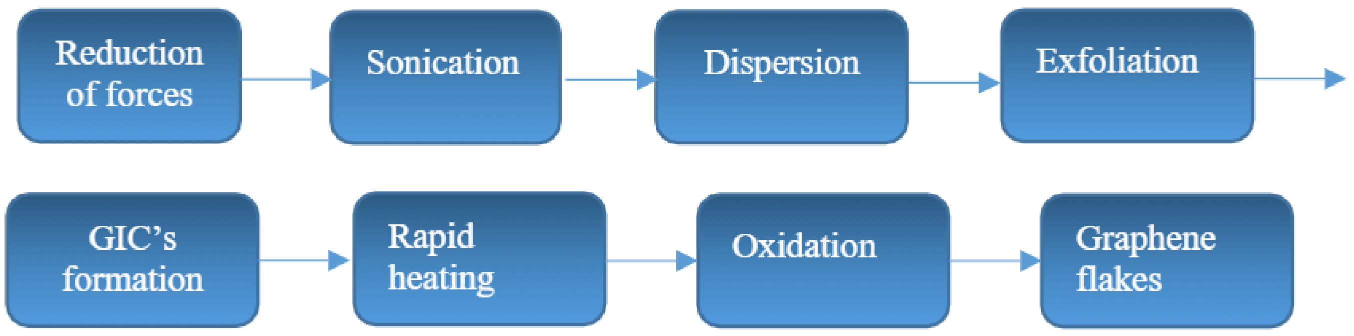

Fig. 2.8. A flowchart of the steps of Chemical Exfoliation

the dispersed solution of graphite is exfoliated followed by sonication using Hummer’s method (oxidation of graphite using oxidizing agents) causing the formation of an intercalated compound (GIC’s). Exfoliation occurs as a result of the transfer of charge from solvent to layers of graphite material leading to charging of graphite sheets which depends upon the composition of the solvent [42]. Then rapid heating and oxidation are done after exfoliation which leads to the decomposition of graphite flakes and the formation of a colloidal solution of graphene oxides (GO) from which Graphene is extracted.

CHAPTER – 3

SYNTHESIS

3.1 CHEMICALS AND MATERIALS

Tungsten hexachloride (WCl_6), Thioacetamide or TAA (C_2H_5NS) and Ammonium Molybdate Tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$) [11] with 99.98% purity were purchased from Sigma Aldrich. Zinc acetate ($ZnC_4H_6O_4$) and Sodium Hydroxide (NaOH) were purchased from Thermo Scientific. Thiourea (CH_4N_2S) was purchased from SRL Pvt. Ltd. Acetone was purchased from Rankem. Ethanol was purchased from Merck. We have used Milli-Q water, (18.2 MΩ cm) as the solvent during our synthesis. All the chemicals used here had an analytical grading and were taken without any further purifications being done.

3.2 WS_2 NANOSTRUCTURE SYNTHESIS

WS_2 nanostructures were synthesized via the Hydrothermal method and their phase was checked using XRD characterization. Fig. 3.1. gives an outline of the hydrothermal process used for WS_2 nanomaterial synthesis in NRL lab, DTU, Delhi, India.

We first weighed the salts/precursors i.e., Tungsten Hexa-chloride and TAA, and added them to two different beakers containing water as solvent. Beakers were then kept for magnetic stirring at room temperature (27-30 ° C) with varied revolutions per second for 1 hour for mixing of salts in water. Two different approaches were followed for the synthesis of WS_2 nanostructures. In one approach of synthesis, the TAA solution was added dropwise into WCl_6 solution after one hour while in the other approach, the WCl_6 solution was added into TAA solution. After this, the mixed solutions were kept for stirring for 1 hour. The pH of the solutions was regulated and optimized to the values ranging from 6 to 8 which was initially 2 by adding liquor ammonia drop by drop. The solution mixtures were then transferred to Teflon-lined autoclaves of different capacities and kept in the oven for 20-24 hours at 220 °C. Then centrifugation and washing of samples was done using De-ionized Water (DI) and ethanol, 3 times with each. Drying of samples was done at 60 °C in an oven for 24 hours. Then the samples were sent for XRD analysis. We tried 5 reaction attempts to synthesize the materials at varied conditions. In the following Table 3.1. we have summarized all 5 reaction attempts and their physical optimization conditions.

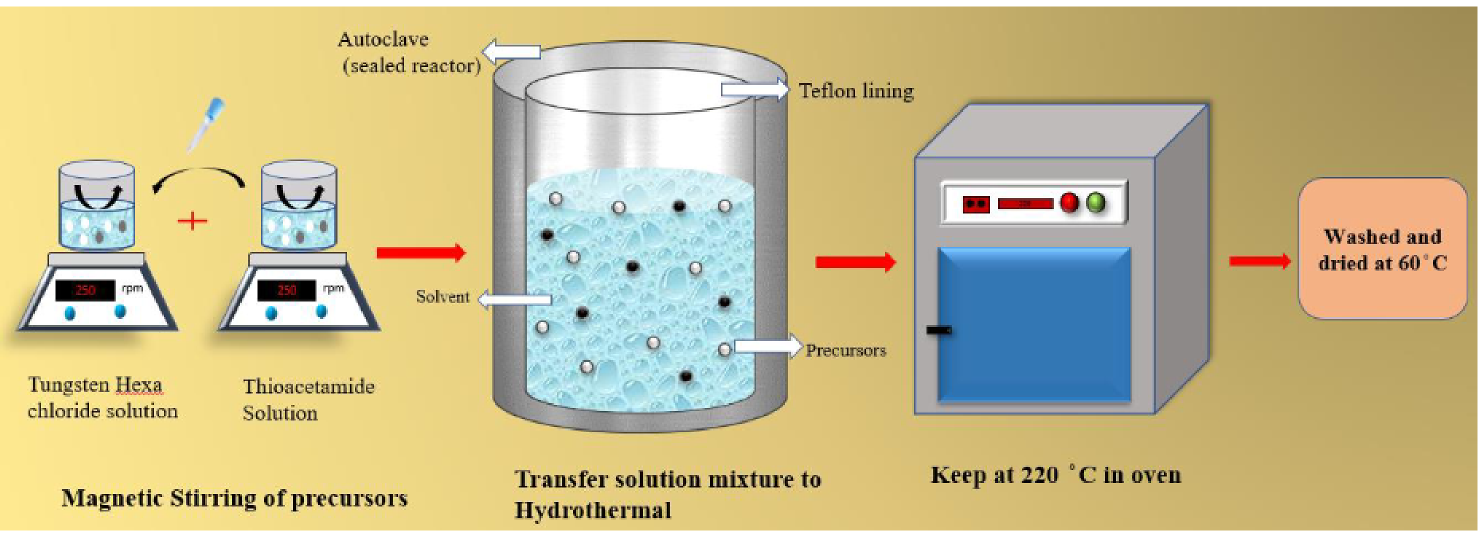

Fig. 3.1 A diagrammatical representation of the general hydrothermal process used for sample preparation in NRL, DTU, Delhi, India.

After 24 hours, samples were cooled down to room temperature. Then the samples were collected via centrifugation at 7,000 rpm for 7 min after washing with DI water and ethanol before drying at 60 °C for 24 hours. The formed samples were collected in Eppendorfs after crushing and named as ‘S4’and ‘S5’ respectively.

Table 3.1: Reaction attempts summary for WS_2 synthesis

Sample	Precursor name	Amount (g)	DI water (mL)	Stirring conditions	pH
S1 (TAA into WCl_6)	WCl_6	0.522	30	stirred at 250 rpm, 30˚C	Initial: 2
	TAA	0.6	30	stirred until fully dissolved	Final: 6
	TAA was added into WCl_6 and the mixture was stirred at 350 rpm at 30˚C.				
	Solution mixture kept at 220˚C for 24 hours in a 100 mL Teflon-lined autoclave.				
S2 (WCl_6 into TAA)	WCl_6	0.522	18	stirred at 350 rpm, 27˚C	Initial: 2
	TAA	1.000	17	stirred at 250 rpm, 27˚C	Final: 8
	WCl_6 was added into TAA and the mixture was stirred at 350 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 24 hours in a 50 mL Teflon-lined autoclave.				
S3 (TAA into WCl_6	WCl_6	1.044	18	stirred at 400 rpm, 27˚C	Initial: 2
	TAA	2.000	17	stirred at 250 rpm, 27˚C	Final: 8
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 24 hours in a 50 mL Teflon-lined autoclave.				
S4 (TAA into WCl_6)	WCl_6	0.632	18	stirred at 400 rpm, 27˚C	Initial: 2
	TAA	1.211	17	stirred at 250 rpm, 27˚C	Final: 6
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 20 hours in a 50 mL Teflon-lined autoclave.				
S5 (TAA into WCl_6)	WCl_6	1.566	17	stirred at 280 rpm, 27˚C	Initial: 2
	TAA	3.000	18	stirred at 400 rpm, 27˚C	Final: 6
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 20 hours in a 50 mL Teflon-lined autoclave.				

3.3 ZnO-MoS_2 COMPOSITE SYNTHESIS

Two synthesis approaches were followed for the synthesis of the ZnO-MoS_2 nanocomposite, first or type-I reactions were adding prepared MoS_2 in the synthesis of ZnO and the type-II were by the vice-versa method i.e., adding prepared ZnO into the synthesis of MoS_2. In total, 15 samples were prepared with different compositions and conditions. Fig. 3.2. gives an outline of the hydrothermal process (type-I) used for ZnO-MoS_2 nanocomposite synthesis in NRL lab, DTU, Delhi, India.

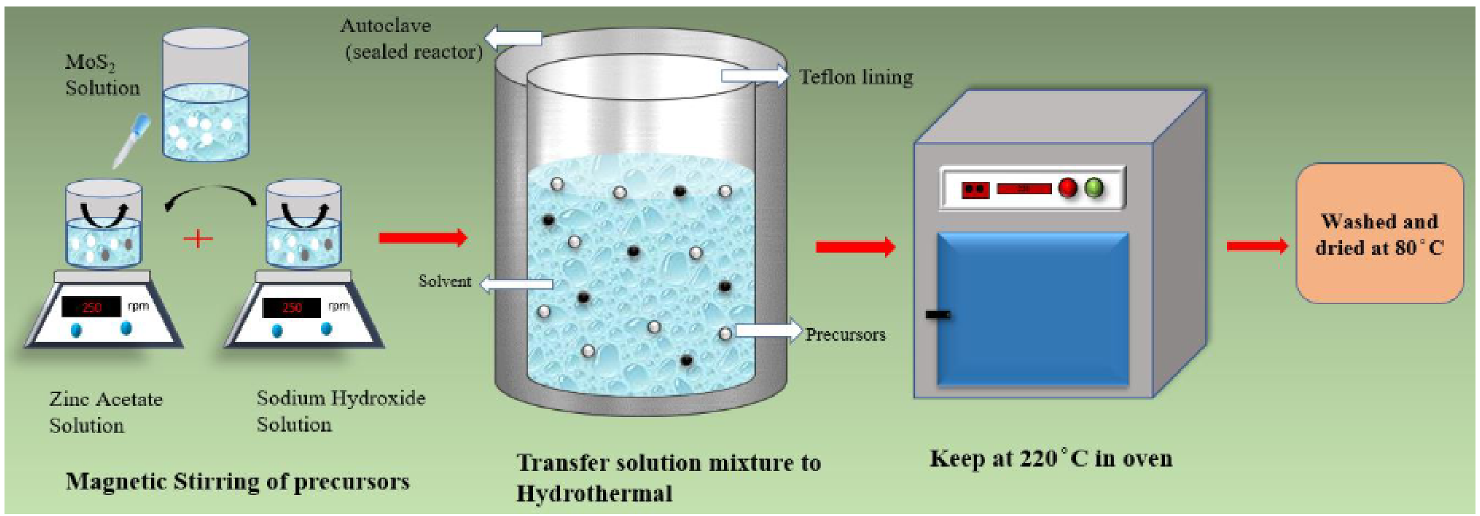

Fig. 3.2. A diagrammatical representation of the general process (type-I) used for sample preparation in NRL, DTU, Delhi, India.

In type-I synthesis, prepared MoS_2 nanoparticles [43] (named as MS1 and MS2) were added in the synthesis of ZnO nanostructure and the resultant nanomaterial obtained was a nanocomposite of ZnO-MoS_2 as can be interpreted by the literature survey [44], [45] and the preliminary XRD results.

We have got the optimized conditions for ZnO nanostructures from our senior, Ms. Nikita Jain. For the synthesis of these ZnO nanoparticles, the two precursors taken were Zinc Acetate ($ZnC_4H_6O_4$) and Sodium Hydroxide (NaOH). These were added to the different amounts of DI water and magnetically stirred until completely dissolved. 11 samples of the nanocomposite were prepared using this approach with varying amounts of precursors, DI water, temperature and stirring conditions. Prepared MoS_2 was added as a liquid solution of varying concentrations (10, 12 and 20 mL) to these solutions of precursors and with weight percentages of 0.5, 1.5, 2, 5 and 10 % with respect to ZnO. In some reactions, MoS_2 solution was ultrasonicated to obtain a homogenous mixture for fast and easy synthesis. The mixture solutions were again magnetically stirred using magnetic beads and then transferred to Teflon-lined autoclaves. The time of reactions was generally kept at 24 hours and varied temperatures ranging from 130 to 220 ° C.

After 24 hours, the samples cooled down naturally to room temperature. Then they were collected via centrifugation after washing with DI water and ethanol, 3 times each. Later, the washed samples were kept for drying. In one reaction of 5 wt % MoS_2, the washed and dried sample was even annealed at 300 ° C for 5 hours to obtain well pronounced XRD peaks. The powdered form of samples was then collected in an Eppendorf after crushing them and sent for XRD.

In type-II synthesis, prepared ZnO nanoparticles (sample named as Z1) were added in the synthesis of MoS_2 nanostructures and the resultant nanomaterial obtained was a nanocomposite of ZnO-MoS_2 as can be interpreted by the literature survey and the preliminary XRD results. Following Table 3.2. is the summary of the reaction attempts for the preparation of the synthesis of the composite by this second approach.

After 24 hours, the samples cooled down naturally to room temperature. Then they ⑦were collected via centrifugation at 10,000 rpm for 10 min after washing with DI water and ethanol, 3 times each. The washed samples were kept for drying at 60˚C for 24 hours. The powdered form of samples was collected in an Eppendorf after crushing them and named as ‘Rn1``, ‘Rn2``, ‘Rn3``, Rn4`` respectively.

Table 3.2: Reaction attempts summary for ZnO-MoS_2 nanocomposite synthesis (type-II)

Sample	Precursor name	Amount (g)	DI water (mL)	Stirring	
1 wt % ZnO in MoS_2 (Rn 1`)	Ammonium Molybdate Tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot4H_2O)$	2.4718	25	stir at 350 rpm, 30 min	(1)
	Thiourea (CH_4N_2S)	2.1504	25		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.0673	20	Stir for 30 min	(4)
	Add (4) into (1) dropwise and stir at 350-450 rpm for 60 min.				
	Transfer the solution mixture of (1) into 100 mL Teflon-lined autoclave and keep at 220˚C for 24 hours				
6 wt % ZnO in MoS_2 (Rn 2`)	Ammonium Molybdate Tetrahydrate	2.4718	25	stir at 350 rpm, 30 min	(1)
	Thiourea	2.1504	25		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.4041	20	Ultrasonicate for 5 min then stir for ½ hr	(4)
	Add (4) into (1) dropwise and stir at 350-450 rpm for 1 hour.				
	Transfer the solution mixture of (1) into 100 mL Teflon-lined autoclaves and keep at 220˚C for 24 hours				
1 wt % MoS_2 in ZnO (Rn 3`)	Ammonium Molybdate Tetrahydrate	2.4718	11	stir at 350 rpm, 30 min	(1)
	Thiourea	2.1504	12		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.0673	12	Ultrasonicate for 30 min then stir for ½ hr	(4)
	Add (4) into (1) dropwise and stir at 350-450 rpm for 1 hour.				
	Transfer the solution mixture of (1) into 50 mL Teflon-lined autoclave and keep at 220˚C for 24 hours.				
6.4 wt % ZnO in MoS_2 (Rn 4`)	Ammonium Molybdate Tetrahydrate	2.4718	11	stir at 350 rpm, 30 min	(1)
	Thiourea	2.1504	12		(2)
	Add (2) into (1) dropwise and stir at 350 rpm for 30 min at room temp.				
	Citric Acid	2.1133	-	Add into (1)	(3)
	ZnO	0.4310	12	Ultrasonicate for 30 min then stir for ½ hr	(4)
	Transfer the solution mixture of (1) into 50 mL Teflon-lined autoclave and keep at 220˚C for 24 hours.				

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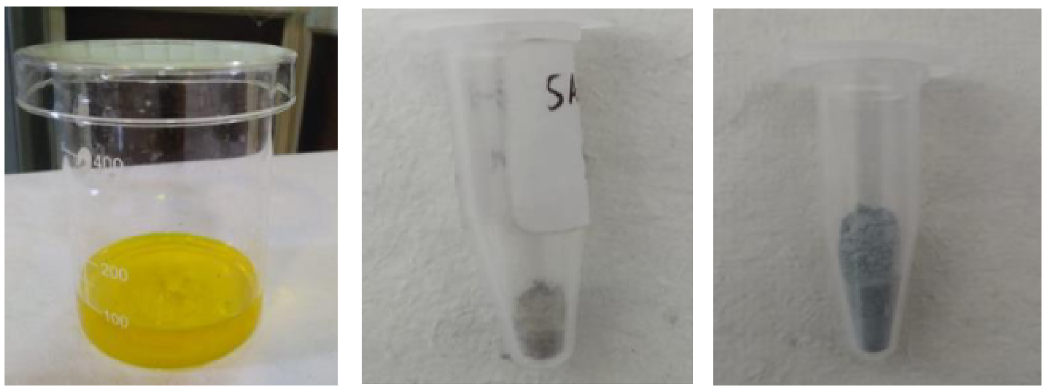
CHAPTER 4

RESULTS AND DISCUSSION

4.1. WS$_2$

In the first three attempts of WS$_2$ synthesis, no sample was obtained at the bottom of the Teflon as shown in Fig. 4.1. (a) but in the 4th attempt, as 37 shown in Fig. 4.1. (b) and 5th attempt, as shown in Fig. 4.1. (c), impressive amounts of greyish-colored samples were formed. Here, we have included the obtained XRD results of our 4th and 5th reaction attempts of the synthesis of WS$_2$ nanomaterial. The phases of the resultant nanomaterials obtained in the last 2 reactions were checked for the confirmation of the WS$_2$ phase as can be interpreted from the preliminary XRD results compiled in the following sections.



(a) (b) (c)

Fig. 4.1. (a) No sample obtained in the first three attempts **(b)** Sample formed in the fourth attempt **(c)** Sample formed in the fifth attempt

4.2. ZnO-MoS$_2$

Several attempts were made to synthesize the nanocomposite by two different calculations as discussed in chapter 3 with varying weight percentages of MoS$_2$ or ZnO. The pictorial representation of one of the resulting prepared sample of ZnO-MoS$_2$ nanocomposite is shown in Fig. 4.2. Here, we are reporting the preliminary XRD results of the prepared MoS$_2$ sample (MS1 and MS2), prepared ZnO sample (Z1) and all 15 reaction attempts in the preparation of the ZnO-MoS$_2$ nanocomposite and the UV results of the nanocomposite. The ZnO-MoS$_2$ phase can be interpreted from the preliminary XRD results compiled in the following sections.

