

POLITECNICO DI TORINO

Master's Degree in Electronic Engineering



Master's Degree Thesis

**Optimization of Thin Film Production from Colloidal Nanomaterial Inks
Using Ultrasonic Spray Coating**

By

Muhammad Omair Awan

Mentors: Micaela Pozzati, Mengjiao Wang

Supervisor: Prof. Teresa Gatti

Abstract

2D layered materials are promising in the field of electronics, photovoltaic and sensing applications, and to produce thin films with 2D layered materials is important to integrate the materials into devices. This research is focused on the optimization of thin films produced from colloidal 2D layered material inks using the process technique of ultrasonic coating. Three major objectives of this work are targeted: uniformity, thickness control, and adhesion of the thin film produced. In this regard, several parameters of the ultrasonic spray coating process are varied and their interaction mechanisms on nanomaterials comprehended with experimental approaches coupled with computational analysis. It follows, therefore, that these findings have key implications on the large-scale production of thin-film quality used in technologies for electronic, photovoltaic and sensing applications.

Acknowledgements

I acknowledge with the deepest sense of gratitude the moral support and direction extended to me during the preparation of this master's degree Thesis at Politecnico di Torino.

I am highly indebted to my mentor's, Micaela Pozzati and Mengjiao Wang, who demonstrated professional expertise, patience, and tolerance in directing me throughout the process of this research. Their meaningful considerations and continued support were very effective in making my thesis into shape.

The deepest sense of gratitude goes to my supervisor, Prof. Teresa Gatti, for her excellent guidance, wisdom, and dedication. She had an enormous treasure of knowledge and critical insights, which somehow seeded the core foundation of this research. Always encouraging, her belief in my potential inspired me to do my best.

I also extend my appreciation to Politecnico di Torino for the support and resources that have greatly helped this study. The facilities and the academic atmosphere at Politecnico di Torino helped a lot toward boosting my potential and impregnability towards learning and researching.

The continued support from my family and friends, I thank very much. The understanding of what I was doing and their motivation all along have impelled force into my strength throughout this academic journey.

Finally, I am thankful that the whole of the faculty staff and students in the Electronic Engineering department were positive and involved in an excellent academic, rich environment.

This thesis is dedicated to the people who believed in me and supported me along the way.

Table of Contents

Chapter 1: Introduction	5
1.1 Introduction to Thin Film Technologies	5
1.2 Introduction to 2D Materials	5
1.3 Evolution of Thin Film Deposition	7
1.4 Overview of Spray Coating Techniques for 2D Materials	9
1.5 Significance of the Study	10
1.6 Scope of the Study	10
Chapter 2: Methodology	11
2.1 Material and Substrate Preparation	11
2.2 Spray Coating Method	11
2.3 Characterization Techniques.....	13
2.4 Energy Conversion Analysis	14
Chapter 3: Results and Discussions.....	15
3.1 Effect of Parameters on MoS ₂ Thin Film Quality	16
3.2 Band Gap and Optical Transitions in MoS ₂ Thin Films	18
3.3 Evaluation of Surface Uniformity in MoS ₂	19
3.4 Raman and SEM Analysis of MoS ₂ Thin Films	25
3.5 Effect of Parameters on WS ₂ Thin Film Quality	27
3.6 Band Gap and Optical Transitions in WS ₂ Thin Films	29
3.7 Evaluation of Surface Uniformity in WS ₂	31
3.8 Raman and SEM Analysis of WS ₂ Thin Films	36
3.9 Photoluminescence Spectra of MoS ₂ and WS ₂ Thin Films	37
Chapter 4: Conclusion	39
REFERENCES	41

Chapter 1: Introduction

1.1 Introduction to Thin Film Technologies

Thin films are the backbone of modern technological advancement, with specific, tailored properties forming the core in many electronic, optoelectronic, and energy conversion devices. In general, thin films have much more excellent functionalities compared to their bulk forms, partially due to increased surface area-to-volume ratio, which may enhance optical, electronic, and catalytic properties. However, those classical deposition techniques have limited scopes for attaining uniformity, scalability, and compatibility for a wide range of materials, especially new bidimensional nanomaterials.¹