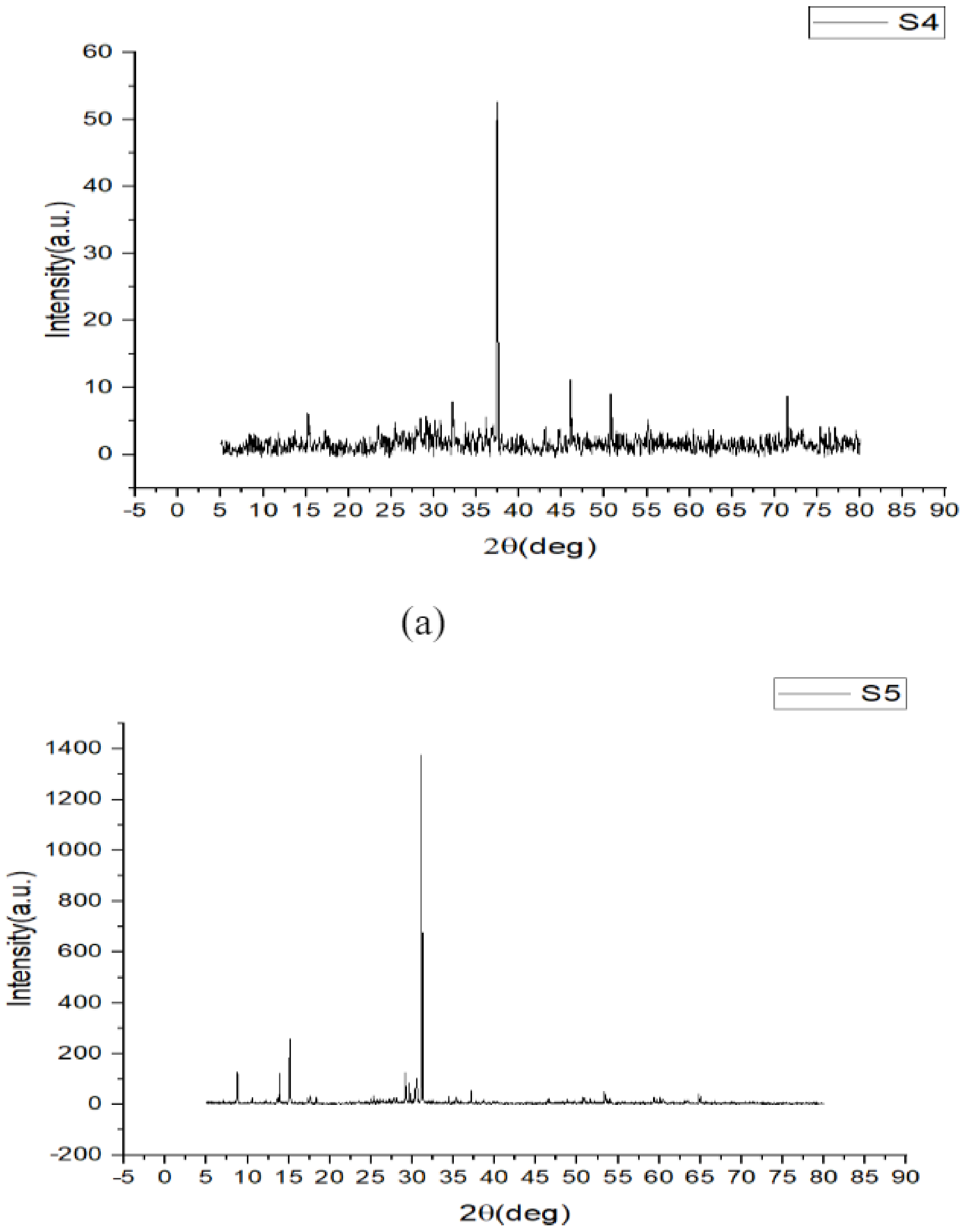
4.3 CHARACTERIZATION

XRD patterns were recorded using Bruker 8D Advance System using CuK{alpha} λ=1.54 Angstrom [16] at 40 kV voltage and 20 mA current with a scan rate of 1° per minute to study and verify the phase of the as-prepared samples and UV-vis spectroscopy is done using Carry-500 spectrometer which can be further studied to know the optical properties of the nanomaterial samples. The diffraction patterns for WS$_2$ are recorded within the 2θ scanning range of -5 to 90 degrees and that of ZnO-MoS$_2$ nanocomposites is 5 to 80 degrees and the UV-vis spectra are recorded for the liquid composite samples within a range of 200-800 nm.

Fig. 4.2 Pictorial representation of resulting prepared sample of ZnO-MoS$_2$.

4.3.1 XRD Characterization of WS_2

XRD results of the prepared WS_2 sample numbers 4 (S4) and 5 (S5) corresponding to reaction attempts 4 and 5 (from Table 3.1) are as shown in Fig. 4.3. (a) and Fig. 4.3. (b). The crystal structure of these samples was interpreted using XRD spectra. In the XRD results of sample 4, diffraction peaks are obtained at 2θ angles of 15.05°, 28.87°, 32.12°, 37.36°, 46.20°, 50.80° and 71.26° whereas, for sample 5, the diffraction peaks are more prominent and are obtained at 2θ angles of 8.81°, 13.80°, 15.29°, 29.00°, 29.63°, 30.63°, 31.12°, 37.23°, 53.43°and 64.89°. The diffraction peaks corresponding to these samples were plotted and labelled using OriginPro-2021 software.



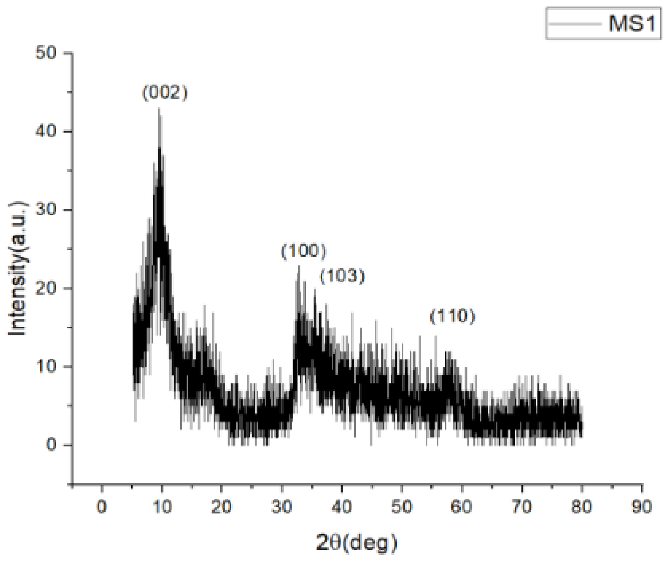
(a)

(b)

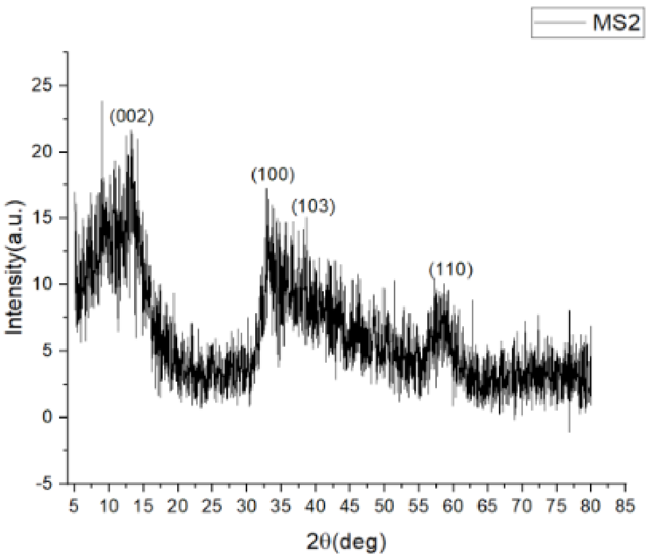
Fig. 4.3. XRD of **(a)** Sample 4 (S4), **(b)** Sample 4 (S5)

4.3.2 XRD Characterization of ZnO-MoS_2

For type-I synthesis, the XRD results of the pre-prepared MoS_2 samples (MS1 and MS2) are as shown in Fig. 4.4 (a) and (b) and that of the ZnO-MoS_2 composites loaded with 0.5%, 1.5%, 2%, 5% and 10% MoS_2 are shown in Fig. 4.4 (c) to Fig. 4.4 (l). The crystal structure of the prepared composite samples is interpreted by these XRD curves. In the diffraction results of pure MoS_2 (Fig. 4.4 (a)), diffraction peaks are obtained at 2θ angles of 13.04°, 32.20°, 38.6° and 58.6° corresponding to the miller planes (002), (100), (103) and (110) respectively which can be interpreted from the literature. The diffraction peaks of ZnO in the composite samples correspond to the 2θ angles of 31.8°, 34.5°, 36.2°, 47.5°, 56.6°, 62.8°, 66.3°, 68.0° and 69.1° which can be indexed to the planes of (100), (002), (101), (102), (110), (103), (112), (201) and (202) respectively.



(a)



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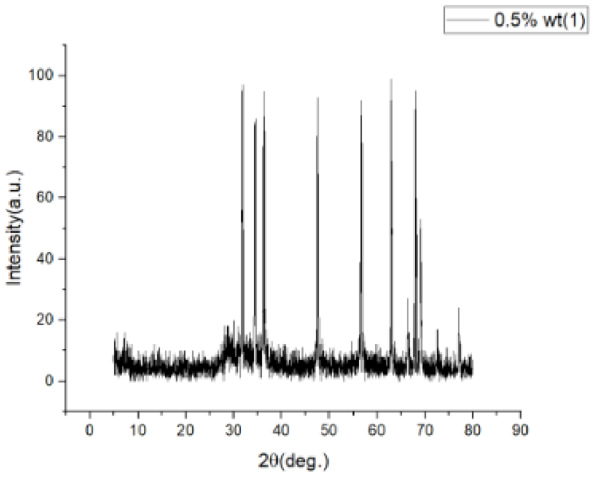
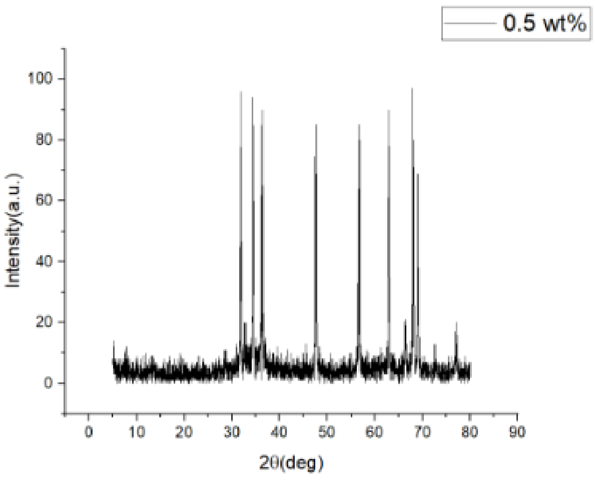
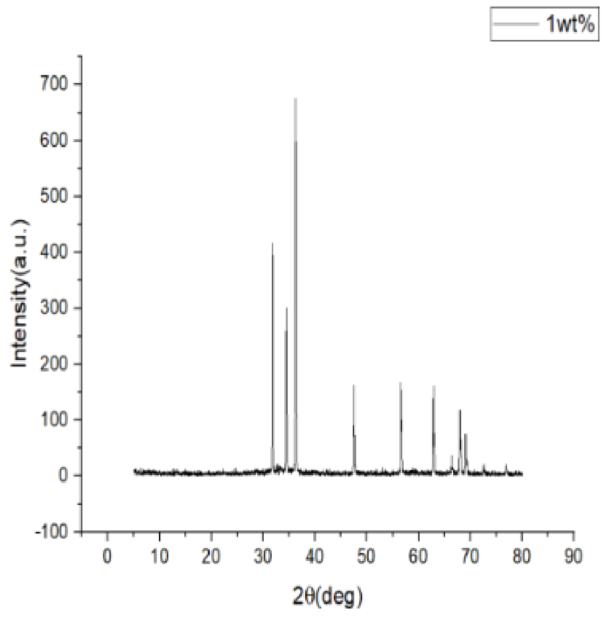


(c)



(d)


1wt%
Intensity(a.u.)
-100
0
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300
400
500
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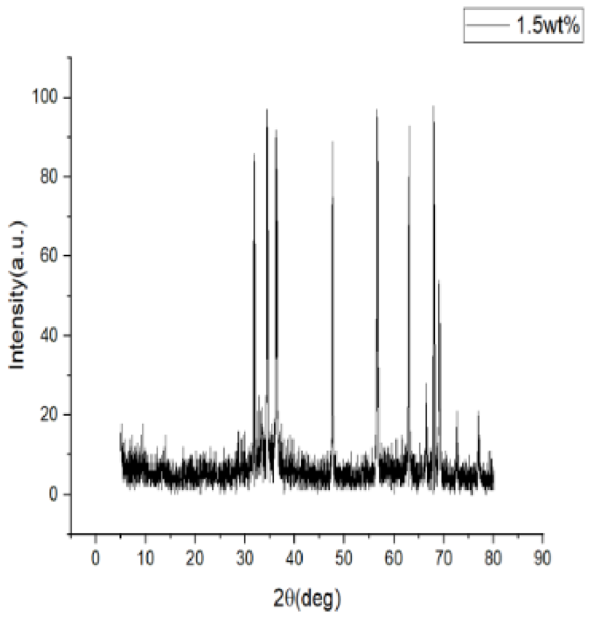
700
0 10 20 30 40 50 60 70 80 90
2θ(deg)

(e)


1.5wt%
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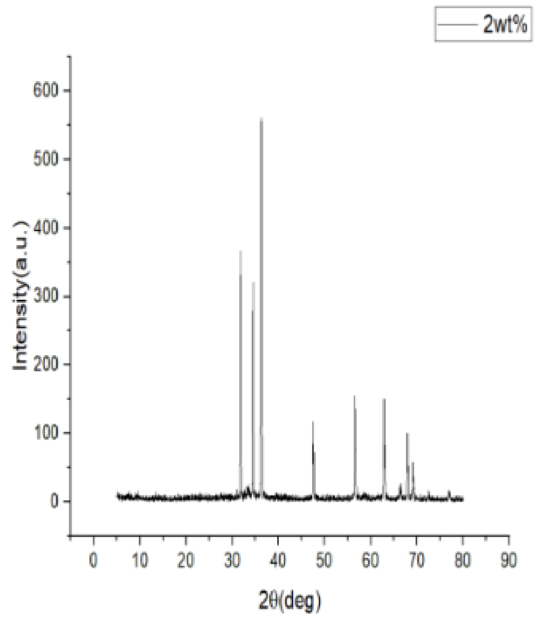
2θ(deg)

(f)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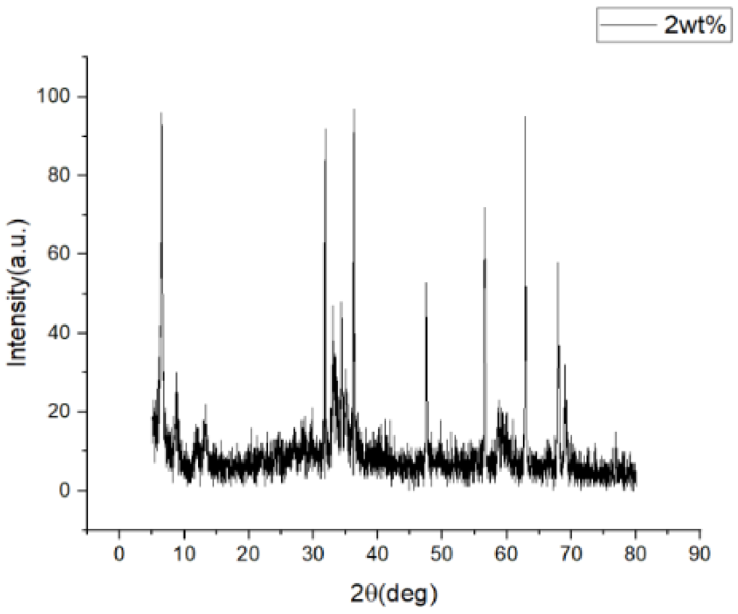
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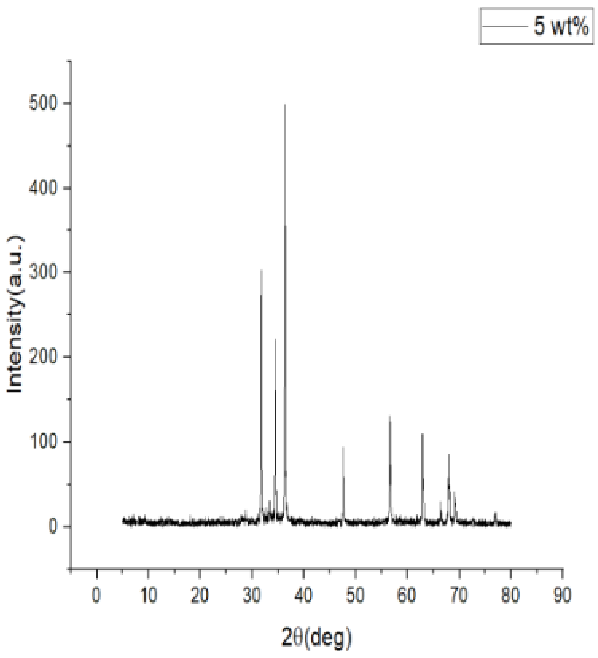
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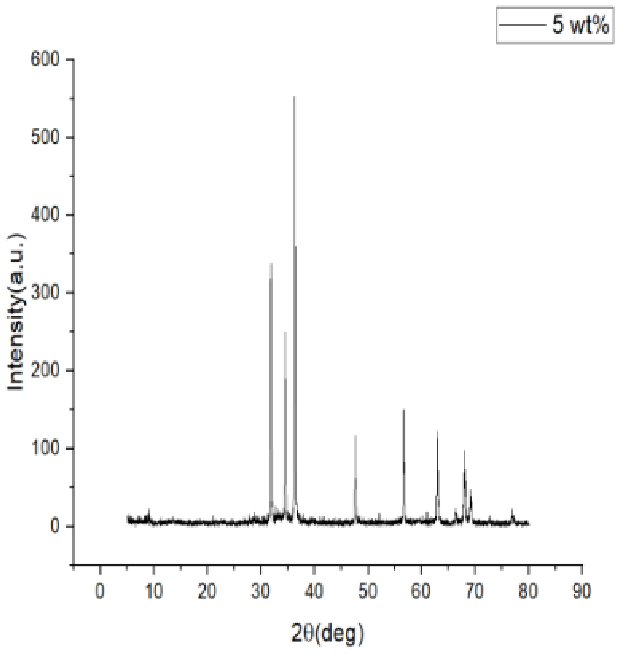
2θ(deg)

(I)


5 wt%
Intensity(a.u.)
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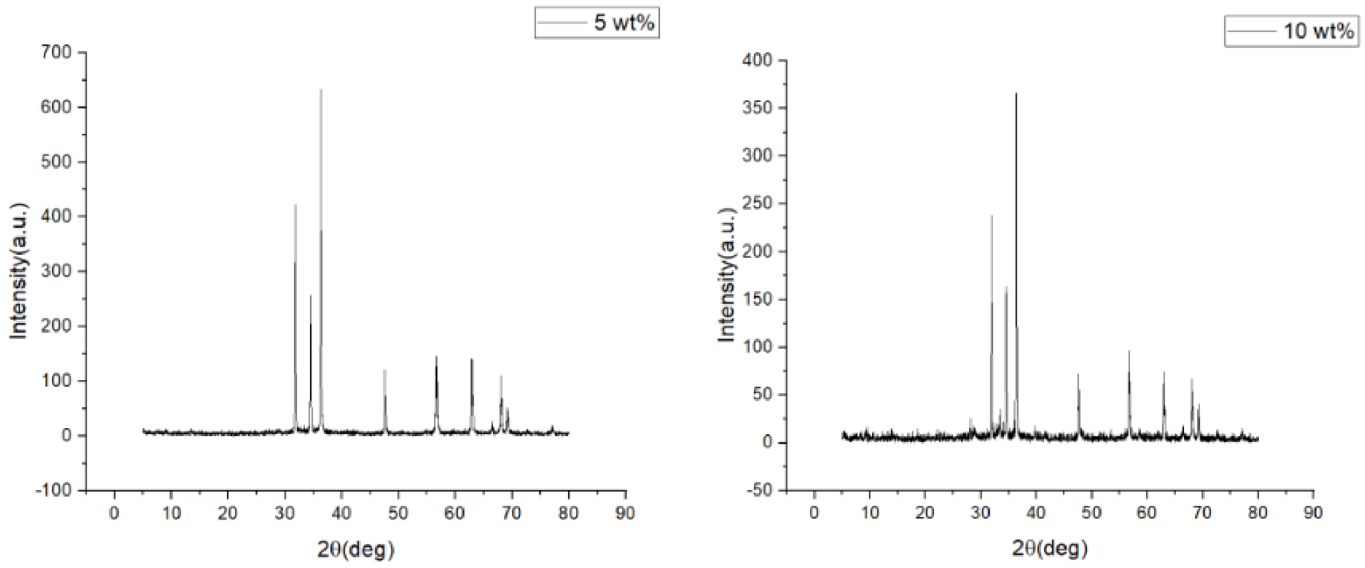
600
0 10 20 30 40 50 60 70 80 90
2θ(deg)

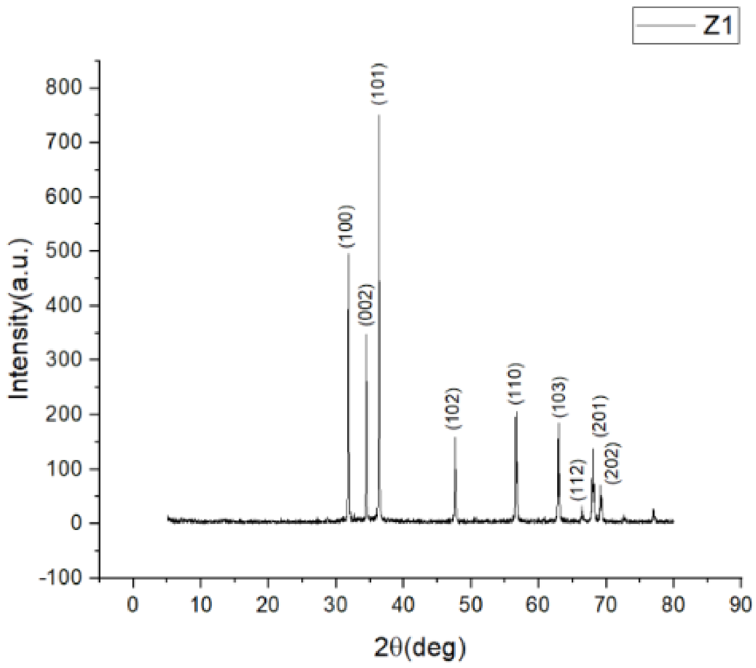
(j)



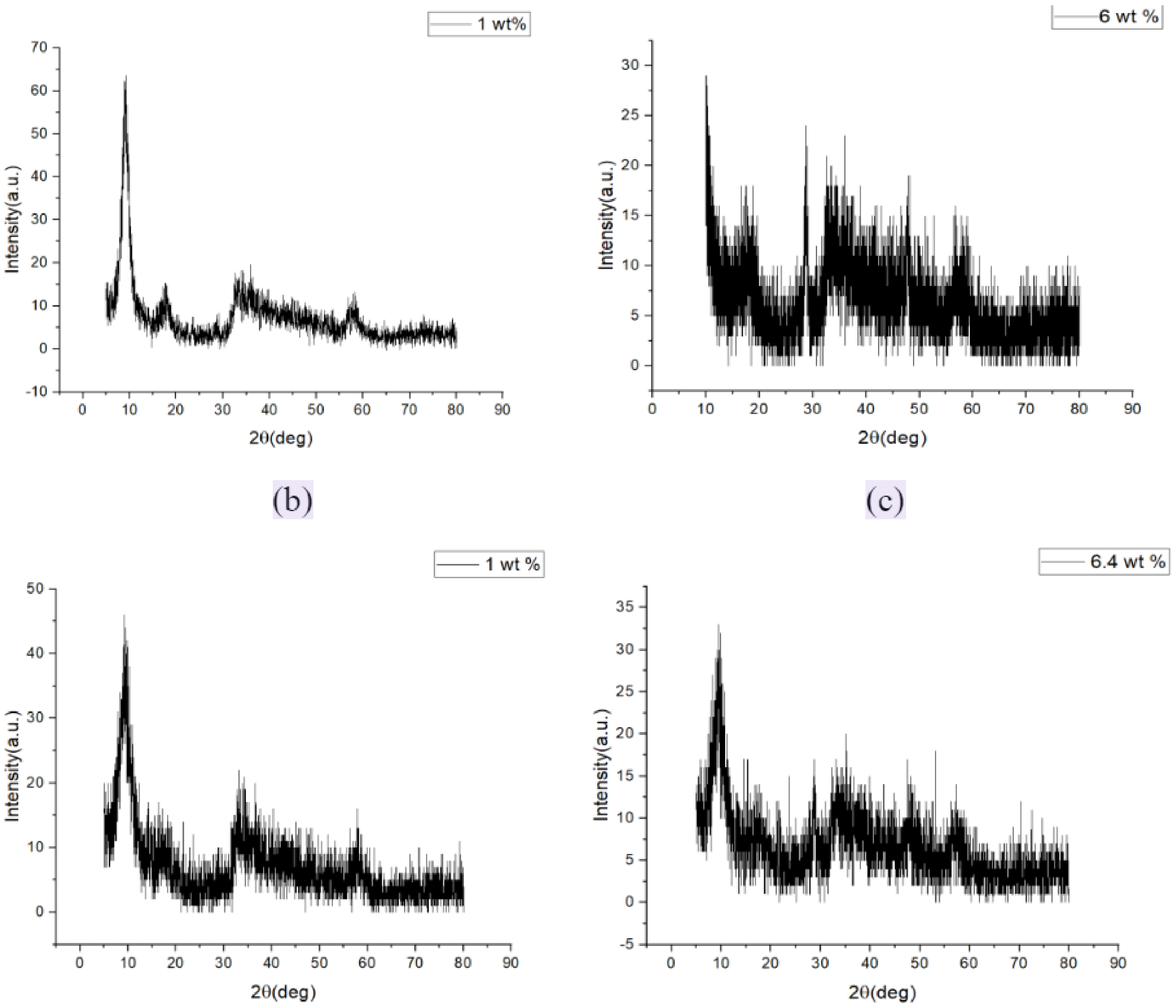
(k) (l)

Fig. 4.4. XRD of **(a)** prepared MoS_2 samples (MS1), **(b)** prepared MoS_2 sample (MS2), **(c)** 0.5 wt % (Rn1), **(d)** 0.5 wt % (Rn2), **(e)** 1 wt % (Rn3), **(f)** 1.5 wt % (Rn4), **(g)** 2 wt % (Rn5), **(h)** 2 wt % (Rn6), **(i)** 5 wt % (Rn7), **(j)** 5 wt % (Rn4), **(k)** 5 wt % (Rn4), **(k)** 5 wt % (Rn4), **(l)** 10 wt % (Rn4) sample.

Now, for type-II reactions, XRD plots of the pre-prepared ZnO samples are as shown in Fig 4.5. (a) and that of all 4 reaction attempts of the ZnO-MoS_2 nanocomposite are as shown in Fig. 4.5 (b), (c), (d) and (e).



(a)



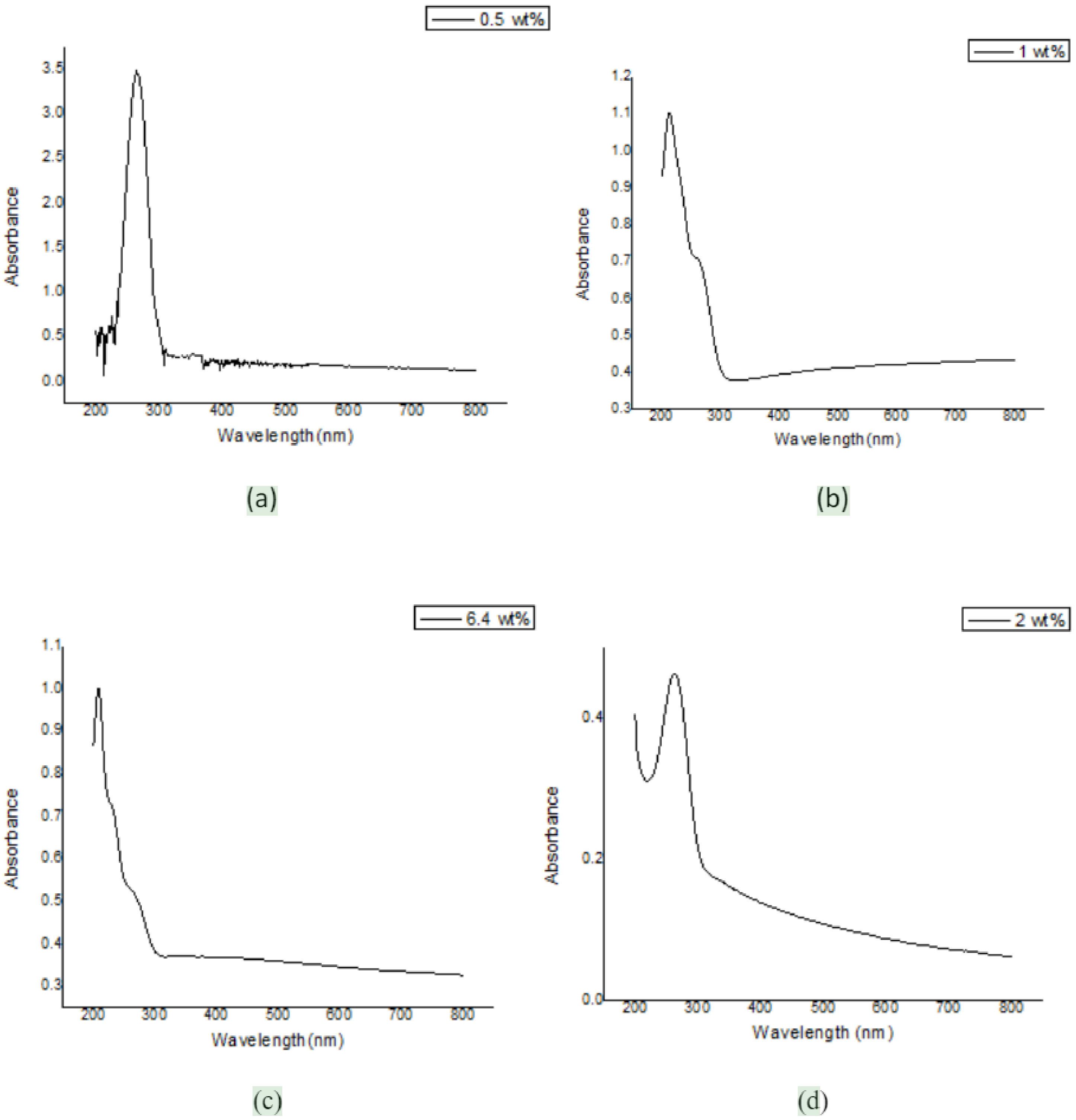
(b) (c)

(d) (e)

Fig. 4.5: XRD results of (a) pre-prepared ZnO nanoparticles (b) Rn 1', (c) Rn 2', (d) Rn 3' and (e) Rn 4'

4.3.3 UV-vis Spectroscopy

The nanoparticles show a broad absorption spectrum due to quantum confinement effects and the absorption peaks shift toward smaller wavelengths (higher energies) as the crystal size of the nanoparticles decreases, while the molar absorption coefficient increases with decreasing size. The peak widths of the nanoparticles also depend on the size distribution of the nanoparticles. The shift of absorption peak from higher to shorter wavelength is called a blueshift. UV–vis spectroscopy is used to determine the concentration, size, purity, and aggregation state of the constituents, and functional groups in molecules. It also provides size- and composition-dependent spectrum for the nanomaterials. The wavelength (λ) of light required for electronic transitions is typically in the ultraviolet (λ = 200–390 nm) and visible region (λ = 390–780 nm) of the electromagnetic radiation spectrum. Uv-vis analysis of a few ZnO-MoS_2 samples was done and their absorbance versus wavelength curves are as shown in the Fig. 4.6 ((a) to ( )). In these UV results of the nanocomposite, the absorption edge of the composite sample was obtained at around 310 nm as is shown in the figure below.



(a) (b)

(c) (d)

Fig. 4.6. UV-vis spectrum for (a) 0.5 wt% MoS_2 in ZnO, (b) 1 wt% MoS_2 in ZnO, (c)6.4 wt% MoS_2 in ZnO (d)2 wt% ZnO in MoS_2

4.4 CONCLUSION AND DISCUSSIONS

There are many Physical and Chemical synthesis techniques for the preparation of nanoparticles namely Hydrothermal, Solvothermal, Sonochemical, CVD, Sol-gel, and Chemical Exfoliation techniques. Some are Top-Down approaches while others are Bottom-Up (56) approaches. Both types of techniques have their advantages and disadvantages offering a variety of options to the users. Different types of nanomaterials like metal oxides, TMDs, etc. can be prepared by these approaches. Among the various metal oxides, Zinc Oxide (ZnO) is the one which has been explored vastly due to their exceptional properties. But on the other side, TMDs like (26) Molybdenum disulfide (MoS_2), Tungsten Disulphide (WS_2), etc. have also attracted attention due to their remarkable optical and electronic properties. Here, various attempts of preparation of the WS_2 nanocomposite and the ZnO-MoS_2 nanocomposite via facile Hydrothermal method are reported with the preliminary XRD and UV results.

In results of reaction of WS_2 nanocomposite, for the first three attempts, no sample was formed while in other attempts, greyish colored powder was obtained after centrifugation and washing. The suspected reason for the improper phase obtained in the XRD results of the WS_2 samples as shown in the previous section is the manual or incomplete stirring of precursors due to unoptimized conditions.

(50) This material can be used for a variety of applications in which solid lubrication is a famous one. The adhesion between Sulfur layers is relatively weak which results in the sliding of layers over each other.

The ZnO-MoS_2 nanostructure's synthesis using two different approaches and characterization results were also presented here. In first approach, MoS_2 powder was synthesized which was then added in the preparation of ZnO and in the second approach, prepared ZnO nanoparticles were added in the preparation of MoS_2. UV-vis spectroscopy was also done of the as-prepared samples of ZnO-MoS_2 nanocomposite which can be used to further study the sample's optical properties.

From these preliminary XRD results, the phase of both the composites can be interpreted from the literature.

CHAPTER 5

CHEMICAL VAPOUR DEPOSITION

5.1 HISTORICAL BACKGROUND

In the twentieth century, revolutionary advancements were going on in the electronics industry. Silicon (Si) was replacing Germanium (Ge) to be used as a basic semiconductor material for all device fabrications due to its remarkable properties like large bandgap and ease in forming the oxide layer on the surface [46], [47]. Soon, the basic requirements of n-, p- doped Si for Si integrated circuit technology was at peak heights to meet the ever-increasing demand for personal computers [34]. It was in the year 1960 that Theurer successfully fabricated good quality Si films which attracted the attention of various industries towards the manufacturing of silicon semiconductor devices [48]. These advancements have created a tremendous urge for highly pure ultra-thin films in the scientific world.

Though various methods like Electroplating [49], Spin coating [50], [51], Vacuum evaporation [52], Sputtering [53], and others have been explored at times to meet the early requirements of film deposition/coatings, many drawbacks and complications like deposition of multiple films, coating of large surface area, and conformal coverage have been observed with them[54]–[56]. This search takes us to the Chemical Vapor Deposition (CVD) technique which was at an early stage at that time. Since the late 1960s, its usage has gained momentum due to various advantages that it offers and it has emerged as the leading candidate for good quality thin film deposition [57]. It involves the deposition of one or more stable solid films on a heated substrate by a suitable chemical reaction at the surface of the substrate [58].

5.2 VARIANTS OF CVD

Various variants of CVD including Thermal Chemical Vapor Deposition, Plasma Enhanced Chemical Vapor Deposition (PECVD), Metal-Organic Chemical Vapor Deposition (MOCVD), and Atomic Layer Chemical Vapor Deposition (ALCVD) have been introduced at times [59]–[63]. Every variant has some advantages as well as disadvantages over others. Thermal CVD can be considered more of kind of a growth process rather than a deposition process in which the chemical reaction takes place at the surface of the substrate. In thermal CVD, the reaction is initiated by thermal energy provided by various means while in PECVD, the electrical energy is used to initiate homogeneous reactions for the production of chemically active ions and radicals that can participate in the heterogeneous reaction. CVD variants can also be differentiated based on zones. (a) Single zone CVD (b) Multiple zone CVD (two or more zones).

Looking at their significant advantages and future scopes, the Double Zone Thermal CVD System and PECVD systems present in the Nanomaterials Research Laboratory (NRL), Department of Applied Physics of Delhi Technological University (DTU), Delhi have been studied. Here, in this chapter, the detailed role of their various components, technical specifications, and working with labelled diagrams, schematics and relevant flowcharts are discussed.

5.2.1 Double Zone Thermal CVD

Double Zone Thermal CVD technique is a versatile, non-line of sight deposition technique by which uniform thin films can be deposited at a reasonable processing cost. Highly dense and pure materials can be obtained by this method. Though this method is a little complex, uniform and conformal deposition of films is possible with good reproducibility which is the biggest advantage [64]–[66]. Since the inception of novel CVD, its market has skyrocketed. The films deposited by the CVD technique have found their applications in numerous fields like the communication industry, optoelectronics industry, synthesis of high-temperature superconductors, coatings, and many interdisciplinary fields [59], [67]–[70]. One of the key reasons for the popularity of this technique comes from the fact that a variety of materials can be used as precursors in this method. Some of them are metals, metal hydrides, halides, halo-hydrides, and metalorganic compounds, and many more [59], [70]–[75]. A typical laboratory Double Zone Thermal CVD in NRL, DTU, Delhi, India is shown in Fig. 5.1.

5.2.2 Plasma Enhanced CVD

PECVD is one of the numerous variants of CVD used to deposit thin films. Like Double Zone Thermal CVD, it is also a non-line of sight technique that involves a chemical reaction at a low temperature activated by a high-energy plasma stream. The stream is produced using electrical energy which later transfers the energy of its species to the precursors. This initiates the homogeneous reaction to free

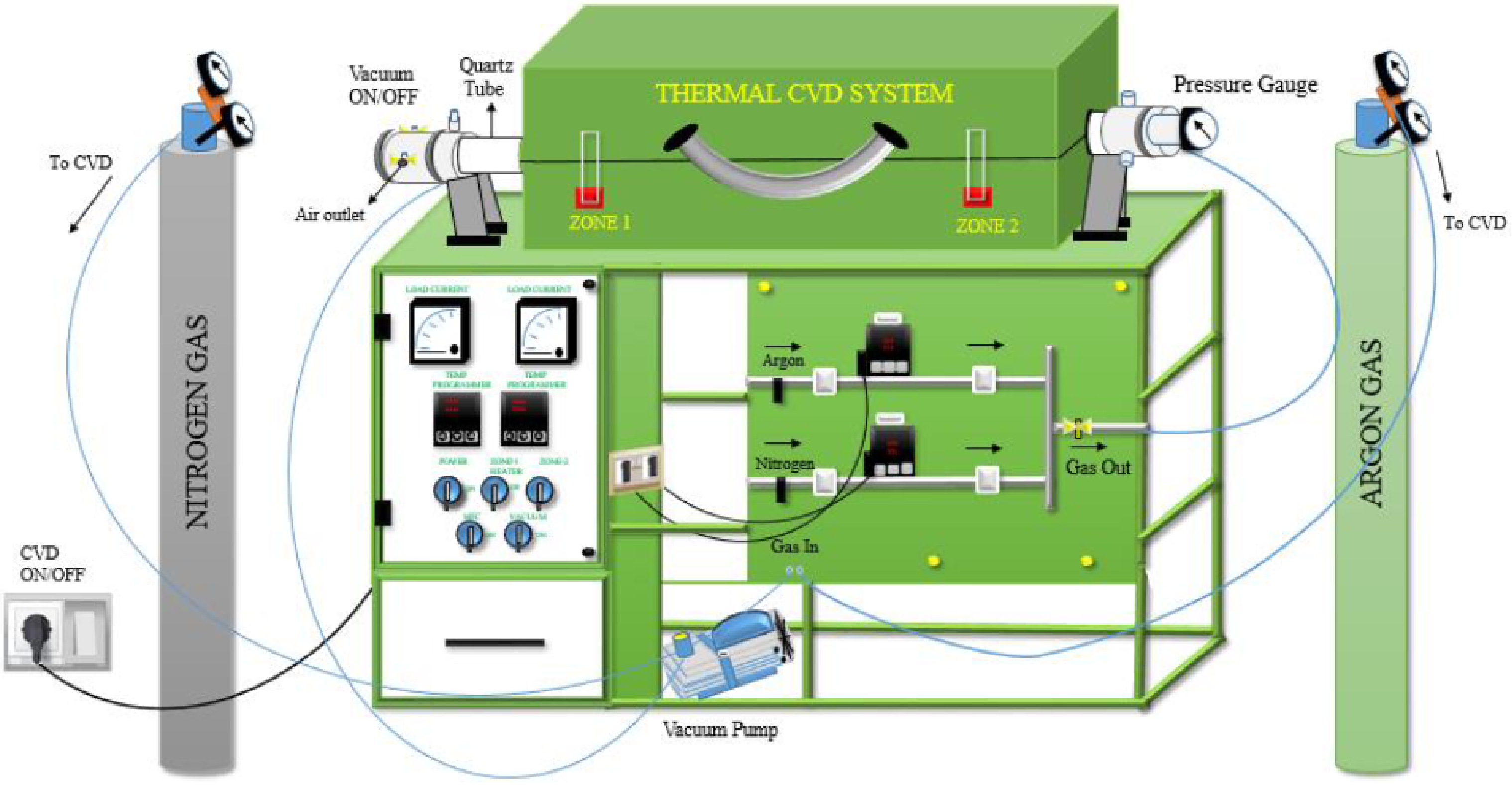


Fig. 5.1. Labelled diagram of typical laboratory Double Zone Thermal Chemical Vapor Deposition (CVD) in NRL, DTU, Delhi, India.

radicals or active ions followed by radical polymerization resulting in the deposition of thin films. It is a widely used technique to fabricate various thin nano-films and modify their properties for diverse applications [76]. A typical laboratory PECVD in NRL, DTU, Delhi, India is shown in Fig.5.2.

5.3 INSTRUMENTATION: IMPLEMENTATION AND FUNCTION

The impetus provided to the phenomenal usage of thermal CVD in diverse areas is due to ease in its installation and simple fabrication process. The most basic requirements for a CVD system are: a gas supplier with a flow controller, some heating mechanism, a reactor chamber, and a temperature controller. In the Double Zone Thermal CVD system in NRL, DTU, Delhi (shown in Fig. 5.1.), there are two independent heating zones with a 31.4-inch chamber size made up of quartz tube that can operate up to 1000℃ which makes it a high-temperature CVD [76]. On one side of the quartz tube, a gauge meter is attached to observe the pressure inside it. It can show the pressure in the range 0 to 1838 mm Hg on the positive side and 0 to -760 mm Hg on the negative side. On the other side, there is a gas outlet valve and a vacuum valve connected to the vacuum pump used for the suction of air inside the

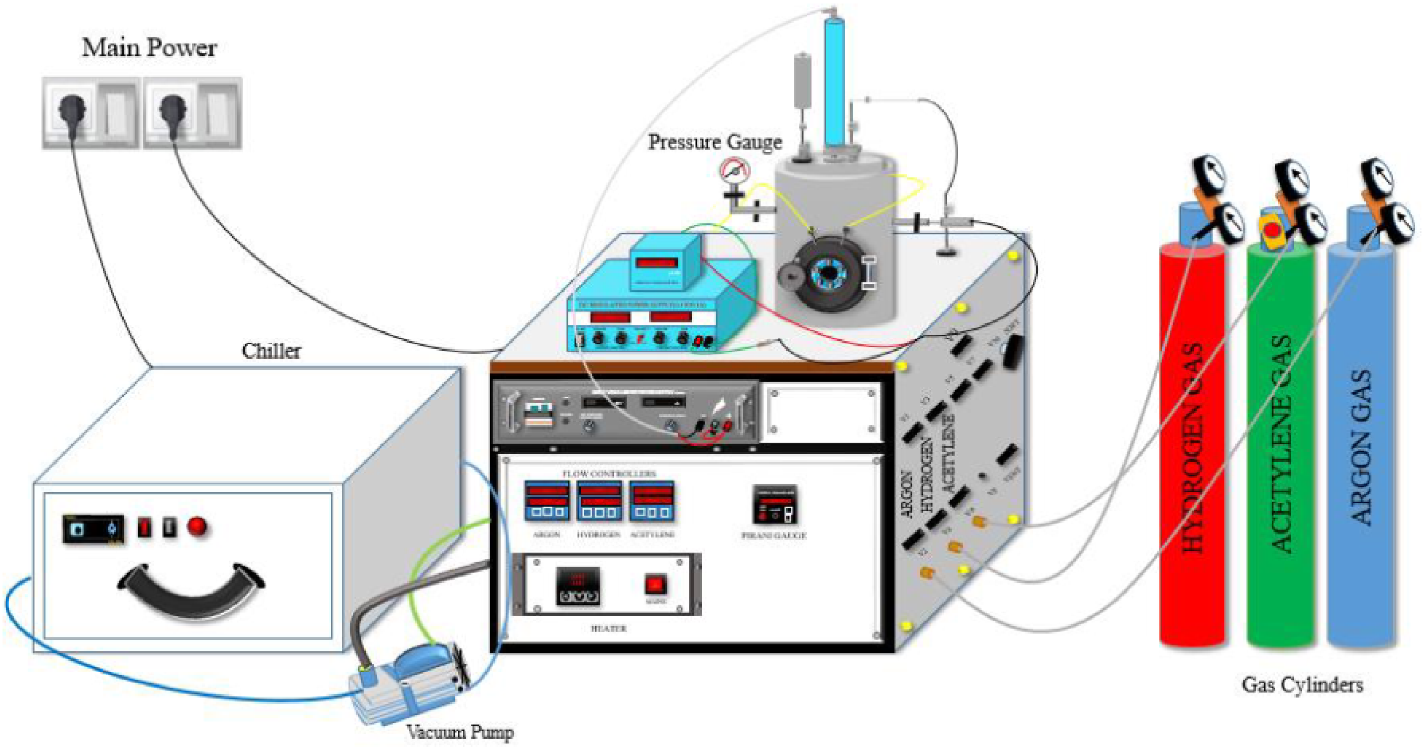


Fig. 5.2. Labelled diagram of PECVD in NRL, DTU, Delhi, India.

tube and creates the desired level of vacuum. There are two load current meters and temperature programmers for both zones respectively. There are two gas cylinders also, containing inert gases, Nitrogen (N_2) and Argon (Ar) respectively. The one filled with N_2 gas has the capacity of 46.7 liters weighing 51.7 kg and the other one filled with Ar has the same capacity weighing 52.2 kg. Complete technical details are presented in Table 5.1. As it is a 58 hot wall reactor, the whole quartz tube is heated uniformly with the precursors and the substrate is placed inside it. Fig. 5.2. shows the PECVD system in NRL, DTU, Delhi. PECVD has three cylinders of gases containing acetylene, hydrogen and argon gas. A chiller and heater are attached to the system for cooling and heating purposes respectively. A vacuum pump is also attached for suction of the air and creating vacuum as per the desired conditions.

5.4 PRINCIPLE

5.4.1 Double Zone Thermal CVD

The basic principle of Thermal CVD is described in the flowchart in Fig. 5.3. Here, volatile precursors are provided thermal energy in the presence of an inert

Table 5.1. Technical details of Double Zone Thermal CVD system

Technical Parameters	**Values**
Zones	2
Chamber Size	31.4 inch
Maximum Temperature	1000°C
Pressure Range (Positive Side)	0 to 1838 mm Hg
Pressure Range (Negative Side)	0 to -760 mm Hg
Volume (Cylinder filled with N_2)	46.7 litres
Volume (Cylinder filled with Ar)	46.7 litres
Weight (Cylinder filled with N_2)	51.7 kg
Weight (Cylinder filled with Ar)	52.2 kg

gas that is used as a carrier gas. At appropriate temperatures, when precursors are in the vapor state, they get mixed with the molecules of inert gas and undergo a homogenous vapor phase reaction. These precursors diffuse to the substrate surface and the gas molecules get adsorbed on the surface of the substrate. The molecules of precursors heterogeneously react with heated substrate forming a thin solid film. After this, the by-products formed, the adsorbed gas molecules and other unwanted

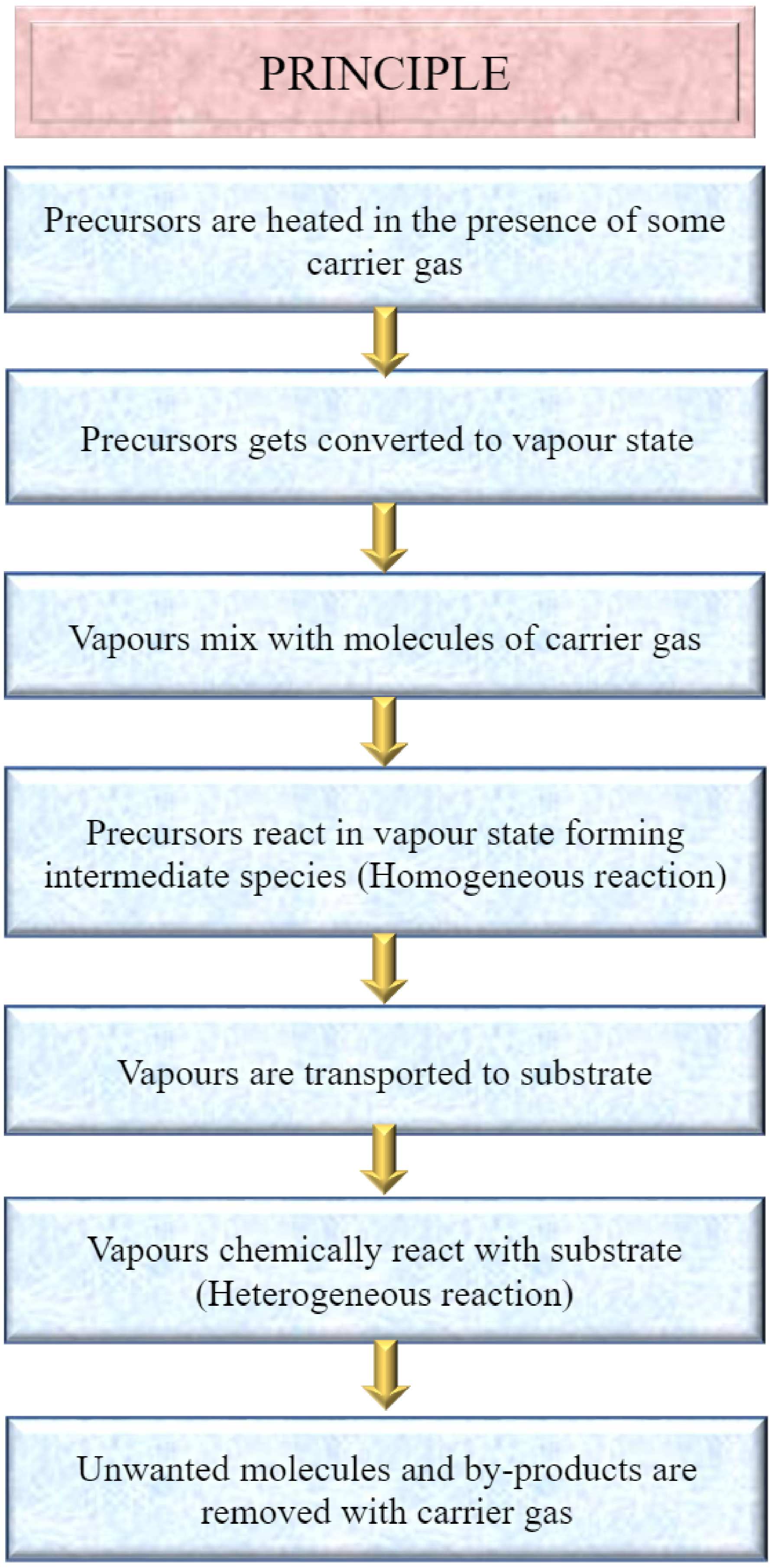


Fig. 5.3. Principle of Thermal CVD

44 materials are carried out of the reactor by outlet valve with the flow of gas [77]. The principle of Double Zone Thermal CVD is no different from the above principle. Double zone CVD is better to control the evaporation moment of the precursors. Here, the precursors that require different temperatures to evaporate can be placed in different zones. Thus, the precursor-1 with lower evaporation temperature is placed in zone-1. The precursor-2 with a higher evaporation temperature is placed in zone-2. Both the precursors are placed in the center of the respective zones. The substrate is placed downstream at an optimized distance from the precursor-2. Both the precursors and the substrate are placed in boats of appropriate material depending on temperature.

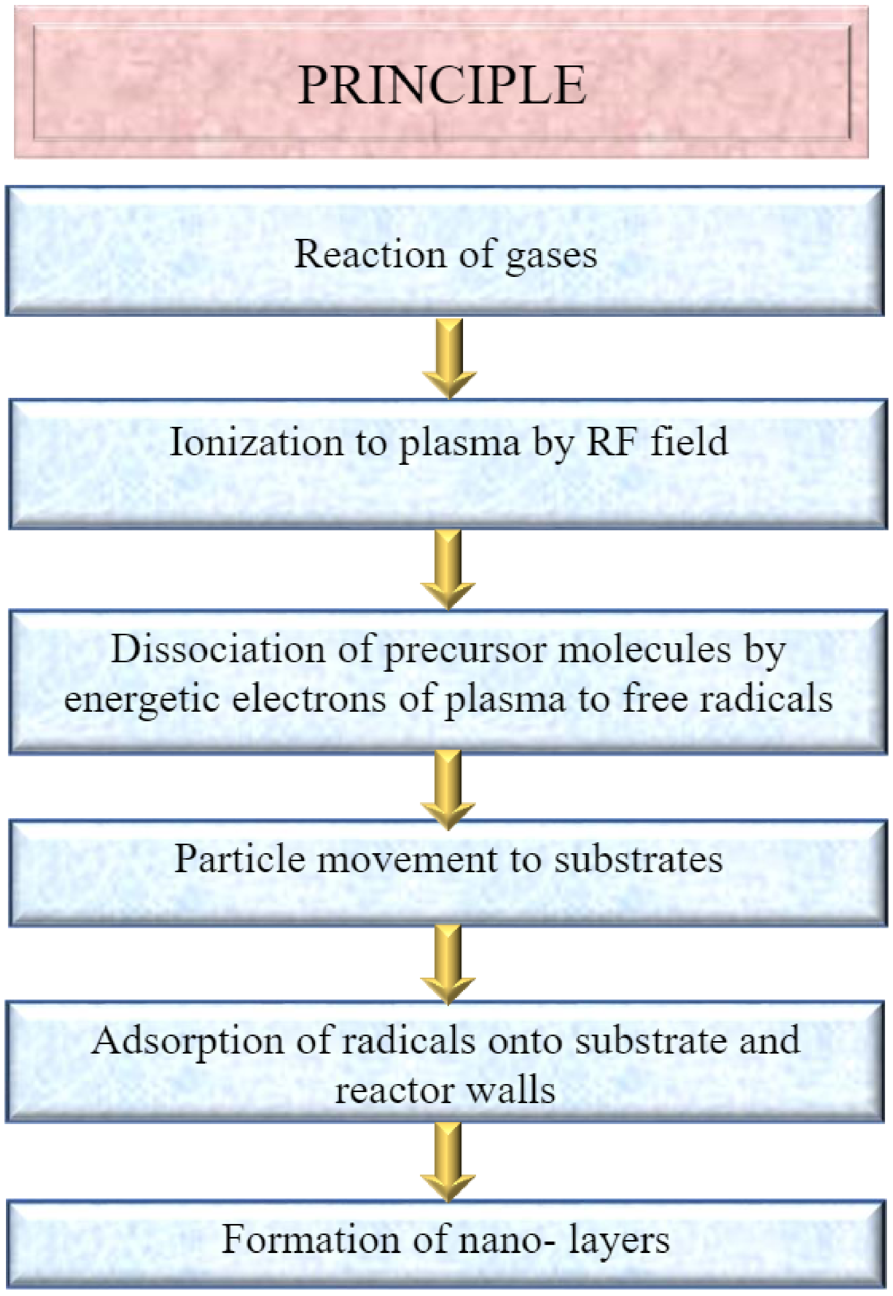


Fig. 5.4. Principle of PECVD

5.4.2 PECVD

The basic principle of the PECVD system is described in Fig. 5.4. The process starts with the reaction of gases followed by the ionization of gases to form the plasma state by DC current. It leads to the dissociation of precursor molecules by energetic electrons of plasma to free radicals which results in the particle movement to the substrates. Finally, the radicals are adsorbed onto the substrate and the reactor walls. Thus, the nano-layers are formed.

5.5 WORKING OF DOUBLE ZONE THERMAL CVD

The working of the Double Zone Thermal CVD system is shown in Fig. 5.5. Here, 'A' denotes the flow of inert gas from cylinders through the gas tubes controlled by flow controllers. 'B' denotes the flow of gas into the quartz tube in the direction shown. 'C' & 'E' denotes the heating of volatile precursors by heating elements attached to the CVD. 'D' & 'F' denotes the conversion of precursors from solid form to vapor form. 'G' denotes the diffusion of precursors in the vapor phase to the substrate's surface. 'H' denotes the heterogeneous reaction ㊴ at the substrate's surface and the formation of a thin solid film. 'I' denotes the removal of by-products and unwanted materials. The complete procedure of depositing the films on the system present in the lab is shown in Fig. 5.6. Initially, the precursors have to be placed inside the boats and then the boats are positioned at the center of the respective zones. In the

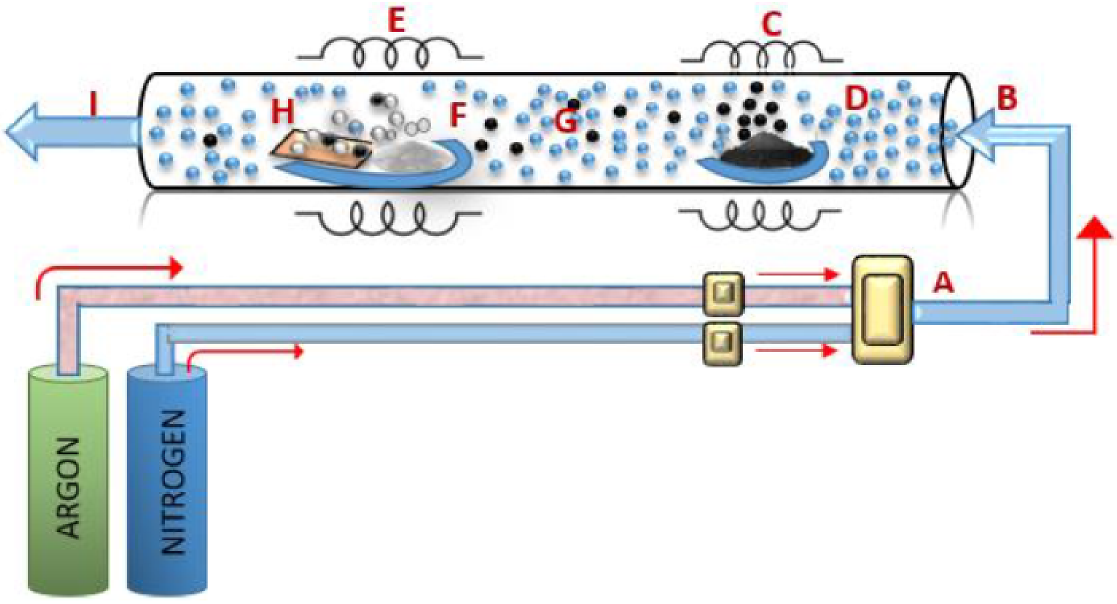


Fig. 5.5. Schematic diagram of Double Zone Thermal CVD

second zone, at some distance from the precursors downstream, the substrate has to be placed. Then, CVD has to be switched ON by turning the power ON knob present on the system. After that, the vacuum inlet valve has to be opened and the vacuum knob has to be turned ON. Then, the pressure gauge has to be checked which should

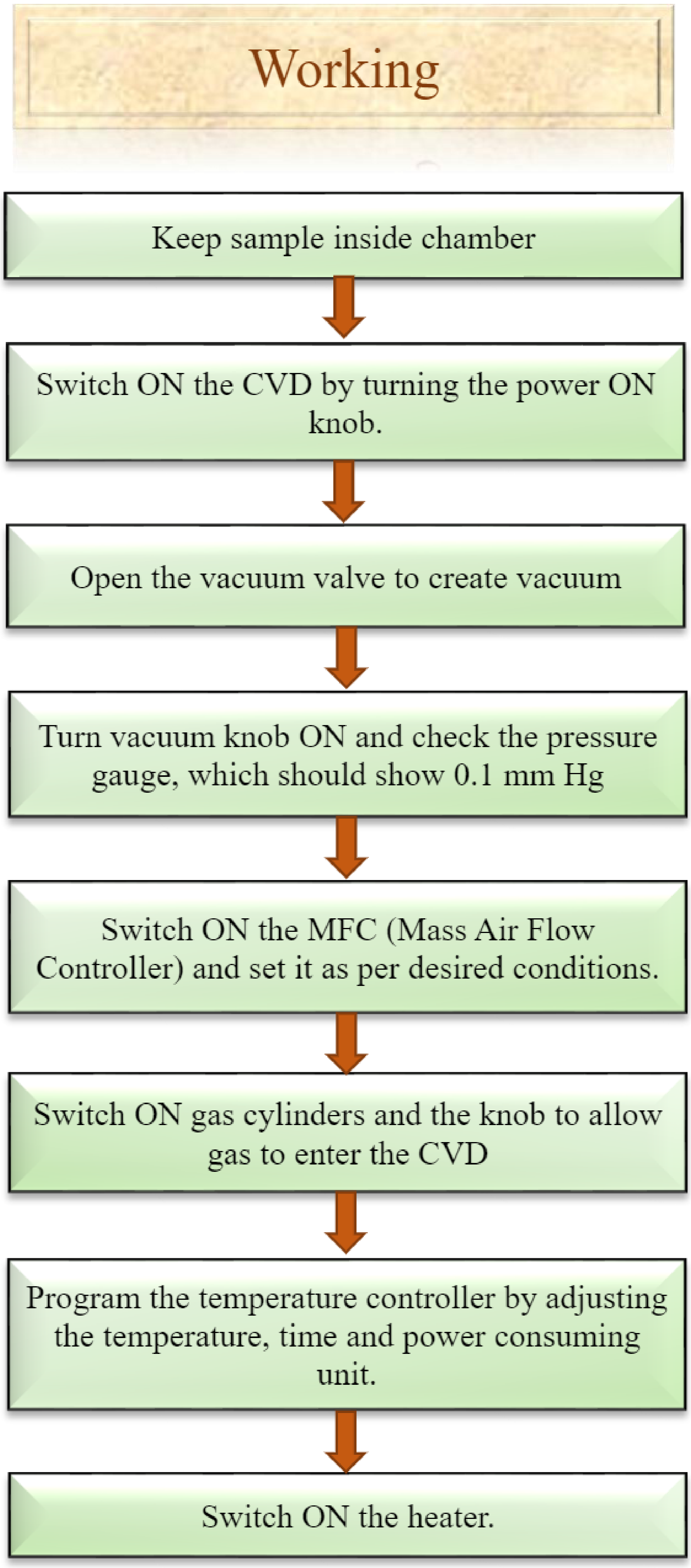


Fig. 5.6. Flow chart of working of Double Zone Thermal CVD system at NRL, DTU

have been showing the reading of 0.1 mm Hg. After checking that, the mass air-flow controller (MFC) has been switched ON and has to be set as per desired conditions. Then, knobs of gas cylinders have to be turned on to allow the gas to enter CVD.

After all the initial steps, finally, temperature controllers have to be programmed to set the temperature, time, and power-consuming unit of both zones. To run the temperature-controlled program, the 'Set' button has to be pressed seven times. After setting the temperature, time, and power consumption unit, the up button has to be pressed to run the program. After looking for all the initial check-points and taking all the precautionary measures, the heater has to be switched on and it starts functioning. The program can be shut off by pressing the "Set" and "Down" buttons simultaneously.

5.6 DIFFERENCES BETWEEN DOUBLE ZONE THERMAL CVD AND PECVD

In conventional CVD, the temperature ranging from 500 to 1000 ° C is taken to thermally decompose the precursor gases. Whereas, in PECVD, much lower temperatures are considered. PECVD technique has some limitations which are listed here:

(a) It requires a sophisticated reactor to contain the plasma.

(b) It is difficult to deposit high purity films using PECVD. The reason could be the 16 incomplete desorption of by-products and unreacted precursors at low temperatures.

(c) Incorporation of impurities like toxic, explosive gases in the plasma stream which can be detrimental for many applications.

(d) High ion energy plasma (< 20eVs) used in PECVD can damage fragile substrates because of ion bombardment, (e) the selection of an appropriate monomer is a challenge.

(f) Suitable inlet instruments are needed to be installed separately.

(g) Films formed may comprise compressive and residual stresses because of low-frequency requirements in PECVD.

(h) If superlattice structures are synthesized using PECVD, it could be time-consuming.

(i) Instability against humidity and aging are two more disadvantages.

(j) Costly parts of equipment and machinery that are generally not desirable.

5.7 PRECURSOR SELECTION

As stated above, one of the key reasons for the popularity of CVD is the variety of precursors used in the technique. The precursors can be inorganic compounds like halides, hydrides, halo-hydrides of metals, and metalloids. The precursors used can also be organic compounds like alkoxides, acetylacetonates, alkyl, aryl-derivatives of metal, carbonyls, arenes, etc. as is shown in the classification in Fig. 5.7.

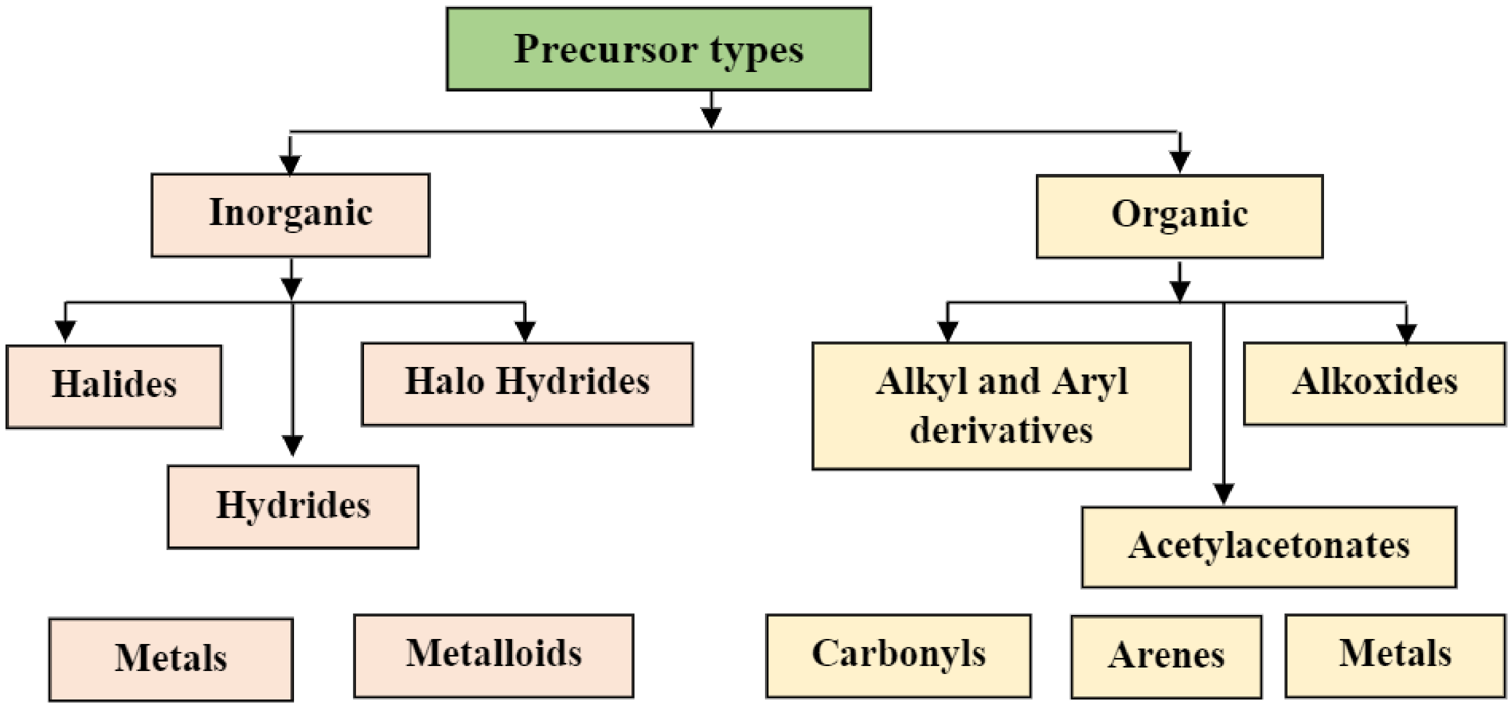


Fig. 5.7. Classification of Precursors used in CVD

Though a large no. of materials can be used as the precursors in this technique, some conditions that are applied to the materials to be used as a precursor are as follows:

(a) At room temperature, the precursor should be stable.

(b) It should have a low evaporation temperature such that it has sufficient volatility.

(c) Its reaction temperature should be ㊹ below the melting point of the substrate.

(d) It should be available in an adequate amount in pure form at a low cost.

(e) It should be non-hazardous [34], [35], [58].

Above stated conditions are applicable on all the precursors irrespective of the variant of CVD, while some more conditions may vary depending upon the variant of CVD in which they will be used.

5.8 PRECAUTIONARY MEASURES

While operating any device, there are always some safety guidelines that must be followed. Failure in doing so may cause trouble to the user and damage to the instrument. Unlike any other device, while operating a double zone thermal CVD system too, there are some safety precautionary measures that must be followed for the safety of the user and the long life of the CVD system. These are listed here:

(a) CVD should not be operated at power-consuming units greater than 60 percent.

(b) The heater should be switched ON only after the last step described in the working procedure. It shouldn’t be switched on in between.

(c) The pressure inside the chamber should be ensured at 0 psi or 0 mmHg. If it increases, the outlet valve should be opened otherwise the quartz tube may get cracked.

(d) If we do not create a vacuum inside the quartz tube in the procedure, the outlet valve should be open so that the moisture doesn't get collected inside the tube. Moisture developed inside the tube might break the quartz tube.

(e) The value of the mass airflow controller should always be set to less than 500 scm.

(f) The main valves of the cylinder should be shut off while not in use.

Some precautions that need to be followed while operating the PECVD system are listed as follows:

(a) UPS should always be kept on.

(b) After starting the rotary pump, the user should open the SOFT valve first and only after a few min of suction ROUGHING valve should be open.

(c) Valves should be operated softly.

(d) V11 valve should be open before injecting gases into the process chamber and it should be closed before opening the VENT valve.

(e) Acetone should be avoided for cleaning purposes, especially for o-rings.

Apart from these instrumental precautions, there are some other rules too that should be followed thumb rule. Especially, while handling hazardous chemicals, extra care needs to be taken to avoid accidents. Some of them are listed here:

(a) Good ventilation should be ensured while handling the hazardous chemicals or the instrument.

(b) Enough equipment should be arranged for the protection of the user's safety like a face shield, glasses for eyes and others.

(c) Fire extinguishers should be installed at various places to ensure people's safety.

(d) Arrangement of first aid treatment should have been ensured in case of any emergency [35], [58].

5.9 CONCLUSION

CVD technique finds potential applications in the deposition of thin films offering many advantages like conformal coverage and coating over the large surface area. There are numerous variants of CVD including Thermal CVD, PECVD, MOCVD, ALD, and others. Two of the variants of CVD i.e., Double Zone Thermal CVD and PECVD were studied and it is concluded that both have their own advantages and disadvantages. However, achieving control over ultimate film properties like thickness and film composition is a challenge in PECVD which is not the case with the thermal CVD system. Furthermore, these systems can be used to synthesize various types of materials ranging from pure-dense materials to thin-nano films for many industries. They find applications in areas like microelectronics (electrical insulation and conductive films, diffusion masks, capacitors, etc.); optoelectronics; protective, decorative, optical coatings (photovoltaics and photonics e.g., notch filters and anti-reflective coatings); synthesis of Transition Metal Dichalcogenides, Carbon films, Graphene-based polymeric nanocomposites, etc.; fabrication of integrated circuits, solar cells, transistors, and some others like food packaging, biosensors, device fabrication and various biomedical applications (immobilization of biomolecules, degradation of biopolymers, etc.).

CHAPTER 6

FUTURE APPLICATION - SENSING

After synthesizing these nanostructures successfully, they can be used to explore the incredible properties and for a variety of applications. We aimed to use the nanostructures for the application in Gas-Sensing, which couldn't be done due to the COVID-19 pandemic. But, it can certainly be achieved in the future. We have studied two types of Gas-Sensing which will be discussed in the current chapter.

6.1 SENSORS

Sensors, similar to human senses in their function, are devices that can sense a signal, be it mechanical or chemical or optical and then converts it into another signal that is electrical in nature. This output signal is received and studied using systems of devices like computers.

The two main parts of a sensor are An active sensing part that acts as a translator for the input signal to convert it into an intermediate signal and the transducer part that converts that intermediate signal into the final output signal.

6.1.1 Working of Sensors

The above-mentioned parts consist of the working process for the sensors. Fig. 6.1 describes the same in the form of a flowchart.

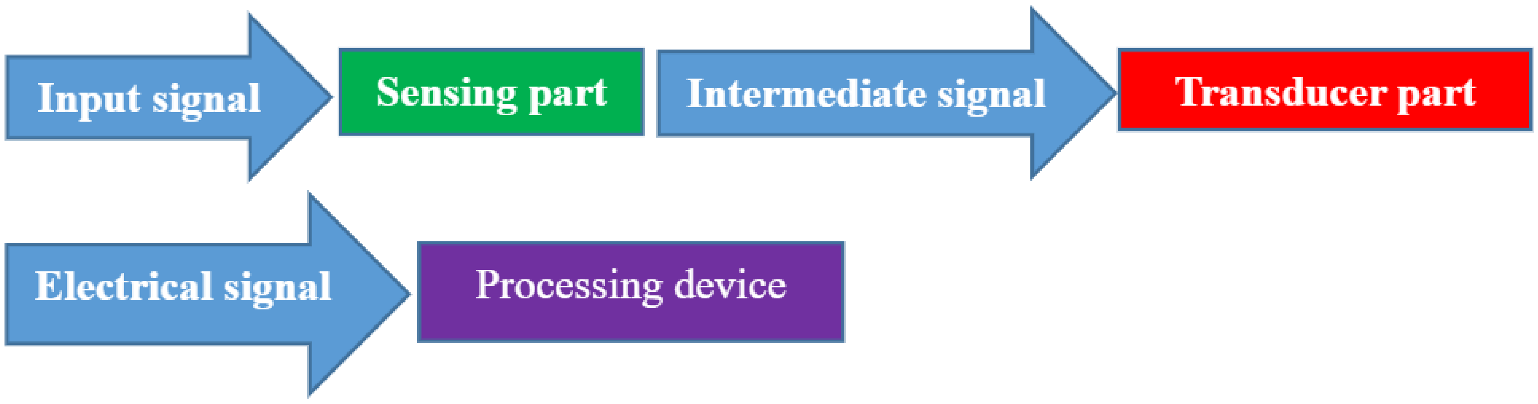


Fig. 6.1: Flowchart of working of sensors

6.1.2 Types of Sensors

There are many types of sensors. Some of them are named as follows:

1. Gas sensor
2. Temperature sensor
3. Bio sensor
4. Chemical sensor
5. Nano sensor
6. Light sensor
7. Touch sensor
8. IR sensor
9. Humidity sensor

6.1.3 Factors influencing the performance of sensors

Many factors affect a sensor's performance like:

(a) Morphology of the material of the sensor - if the morphology is not developed appropriately then it may cause functioning issues in some particular sensors like gas sensors and decrease their sensitivity.

(b) Its structure – similar sensitivity issues could be faced as that of morphological ones.

(c) Surface area – they must have huge surface areas as they function at low ppb so high surface areas are required for maximum adsorption of analytes to obtain quick and strong sensitivity.

6.2 ELECTROCHEMICAL-BIO SENSORS

Electrochemical-bio sensors are an important class of Bio-sensors that converts biological information into an electric signal with the help of an electrochemical transducer. That output signal is then processed using a detecting device. These are used to detect a variety of biological materials like enzymes, ligands, tissues, etc. Generally, enzymes are used as bioreceptors in electrochemical biosensing because of their biocatalytic and binding nature [36]. Some main components of Electrochemical Bio Sensors are:

1. Bioreceptors – enzymes, antibodies, nucleic acids, etc.
2. Analytes – biological samples e.g., blood, saliva, food samples, etc.
3. Electrolytes – salts, acids or bases in aqueous format room temperature acts as electrolytes.
4. Transducers – to integrate these biochemical materials.
5. Computer software – to detect and process the converted output electrical signal
6. Electrodes – provide surfaces for the chemical reactions to occur. An electrochemical bio sensor's sensing ability majorly depends upon the material and dimensions of the electrodes used.

Electrodes are used at three different places in the mechanism : (a) as a reference electrode (Ag/AgCl) to maintain the desired potential and is kept near the reaction site. (b) as a working/redox electrode that acts as the transducer and (c) as an auxiliary electrode to connect the working electrode to the analytic solution. Generally, depending on the requirement of analyte solution, metals like gold, platinum, carbon and silicon are used as electrodes as they possess properties like conductivity and stability.

6.2.1 Working of Electrochemical-bio Sensors

The above components follow the following process for the working of the electrochemical sensors:

Step 1: First, selective binding of the bioreceptor and the analyte takes place. Only the target analyte attaches to the surface of the bioreceptor layer.

Step 2: A specific biological event occurs at the interface and an intermediate signal is formed which is then measured in an electrochemical transducer, amplified and converted in the form of an electronic signal.

Step 3: The amplified output signal is fed into a detecting device like a computer.

Step 4: The computer software converts the electronic signal into a readable notation that is interpreted easily.

Step 5: This is then presented through the user interface to the operator.

This is the complete working mechanism of an electrochemical biosensor as depicted in Fig. 6.2 below:

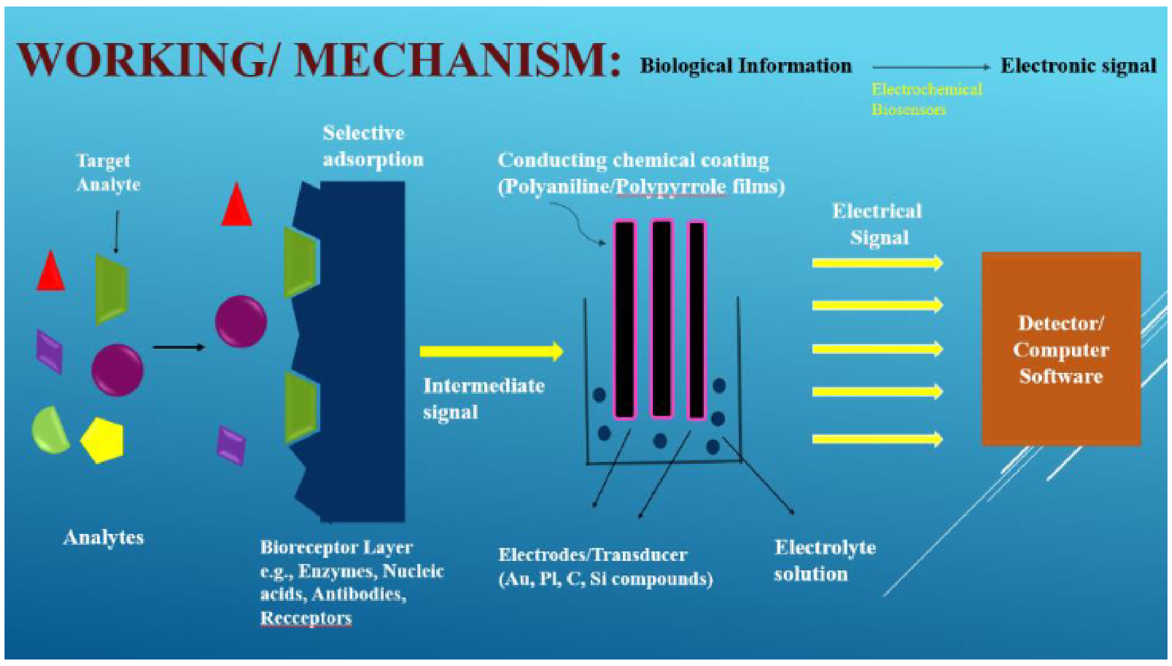


Fig. 6.2: Working of the electrochemical-bio sensor

6.2.2 Advantages of Electrochemical Biosensors:

- They are small and compact in size and mechanically robust.
- These are simple and cheap electronic gadgets are used for their production.
- They have a user-friendly interface.
- They are easy in operating and have conventional processing.
- They have a very good resolution.
- They have negligible external heating.
- They have very low power requirements.

6.2.3 Disadvantages of Electrochemical Biosensors:

- They have a very narrow temperature range.
- They have a short shelf life.

6.3 CONDUCTOMETRIC GAS SENSING

㊱Chemiresistor is a material whose internal resistance is modulated by the change in chemical composition in its surroundings. Here, the carrier concentration at the surface changes on the interaction between material and analyte. The sensing material acts as a bridge covering the fine gap between electrodes as shown in fig. 6.3. and it controls the conductance. It is generally made up of metal oxide and is thus also known as a (63)metal oxide gas sensor. The metal oxide gas sensors have many

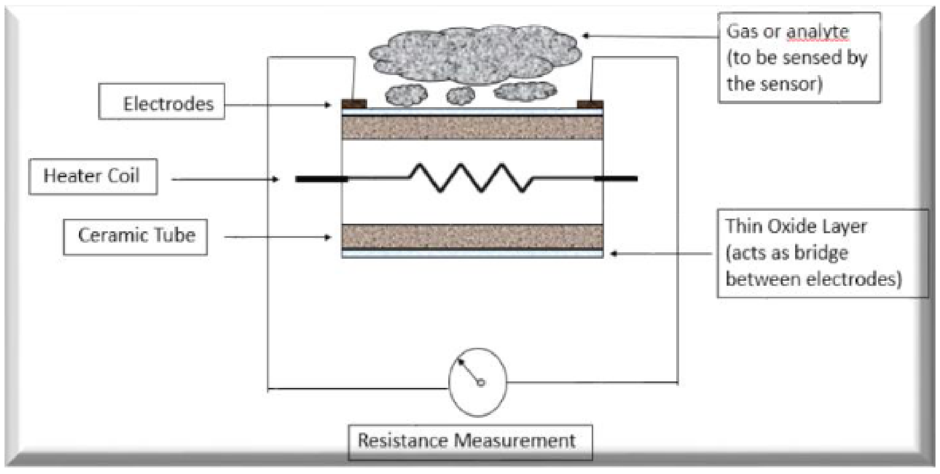


Fig. 6.3 Principle of Conductometric gas sensing

advantages over other sensors. They are highly selective, sensitive, compact in size and their fabrication is quite simple. A simple dc circuit can be used as a resistance measuring device. It can also be a simple Op-Amp circuit that is used as a voltage-current converter.

Initially, ⑤ a film of metal oxide is deposited on a substrate, often silica, by any of the myriad techniques present. It can be done either by any of the physical methods like evaporation, sputtering, etc. or chemical methods like sol-gel method, solvothermal method, etc. The substrate should be heat stable and electrical insulator. There are two physical interactions in the process of gas sensing, the gas-solid interaction which ㊺ changes the physical properties of the surface, and transduction which modifies the resistance.

The material is heated in the presence of ambient oxygen and the molecules are adsorbed at the surface and active oxygen species are formed like O^{2-}, O^{-}, etc. This results in the trapping of electrons by the molecules and thus forming a potential barrier.

It is heated till saturation. The temperature is required to overcome the activation energy and change the resistivity. Some apparatus include microheaters to improve the sensing response.

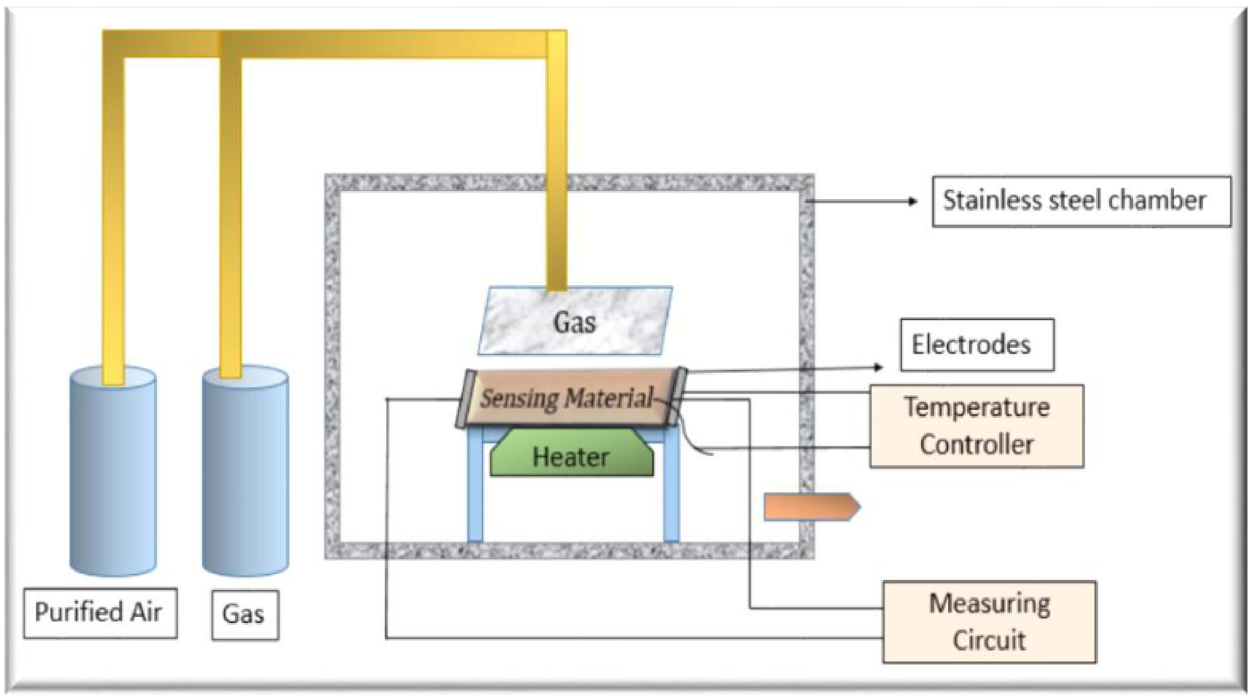


Fig. 6.4 Schematic Diagram of Conductometric gas sensing

When it is placed in a gaseous environment to detect or sense as shown in Fig. 6.4, it interacts with the gas present there and its molecules are adsorbed at the surface. These molecules form a bond [6] with the adsorbed oxygen molecules and the trapped electrons are made free. This decreases the potential barrier and the carrier concentration increases resulting in reduced resistance. The change in resistance is measured which gives an idea of the presence of the analyte and its concentration.

Oxidizing and reducing gases, both can be detected using these sensors. The difference is that in the presence of oxidizing gases, electron depletion is increased in the presence of the analyte, which increases the resistance instead of reducing it. [53] In the presence of reducing gases, the resistance of the material [40] decreases with an increase in the concentration of the analyte.

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LIST OF PUBLICATIONS

(in series of work written in thesis and not in the order of dates of acceptances)

1. Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials.

Author's Names (in sequence as per research paper): Anukool Yadav, Shreya, Nitin K. Puri

Name of Conference: 6th International Conference on Advanced Production and Industrial Engineering (ICAPIE) – 2021

Conference Index: Scopus

Status of Paper: Accepted in Conference

Date of Communication: 25th April, 2021

Date of Acceptance: 13th May, 2021

Date of Conference: 18-19 June, 2021

Date of Publication: October, 2021

2. Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage

Status of Paper: Accepted in Conference

Author's Names (in sequence as per research paper): Shreya, Anukool Yadav, Ritika Khatri, Nikita Jain, Anurag Bhandari, Nitin K. Puri

Name of Conference: 6th International Conference on Advanced Production and Industrial Engineering (ICAPIE)- 2021

Conference Index: Scopus

Status of Paper: Accepted in Conference

Date of Communication: 15th March, 2021

Date of Acceptance: 12th May, 2021

Date of Conference: 18-19 June, 2021

Date of Publication: October, 2021

ACCEPTANCE PROOFS

Paper 1: Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials.

Certificate

Dear Author(s): Anukool Yadav, Shreya and Nitin K. Puri

Paper ID: 395

Paper Title: Preliminary Observations of Synthesized WS2 and Various Synthesis Techniques for Preparation of Nanomaterials.

This is to enlighten you that the above manuscript has been appraised by the editors of LNME and is accepted for the **6th International Conference on Advanced Production and Industrial Engineering (ICAPIE)- 2021 to be held during June 18-19, 2021**. The paper is recommended for publication in **Lecture Notes in Mechanical Engineering (Scopus Indexed publication of Springer Nature), ISSN: 2195-4356**. The manuscript has been submitted to Springer in May 2021 and will be online during October 2021.

Finally, the team of CAPIER DTU and ICAPIE-2021 would like to extend congratulations to you.

Prof. Ranganath M Singari
(Conference Chair, ICAPIE-2021)

Dr. Harish Kumar
(Convener, ICAPIE-2021)

Paper 2: Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage

Certificate

Dear Author(s): Shreya, Anukool Yadav, Ritika Khatri, Nikita Jain, Anurag Bhandari and Nitin K. Puri

Paper ID: 168

Paper Title: Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage

This is to enlighten you that the above manuscript has been appraised by the editors of LNME and is accepted for the **6th International Conference on Advanced Production and Industrial Engineering (ICAPIE)- 2021 to be held during June 18-19, 2021**. The paper is recommended for publication in **Lecture Notes in Mechanical Engineering (Scopus Indexed publication of Springer Nature), ISSN: 2195-4356**. The manuscript has been submitted to Springer in May 2021 and will be online during October 2021.

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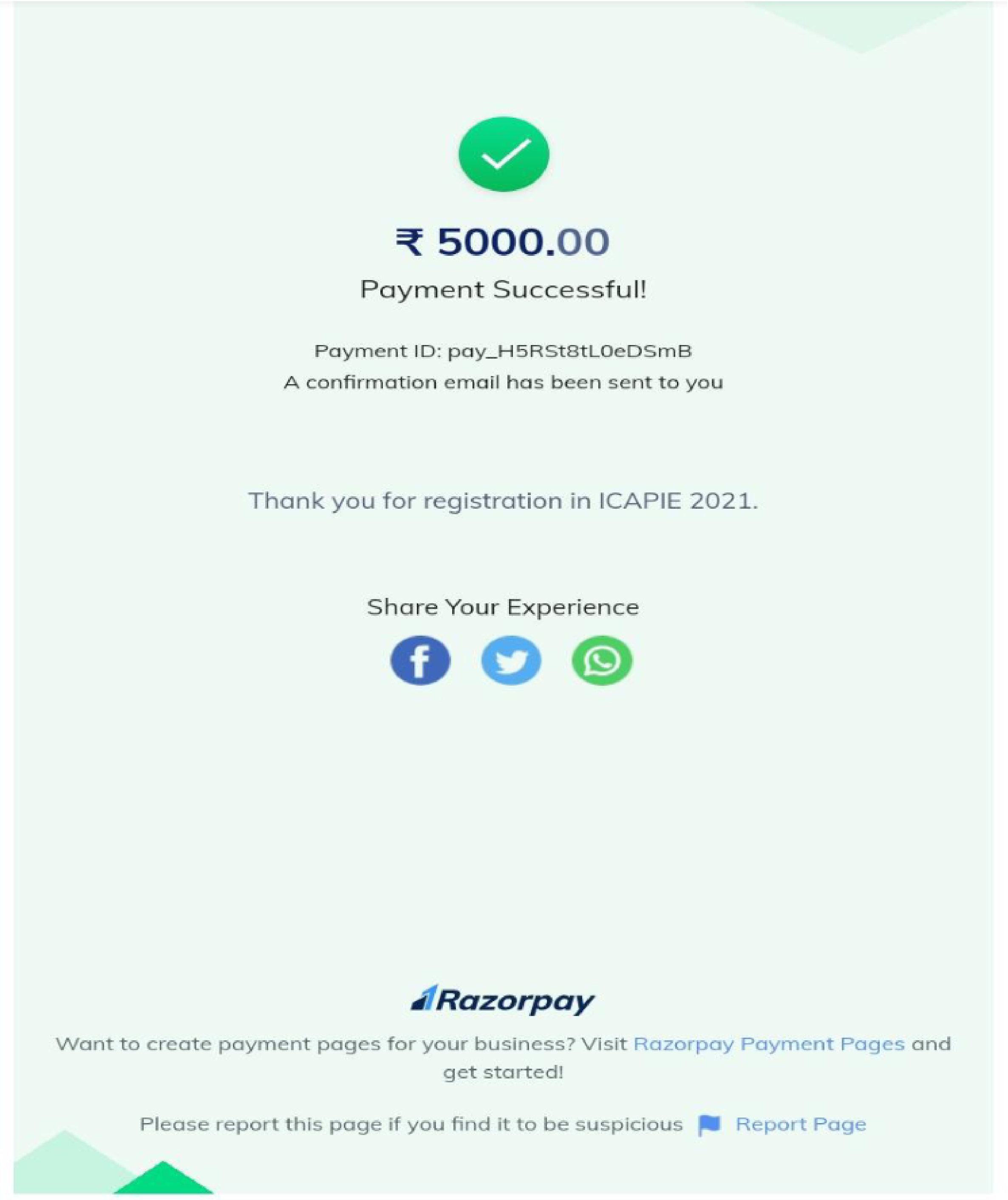
REGISTRATION PROOFS

Paper 1 : Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials.



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PLAGIARISM REPORT OF THESIS

Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage

Shreya[1,†], Anukool Yadav[1,†], Ritika Khatri[1], Nikita Jain[1], Anurag Bhandari[1] and Nitin K. Puri[1,*]

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Abstract. The present work is regarding the study of Double Zone Thermal Chemical Vapor Deposition (CVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD) systems. Here, we have tried to describe the principle, working and technical details as well as the advantages and disadvantages associated with the above mentioned systems. Both the deposition variants i.e., Double Zone Thermal CVD and PECVD offers a wide range of advantages like the uniformity of thin films along with easy accessibility over a wide range of precursors for nanomaterial synthesis. It is also concluded that the former system has an edge over other existing conventional deposition techniques as we can control the migration of the source particles whereas PECVD offers the advantage of performing the deposition of thin films over comparatively low temperature which allows the usage of the substrate having a low melting point.

Keywords: Thin films, Chemical Vapor Deposition, Double Zone Thermal CVD, PECVD.

1 Introduction

In the twentieth century, revolutionary advancements were going on in the electronics industry. Silicon (Si) was replacing Germanium (Ge) to be used as a basic semiconductor material for all device fabrications due to its remarkable properties like large bandgap and ease in forming the oxide layer on the surface [1], [2]. Soon, the basic requirements of n-, p- doped Si for Si integrated circuit technology was at peak heights to meet the ever-increasing demand for personal computers [3]. It was in the year 1960 that Theurer successfully fabricated good quality Si films which attracted the attention of various industries towards the manufacturing of silicon semiconductor devices [4]. These advancements have created a tremendous urge for highly pure ultra-thin films in the scientific world.

Though various methods like Electroplating [5], Spin coating [6] Vacuum evaporation [7], Sputtering [8] and others have been explored at times to meet the early re-

† These authors have contributed equally.

quirements of film deposition/coatings, many drawbacks and complications like deposition of multiple films, coating of large surface area, and conformal coverage have been observed with them [9]. This search takes us to the Chemical Vapor Deposition technique which was at an early stage at that time. Since the late 1960’s, its usage has gained momentum due to various advantages that it offers and it has emerged as the leading candidate for good quality thin film deposition [10]. It involves the deposition of one or more stable solid films on a heated substrate by a suitable chemical reaction at the surface of the substrate [11].

1.1 Double Zone Thermal CVD

Double Zone Thermal CVD technique is a versatile, non-line of sight deposition technique by which uniform thin films can be deposited at a reasonable processing cost. Highly dense and pure materials can be obtained by this method. Though this method is a little complex, uniform and conformal deposition of films is possible with good reproducibility which is the biggest advantage [12]–[14]. Since the inception of novel CVD, its market has skyrocketed. The films deposited by CVD technique have found their applications in numerous fields like the communication industry, optoelectronics industry, synthesis of high-temperature superconductors, coatings, and many interdisciplinary fields [15]–[17]. One of the key reasons for the popularity of this technique comes from the fact that a variety of materials can be used as precursors in this method. Some of them are metals, metal hydrides, halides, halo-hydrides and metalorganic compounds and many more [18]–[22].

1.2 PECVD

PECVD is one of the numerous variants of CVD used to deposit thin films. Like Double Zone Thermal CVD, it is also a non-line of sight technique which involves a chemical reaction at a low temperature activated by a high-energy plasma stream. The stream is produced using electrical energy which later transfers the energy of its species to the precursors. This initiates the homogeneous reaction to produce free radicals or active ions followed by radical polymerization resulting in the deposition of thin films. It is a widely used technique to fabricate various thin nano-films and modify their properties for diverse applications [29].

1.3 Variants of CVD

Various variants of CVD including Thermal Chemical Vapor Deposition, Plasma Enhanced Chemical Vapor Deposition (PECVD), Metal-Organic Chemical Vapor Deposition (MOCVD) and Atomic Layer Chemical Vapor Deposition (ALCVD) have been introduced at times [23]–[26]. Every variant has some advantages as well as disadvantages over others. Thermal CVD can be considered more of kind of a growth process rather than a deposition process in which the chemical reaction takes place at the surface of the substrate. In thermal CVD, the reaction is initiated by thermal energy provided by various means while in PECVD, the electrical energy is used to initiate homogeneous reactions for production of chemically active ions and radicals that can participate in heterogeneous reaction. CVD variants can also be differentiated based on zones. (a) Single zone CVD (b) Multiple zone CVD (two or more zones).

Looking at their significant advantages and future scopes, the Double Zone Thermal CVD System and PECVD systems present in the Nanomaterials Research Laboratory (NRL), Department of Applied Physics of Delhi Technological University (DTU), Delhi have been studied. Here, in this report, we present the detailed role of their various components, technical specifications and working with labelled diagrams, schematics and relevant flowcharts.

2 Instrumentation of Double Zone Thermal CVD and PECVD

The impetus provided to the phenomenal usage of thermal CVD in diverse areas is due to ease in its installation and simple fabrication process. The most basic requirements for a CVD system are: a gas supplier with a flow controller, some heating mechanism, a reactor chamber and a temperature controller. In the Double Zone Thermal CVD system in NRL, DTU, Delhi (shown in Fig. 1.), there are two independent heating zones with a 31.4-inch chamber size made up of quartz tube that can operate up to 1000℃ which makes it a high-temperature CVD [29]. On one side of the quartz tube, a gauge meter is attached to observe the pressure inside it. It can show the pressure in the range 0 to 1838 mm Hg on the positive side and 0 to -760 mm Hg on the negative side. On the other side, there is a gas outlet valve and a vacuum valve connected to the vacuum pump used for the suction of air inside the tube and creates the desired level of vacuum. There are two load current meters and temperature programmers for both zones respectively. There are two gas cylinders also, containing inert gases, Nitrogen (N_2) and Argon (Ar) respectively. The one filled with N_2 gas has the capacity of 46.7 liters weighing 51.7 kg and the other one filled with Ar has the same capacity weighing 52.2 kg. Complete technical details are presented in Table 1. As it is a hot wall reactor, the whole quartz tube is heated uniformly with the precursors and the substrate is placed inside it. Fig. 2. shows the PECVD system in NRL, DTU, Delhi. PECVD has three cylinders of gases containing acetylene, hydrogen and argon gas. A chiller and heater are attached to the system for cooling and heating purposes respectively. Vacuum pump is also attached for suction of the air and creating vacuum as per desired conditions.

Table 1. Technical details of Double Zone Thermal CVD system

Technical Parameters	**Values**
Zones	2
Chamber Size	31.4 inch
Maximum Temperature	1000°C
Pressure Range (Positive Side)	0 to 1838 mm Hg
Pressure Range (Negative Side)	0 to -760 mm Hg
Volume (Cylinder filled with N_2)	46.7 litres

Volume (Cylinder filled with Ar)	46.7 litres
Weight (Cylinder filled with N_2)	51.7 kg
Weight (Cylinder filled with Ar)	52.2 kg

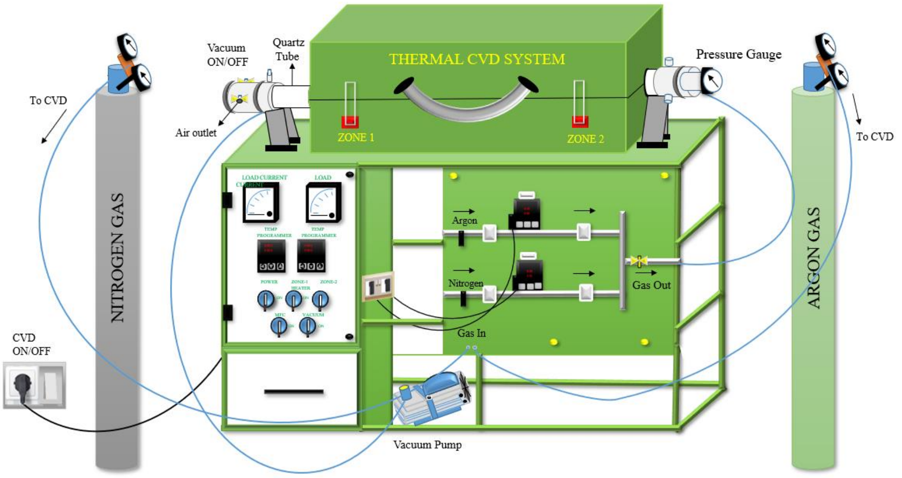


Fig. 1. Labelled diagram of typical laboratory Double Zone Thermal Chemical Vapor Deposition (CVD) at NRL, DTU, Delhi, India.

3 Principle

3.1 Double Zone Thermal CVD

The basic principle of Thermal CVD is described in the flowchart in Fig. 3. Here, volatile precursors are provided thermal energy in the presence of an inert gas that is used as a carrier gas. At appropriate temperature, when precursors are in the vapor state, they get mixed with the molecules of inert gas and undergo a homogenous vapor phase reaction. These precursors diffuse to the substrate surface and the gas molecules get adsorbed on the surface of the substrate. The molecules of precursors heterogeneously react with heated substrate forming a thin solid film. After this, the by-products formed, the adsorbed gas molecules and other unwanted materials are carried out of the reactor by outlet valve with the flow of gas [28]. The principle of Double Zone Thermal CVD is no different from the above principle. Double zone CVD is better to control the evaporation moment of the precursors. Here, the precursors that require different temperatures to evaporate can be placed in different zones. Thus, the precursor-1 with lower evaporation temperature is placed in zone-1. The precursor-2 with a higher evaporation temperature is placed in zone-2. Both the precursors are placed in the center of the respective zones. The substrate is placed downstream at an optimized distance from the precursor-2. Both the precursors and the substrate are placed in boats of appropriate material depending on temperature.

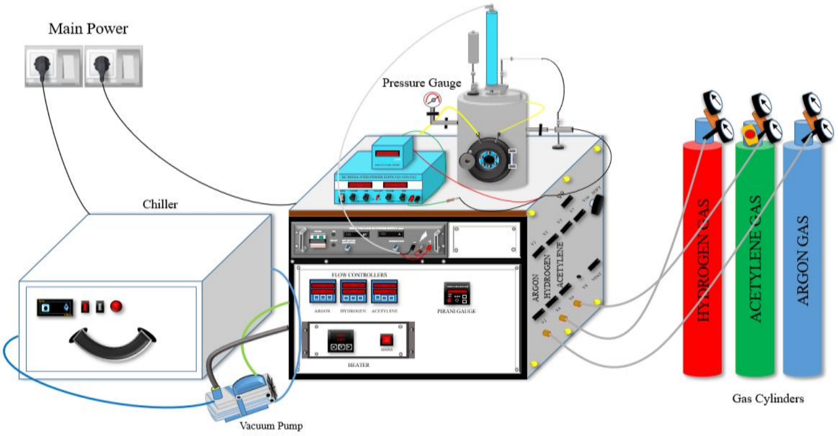


Fig. 2. Labelled diagram of PECVD in NRL, DTU, Delhi, India

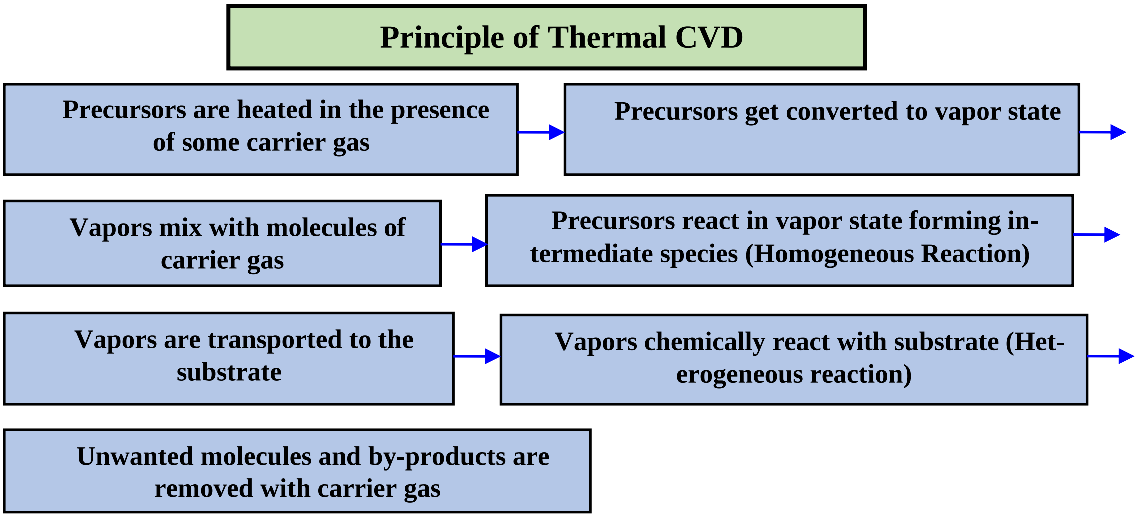
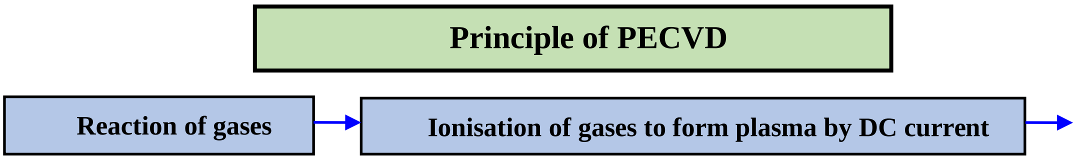


Fig. 3. Principle of Thermal CVD

3.2 PECVD

The basic principle of the PECVD system is described in Fig. 4. The process starts with the reaction of gases followed by ionization of gases to form the plasma state by DC current. It leads to the dissociation of precursor molecules by energetic electrons of plasma to free radicals which results in the particle movement to the substrates. Finally, the radicals are adsorbed onto the substrate and the reactor walls. Thus, the nano-layers are formed in this way.



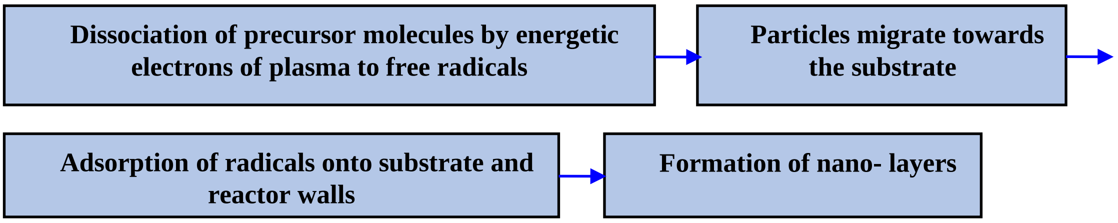


Fig. 4. Principle of PECVD.

4 Working of Double Zone Thermal CVD

The working of the Double Zone Thermal CVD system is shown in Fig. 5. Here, 'A' denotes the flow of inert gas from cylinders through the gas tubes controlled by flow controllers. 'B' denotes the flow of gas into the quartz tube in the direction shown. 'C' & 'E' denotes the heating of volatile precursors by heating elements attached to the CVD. 'D' & 'F' denotes the conversion of precursors from solid form to vapor form. 'G' denotes the diffusion of precursors in the vapor phase to the substrate's surface. 'H' denotes the heterogeneous reaction at substrate's surface and formation of a thin solid film. 'I' denotes the removal of by-products and unwanted materials.

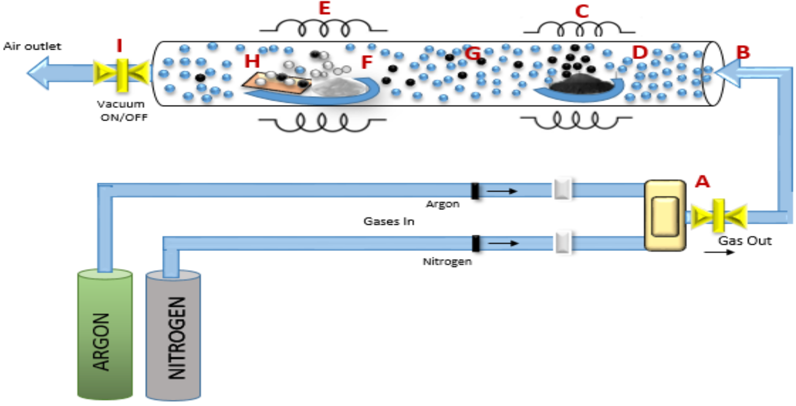
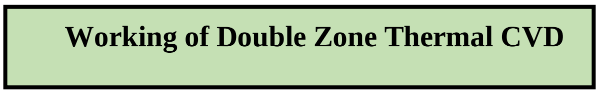


Fig. 5. Schematic diagram of Double Zone Thermal CVD

The complete procedure of depositing the films on the system present in the lab is shown in the Fig. 6. Initially, the precursors have to be placed inside the boats and then the boats are positioned at the centre of the respective zones. In the second zone, at some distance from the precursors downstream, the substrate has to be placed. Then, CVD has to be switched ON by turning the power ON knob present on the system. After that, the vacuum inlet valve has to be opened and the vacuum knob has to be turned ON. Then, the pressure gauge has to be checked which should have been showing the reading of 0.1 mm Hg. After checking that, the mass air-flow controller (MFC) has been switched ON and has to be set as per desired conditions. Then, knobs of gas cylinders have to be turned on to allow the gas to enter CVD.



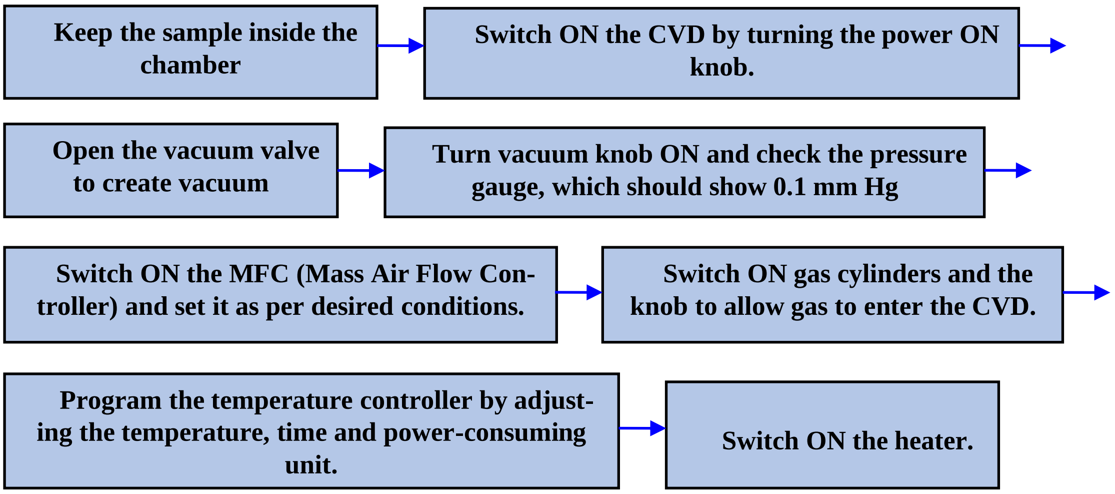


Fig. 6. Flow chart of working of Thermal CVD system at NRL in DTU, Delhi.

After all the initial steps, finally, temperature controllers have to be programmed to set the temperature, time and power-consuming unit of both zones. To run the temperature-controlled program, the ‘Set’ button has to be pressed seven times. After setting the temperature, time and power consumption unit, the up button as shown in Fig. 1. has to be pressed to run the program. After looking for all the initial checkpoints and taking all the precautionary measures, the heater has to be switched on and it starts functioning. The program can be shut off by pressing the “Set” and “Down” buttons simultaneously.

5 Differences between Double Zone Thermal CVD and PECVD system

In conventional CVD, the temperature ranging from 500 to 1000°C is taken to thermally decompose the precursor gases. Whereas, in PECVD, much lower temperatures are considered as the energetic electron gas of plasma can highly dissociate the feed gas. Even when the feed gas and the substrate are near room temperature, the PECVD can deposit films on sensitive substrates that are damaged by high temperature or in the case of semiconductor production where dopant redistribution is an important concern, so high temperatures are not needed here. During the deposition process, the consistent ‘ion bombardment’ of the PECVD film by the plasma may also modify the properties of the film. PECVD technique has some limitations too which are listed here: (a) It requires a sophisticated reactor to contain the plasma. (b) It is difficult to deposit high purity films using PECVD. The reason could be the incomplete desorption of by-products and unreacted precursors at low temperatures. (c) Incorporation of impurities like toxic, explosive gases in the plasma stream which can be detrimental for many applications. (d) High ion energy plasma (< 20eVs) used in PECVD can damage fragile substrates because of ion bombardment. (e) The selection of an appropriate monomer is a challenge. (f) Suitable inlet instruments are needed to be installed separately. (g) Films formed may comprise compressive and residual stresses because of low-frequency requirements in PECVD. (h) If super lattice structures are synthesized using PECVD, it could be time-consuming. (i) Instability against humidity and ageing are two more disadvantages. (j) Costly parts of equipment and machinery that are generally not desirable.

6 Precursor Selection

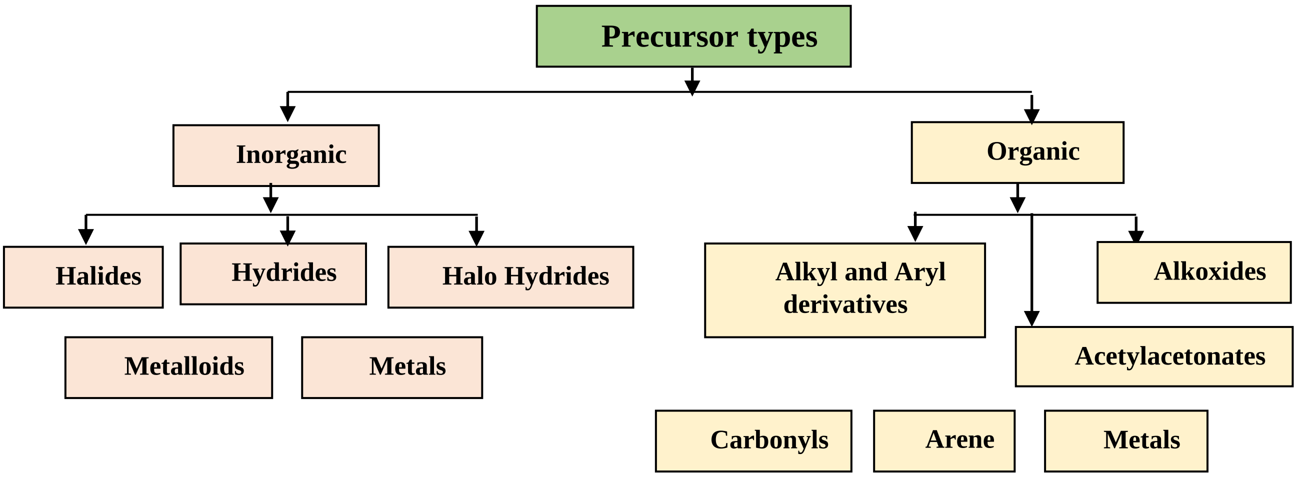


Fig. 7. Classification of Precursors used in CVD

As stated above, one of the key reason for the popularity of CVD is the variety of precursors used in the technique. The precursors can be inorganic compounds like halides, hydrides, halo-hydrides of metals and metalloids. The precursors used can also be organic compounds like alkoxides, acetylacetonates, alkyl, aryl-derivatives of metal, carbonyls, arenes, etc. as is shown in the classification in Fig. 7. Though a large no. of materials can be used as precursor in this technique, some conditions that are applied to the materials to be used as precursor are as follows: (a) At room temperature, the precursor should be stable. (b) It should have a low evaporation temperature such that it has sufficient volatility. (c) Its reaction temperature should be below the melting point of the substrate. (d) It should be available in an adequate amount in pure form at a low cost. (e) It should be non-hazardous. [3], [11], [27]. Above stated conditions are applicable on all the precursors irrespective of the variant of CVD, while some more conditions may vary depending upon the variant of CVD in which they will be used.

7 Precautionary Measures

While operating any device, there are always some safety guidelines that must be followed. Failure in doing so may cause trouble to the user and damage to the instrument. Unlike any other device, while operating a double zone thermal CVD system too, there are some safety precautionary measures that must be followed for the safety of the user and the long life of the CVD system. These are listed here: (a) CVD should not be operated at power consuming unit greater than 60 percent. (b) Heater should be switched ON only after the last step described in the working procedure. It shouldn’t be switched on in between. (c) It should always be ensured that the pressure inside the chamber is 0 psi or 0 mmHg. If it increases, the outlet valve should be opened otherwise the quartz tube may get cracked. Some precautions that need to be followed while operating PECVD system are listed as follows: (a) UPS should always be kept on. (b) After starting rotary pump, user should open SOFT valve first and only after few min of suction ROUGHING valve should be open. (c) V11 valve should be open before injecting gases into process chamber and it should be closed before opening VENT valve. (d) Acetone should be avoided for cleaning purposes, especially for o-rings. Apart from these instrumental precautions, there are some other rules too that should be followed as thumb rule. Especially, while handling hazardous chemicals, extra care needs to be taken to avoid accidents. Some of them are listed here: (a) Good ventilation should be ensured while handling the hazardous chemicals or the instrument. (b) Enough equipment should be arranged for the protection of user’s safety like face shield, glasses for eyes and others. (c) Fire extinguishers should be installed at various places to ensure people’s safety. (d) Arrangement of first aid treatment should have been ensured in case of any emergency [11], [27].

8 Conclusion

CVD technique finds potential applications in the deposition of thin films offering many advantages like conformal coverage and coating over the large surface area. There are numerous variants of CVD including Thermal CVD, PECVD, MOCVD, ALD and others. Two of the variants of CVD i.e., Double Zone Thermal CVD and PECVD were studied and it is concluded that both have their own advantages and disadvantages. However, achieving control over ultimate film properties like thickness and film composition is a challenge in PECVD which is not the case with the thermal CVD system. Furthermore, these systems can be used to synthesize various types of materials ranging from pure-dense materials to thin-nano films for many industries. They find applications in areas like microelectronics (electrical insulation and conductive films, diffusion masks, capacitors, etc.); optoelectronics; protective, decorative, optical coatings (photovoltaics and photonics e.g., notch filters and anti-reflective coatings); synthesis of Transition Metal Dichalcogenides, Carbon films, Graphene-based polymeric nanocomposites, etc.; fabrication of integrated circuits, solar cells, transistors, and some others like food packaging, biosensors, device fabrication and various biomedical applications (immobilization of biomolecules, degradation of biopolymers, etc.).

Acknowledgments

We are indebted to Prof. Yogesh Singh, Vice-chancellor, Delhi Technological University, Delhi, India for providing us the research opportunities. Our sincere gratitude to the companies, Nano Tec, Perungudi, Chennai, Tamil Nadu, India for designing and employing the Double Zone Thermal CVD system and TechnoS Instruments, J-422, RIICO Industrial Area, Sitapur, Jaipur-302022, India, APLab and Crown for assembling the PECVD in NRL lab.

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Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials.

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Abstract. The present work reports various attempts to synthesize WS_2 nanostructures via simple and facile Hydrothermal Method. The preliminary observations and the X-ray Diffraction (XRD) results of nanostructures formed are also discussed here. As the future is more about making things smaller and tinier for various applications, the hunt for better methods is always a hot topic of research. Different approaches are used for the synthesis depending upon the factors like the type of precursors, structure, composition and morphology of the product required, and others. Each technique offers a wide range of advantages and disadvantages, thus, learning about them and their usage in some specific conditions is mandatory in this field. So, here, along with WS_2 synthesis, an attempt to better understand some basic synthesis techniques used for the preparation of nanomaterials has also been made.

Keywords: Hydrothermal, Solvothermal, Sonochemical, Chemical Vapour Deposition (CVD), Sol-gel, Chemical Exfoliation, WS_2

1 Introduction

All the technological advancements of the future that seem impossible right now can indeed become a reality by the discoveries of today. These discoveries in the field of nanotechnology have a very promising future where the arrangement of atoms in the desired way can show some amazing results. There are a large number of pieces of evidence that show how the world’s smallest materials are changing our lives including the nano-machines that defeat the cancer cells, tiny computer chips, a few inches long high definition cameras and others. Synthesis of these nanomaterials is in itself a huge topic of research where the change in a single parameter like temperature can also make a difference in the structure and morphology of the product [1]. There are various synthesis techniques with different working principles that give very different products at specific conditions [2]. The hunt for new tiny gadgets creates a need for new and better synthesis techniques to get products of high purity and controlled dimensions. Initially, it was believed that 2D materials are not stable but after the successful synthesis of graphene as a 2D material, the search for the other 2D materials with enhanced properties like wider band-gap began. We got other potential materials in the form of Transition Metal Dichalcogenides (TMDs) with wonderful electronic and optical properties [3]. Amongst these, MoS_2 and WS_2 have attracted considerable attention because of the peculiar layered structure, an impressive rate of electron transfer and layer-dependent band-gap. Various applications of these materials include solid lubrication, optical devices, gas sensing, and others [4], [5]. The schematic structure of WS_2 is shown in Fig. 1.

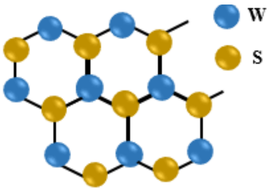
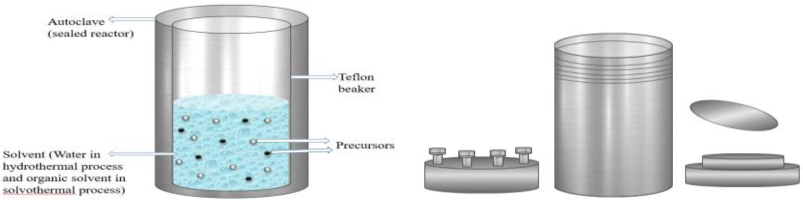


Fig. 1. The schematic layered structure of WS_2

1.1 Hydrothermal and Solvothermal Method

These are two promising inorganic synthesis methods that involve the synthesis via chemical reaction as shown in Fig. 2. (a). These are the green processes as the reaction takes place in a sealed reactor known as Autoclave shown in Fig. 2. (b). The autoclave is generally made up of metal and is employed with Teflon or alloy lining to protect it from highly corrosive solvent. These processes offer numerous advantages over other techniques apart from being the green processes: (a) these are relatively low-cost processes, (b) an environment-friendly process as it takes place inside a sealed reactor, (c) high purity products are formed [6]. In the hydrothermal method, the solvent used is water while the solvothermal process uses aqueous and non-aqueous organic solvents like ethylenediamine, ethanol, diethylenetriamine [7], polyethylene glycol [8], etc. Furthermore, the solvothermal process has some additional advantages over the hydrothermal process: (a) it requires relatively low temperature and pressure, (b) precursors which are sensitive to water can be used in this process, (c) the crystallinity of products formed is very well controlled in this process.



(a) (b)

Fig. 2. (a) A diagrammatical representation of Hydrothermal/Solvothermal synthesis **(b)** A diagrammatical representation of an autoclave in Nanomaterials Research Laboratory (NRL), DTU, India.

1.2 Sonochemical Method

This is a method which neither requires high temperature and pressure nor long reaction times. In this process, the precursors are mixed and put together in solution form and then the sonochemical treatment is given. It involves passing ultrasonic waves through the solution using an ultrasonicator as shown in Fig. 3. In this way, the hotspots are generated which can achieve very high pressure and temperature. The hotspots are the places where the reaction takes place at sufficiently high temperature and pressure conditions and the products are formed [9]. It is a powerful tool for synthesis or modification of nanomaterials where even a little variation in the reaction conditions can lead us to the change in morphologies and compositions of the product formed.

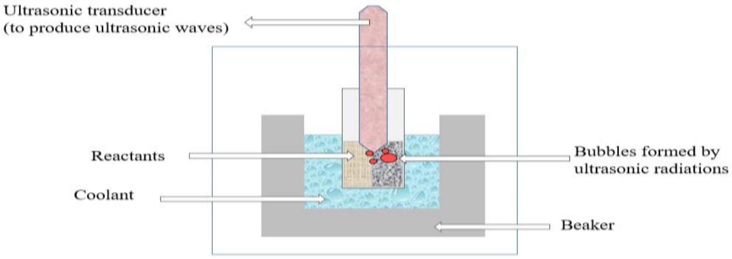


Fig. 3. A diagrammatical representation of the Sonochemical method

1.3 Chemical Vapour Deposition (CVD)

It is a vacuum deposition method that involves a chemical reaction inside a vacuum chamber. It is used for the production of various materials like alloys, carbides, oxides, nanoparticles, etc. Layers of materials are deposited on a solid surface called substrate below atmospheric pressure i.e., vacuum. There are many types of CVD's namely Thermal CVD, Metal-Organic CVD (MOCVD), Plasma Enhanced CVD (PECVD),

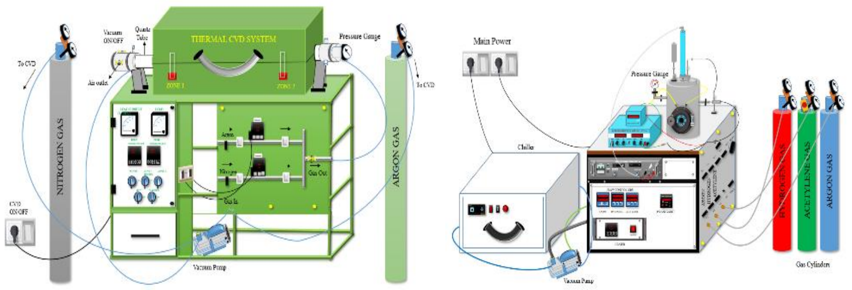


Fig. 4. (a) Labelled diagram of Double Zone Thermal CVD at NRL, DTU, Delhi, India. **(b)** Labelled diagram of PECVD in NRL, DTU, Delhi, India

Atomic Layer CVD (ALCVD), etc. [10], [11]. Among these CVD variants, Double Zone Thermal CVD and PECVD are present in our Lab at DTU whose diagrammatical images are as shown in Fig. 4. (a) and (b) respectively. The technical details and working of the above two instruments are reported in detail in our previous work, *"Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage"*. This bottom-up approach involves the deposition of one or more stable solid films on a substrate at high temperatures by a suitable chemical reaction as shown in Fig. 5.

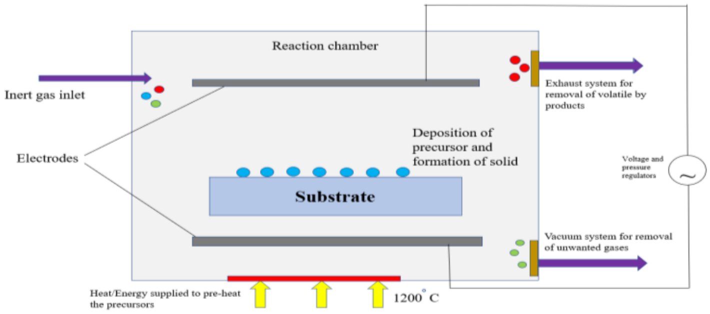


Fig. 5. A diagrammatic representation of the working principle of the CVD process.

1.4 Sol-Gel Method

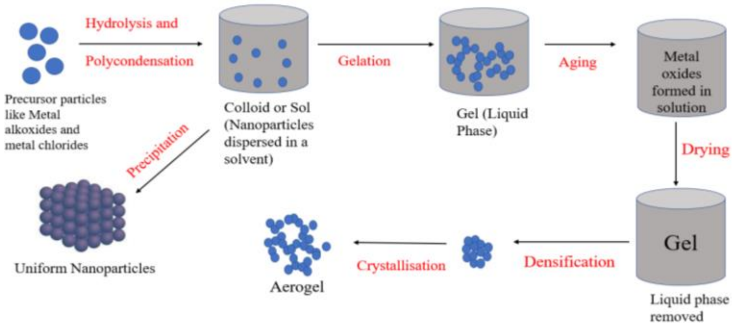


Fig. 6. A diagrammatical representation of the working principle of the Sol-Gel process.

The Sol-Gel method or Chemical Solution Deposition Method is a low-temperature, nanomaterial synthesis process in which solid materials are produced from small molecules. It is a bottom-up approach for material synthesis whose working principle is shown in Fig. 6. The Sol-gel method, as is evident from the name, involves two materials i.e., 'sols' (solid particles suspended in liquid) and 'gels' (porous network of particles having liquid between the pores). First, sols are formed inside a liquid which are then connected after some process to form a network of gels. The liquid then gets evaporated and we are left with the powder or thin-film formation. This method requires less energy consumption leading to less pollution and is generally used to generate highly pure and well-contained ceramic materials [10], [12].

1.5 Chemical Exfoliation Method

It is a top-down nanomaterials synthesis process where the reduction of interlayer forces takes place followed by the formation of intercalated compounds and then exfoliation occurs by rapid heating and sonication. This synthesis mechanism (as shown in Fig. 7.) is mainly done for graphene as the process produces a large amount of graphene at low temperatures [13]. Exfoliation is a phase transition, which takes place when there is a layer to solvent molecule charge transfer and a minimum mixing enthalpy at well-defined elevated temperatures.

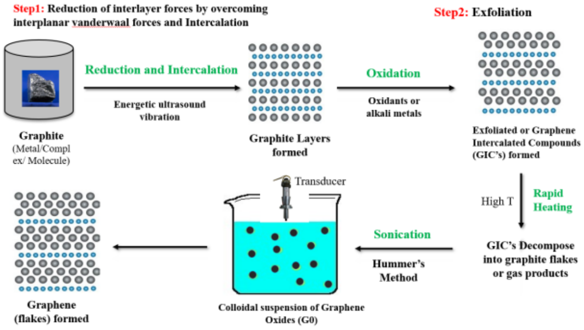


Fig. 7. A diagrammatical representation of the working principle of the Chemical Exfoliation method.

2 Experimental

2.1 Chemicals and Materials

Tungsten Hexa-chloride (WCl_6) and Thioacetamide or TAA (C_2H_5NS) were purchased from Sigma Aldrich. Acetone was purchased from Rankem. Ethanol was purchased from Merck. We have used Milli-Q water, (18.2 MΩ cm) as the solvent during our synthesis. All the chemicals used here had an analytical grading and were taken without any further purifications being done.

2.2 WS_2 Nanostructure Synthesis

WS_2 nanostructures were synthesized via the Hydrothermal method and their phase was checked using XRD characterization. Fig. 8. gives an outline of the hydrothermal process used for WS_2 nanomaterial synthesis in NRL lab, DTU, Delhi, India.

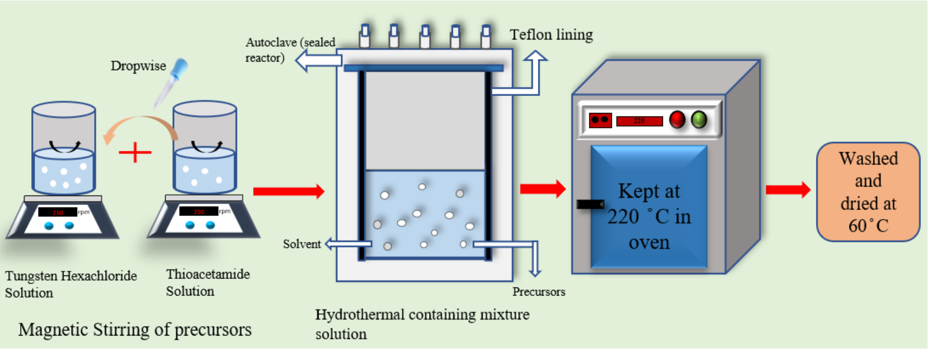


Fig. 8. A diagrammatical representation of the general hydrothermal process used for sample preparation in NRL, DTU, Delhi, India.

We first weighed the salts/precursors i.e., Tungsten Hexa-chloride and TAA, and added them to two different beakers containing water as solvent. Beakers were then kept for magnetic stirring at room temperature (27-30˚C) with varied revolutions per second for 1 hour for mixing of salts in water. Two different approaches were followed for the synthesis of WS_2 nanostructures. In one approach of synthesis, the TAA solution was added dropwise into WCl_6 solution after one hour while in the other approach, the WCl_6 solution was added into TAA solution. After this, the mixed solutions were kept for stirring for 1 hour. The pH of the solutions was regulated and optimized to the values ranging from 6 to 8 which was initially 2 by adding liquor ammonia drop by drop. The solution mixtures were then transferred to Teflon lined autoclaves of different capacities and kept in the oven for 20-24 hours at 220˚C. Then centrifugation and washing of samples was done using De-ionized Water (DI) and ethanol, 3 times with each. Drying of samples was done at 60˚C in an oven for 24 hours. Then the samples were sent for XRD analysis. We tried 5 reaction attempts to synthesize the materials at varied conditions. In the following Table 1. we have summarised all 5 reaction attempts and their physical optimization conditions.

Table 1: Reaction attempts summary for WS_2 synthesis

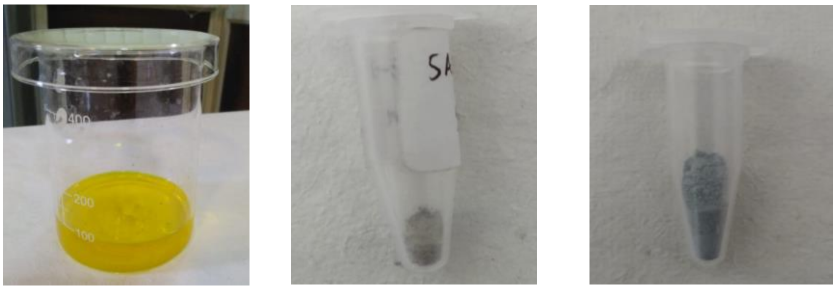
Sample	Precursor name	Amount (g)	DI water (mL)	Stirring conditions	pH
S1 (TAA into WCl_6)	WCl_6	0.522	30	stirred at 250 rpm, 30˚C	Initial: 2 Final: 6
	TAA	0.6	30	stirred until fully dissolved	
	TAA was added into WCl_6 and the mixture was stirred at 350 rpm at 30˚C.				
	Solution mixture kept at 220˚C for 24 hours in a 100 mL Teflon-lined autoclave.				
S2 (WCl_6 into TAA)	WCl_6	0.522	18	stirred at 350 rpm, 27˚C	Initial: 2 Final: 8
	TAA	1.000	17	stirred at 250 rpm, 27˚C	
	WCl_6 was added into TAA and the mixture was stirred at 350 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 24 hours in a 50 mL Teflon-lined autoclave.				
	WCl_6	1.044	18	stirred at 400 rpm, 27˚C	Initial: 2

S3 (TAA into WCl_6	TAA	2.000	17	stirred at 250 rpm, 27˚C	Final: 8
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 24 hours in a 50 mL Teflon-lined autoclave.				
S4 (TAA into WCl_6)	WCl_6	0.632	18	stirred at 400 rpm, 27˚C	Initial: 2 Final: 6
	TAA	1.211	17	stirred at 250 rpm, 27˚C	
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 20 hours in a 50 mL Teflon-lined autoclave.				
S5 (TAA into WCl_6)	WCl_6	1.566	17	stirred at 280 rpm, 27˚C	Initial: 2 Final: 6
	TAA	3.000	18	stirred at 400 rpm, 27˚C	
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27˚C.				
	Solution mixture kept at 220˚C for 20 hours in a 50 mL Teflon-lined autoclave.				

After 24 hours, samples were cooled down to room temperature. Then the samples were collected via centrifugation at 7,000 rpm for 7 min after washing with DI water and ethanol before drying at 60˚C for 24 hours. We then collected the formed samples in Eppendorfs after crushing and named them 'S4'and 'S5' respectively.

3 Results and Discussions

In the first three attempts, no sample was obtained at the bottom of the Teflon as shown in Fig. 9. (a) but in the 4th attempt, as shown in Fig. 9. (b) and 5th attempt, as shown in Fig. 9. (c), an impressive amount of greyish coloured samples were formed. The suspected reason for failures is the manual or incomplete stirring of precursors due to unoptimized conditions. Here, we have included the preliminary XRD results of our 4th and 5th reaction attempts of the synthesis of WS_2 nanomaterial. The phases of the resultant nanomaterials obtained in the last 2 reactions are checked for the confirmation of WS_2 phase as can be interpreted from the preliminary XRD results.



(a) (b) (c)

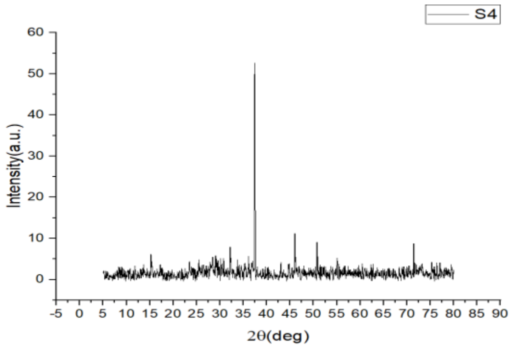
Fig. 9. (a) No sample obtained in first three attempts **(b)** Sample formed in the fourth attempt **(c)** Sample formed in the fifth attempt

3.1 Characterization

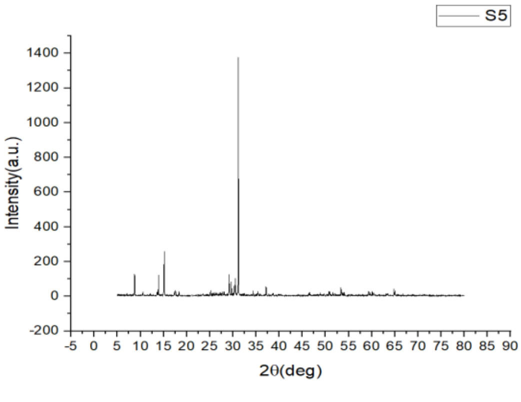
XRD patterns were recorded using Bruker 8D Advance System using CuK{alpha) λ=1.54 Angstrom at 40 kV voltage and 20 mA current with a scan rate of 1° per minute to study the phase of the as-prepared samples. In our results, we present the diffraction patterns as recorded within the 2θ scanning range of -5 to 90 degrees.

3.1.1 XRD

XRD results of the prepared WS_2 sample numbers 4 (S4) and 5 (S5) are as shown in Fig. 10. (a) and Fig. 10. (b). The crystal structure of these samples was interpreted using XRD spectra. In the XRD results of sample 4, diffraction peaks are obtained at 2θ angles of 15.05°, 28.87°, 32.12°, 37.36°, 46.20°, 50.80° and 71.26° whereas, for sample 5, the diffraction peaks are more prominent and are obtained at 2θ angles of 8.81°, 13.80°, 15.29°, 29.00°, 29.63°, 30.63°, 31.12°, 37.23°, 53.43°and 64.89°. The diffraction peaks corresponding to these samples were plotted and labelled and using OriginPro-2021 software.



(a)



(b)

Fig. 10. XRD of **(a)** Sample 4 (S4), **(b)** Sample 4 (S5)

4 Conclusions

There are many Physical and Chemical synthesis techniques for the preparation of nanoparticles namely Hydrothermal, Solvothermal, Sonochemical, CVD, Sol-gel, and Chemical Exfoliation techniques. Some are Top-Down approaches while others are Bottom-Up approaches. Both types of techniques have their advantages and disadvantages offering a variety of options to the users. Different types of nanomaterials like metal oxides, TMDs, etc. can be prepared by these approaches. Here, various attempts of preparation of WS_2 via facile Hydrothermal method are reported with XRD results. In some of the reactions, no sample was formed while in some other attempts greyish coloured powder was obtained after centrifugation and washing. This material can be used for a variety of applications in which solid lubrication is a famous one. The adhesion between Sulfur layers is relatively weak which results in the sliding of layers over each other.

Acknowledgments

We are extremely grateful to Prof. Yogesh Singh, Vice-Chancellor, Delhi Technological University, Delhi, India for providing us the opportunity to work in this enchanting environment and gain experience in the field of research. Two of the authors, Anukool and Shreya also want to thank Mr. Sandeep Mishra for helping us in the characterization of our samples and our senior Ph.D. Scholars, Ms. Ritika Khatri and Mrs. Nikita Jain in the NRL lab, DTU, Delhi who guided and supported us at every possible step.

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