Traditionally, thin films are deposited by methods like physical vapor deposition (PVD)—thermal evaporation and sputtering—and chemical vapor deposition (CVD). Spin coating, dip coating, and electrodeposition are other methods that are found in research and laboratory-scale work. Though efficient under most conditions, these traditional methods tend to be limited in scalability, material compatibility, and in attaining high uniformity on large surface areas. They are particularly acute in the case of working with new two-dimensional (2D) nanomaterials and solution-based precursor systems, where the formation of uniform films and precise control over morphology are critical.

To overcome these problems, the present study investigates ultrasonic spray coating (USC) as a substitute for the deposition method. USC has high material utilization, easy droplet formation control, and suitability with most nanomaterial inks, rendering it a viable method for scalable production of advanced thin films.

The objectives of this research are to investigate the impact of USC parameters on the morphology, structure, and composition of thin films; identify optimal USC settings to produce uniform, reproducible thin films suitable for photovoltaic and (photo)electrocatalytic applications; and compare the performance and properties of thin films created with USC against those made using traditional deposition methods.

1.2 Introduction to 2D Materials

The 2D materials have brought ultra-thin and layered into the advanced materials science realm. Some prominent examples include graphene, MoS₂, and WS₂, showing unique properties directly related to very high mechanical strength, exceptionally good electrical conductivity, and remarkable thermal properties. These materials have gigantic potential in applications relating to electronics, photonics, catalysis, and energy storage. It means that they can deliver enhanced performance and new functionality compared with conventional bulk materials.²

Two-dimensional (2D) materials have attracted considerable attention owing to their distinct structural and functional characteristics. A particular benefit is their large surface area, which increases reactivity and overall performance for applications like catalysis, sensing, and energy

storage.³ They are also extremely mechanically strong, rendering them durable and highly flexible traits of value for the creation of flexible electronics and other new technologies.⁴ 2D materials further have superior electrical and thermal conductivity, for which they are well-suited for use in next-generation electronics and thermal management systems.^{3,5} Yet several difficulties hamper their wider use. Scalability is also a major issue because large-scale production while ensuring uniform quality of these materials can be challenging.⁶ Further, manufacturing and processing of high purity 2D materials may prove costly, thereby causing cost implications that limit their industrial application.⁷

This research focuses on the utilization of Transition Metal Dichalcogenides (TMDCs), specifically molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), due to their outstanding electrical properties and catalytic activities. TMDCs are layered materials with a general formula MX_2 , where M represents a transition metal (such as molybdenum or tungsten) and X represents a chalcogen (such as sulfur).⁸

In this study, two widely researched transition metal dichalcogenides (TMDs), MoS_2 and WS_2 , were chosen for their favorable optoelectronic and catalytic properties, making them suitable candidates for thin film development in energy-related applications.¹⁰ Their similar structural characteristics, coupled with distinct electronic behaviors, allow for a comparative analysis that highlights the influence of the transition metal on the performance of the resulting thin films.¹¹

MoS_2 belongs to a class of TMDC with the graphite-like layer structure. In one such layer, molybdenum atoms are sandwiched between two layers of sulfur atoms and are arranged hexagonally. This special structure consists in weak van der Waals bonds between layers, which makes it easy for exfoliation into monolayers. The semiconducting properties in the monolayer form are excellent; for example, MoS_2 has a direct bandgap of about 1.8 eV, which makes applications possible in transistors and sensors, or even photovoltaic devices.¹²

WS_2 also demonstrates a similar layer structure. Like MoS_2 , WS_2 can be further exfoliated down to monolayers and show semiconductor properties. However, WS_2 shows a slightly higher direct bandgap value of about 2.1 eV in the monolayer configuration. This higher bandgap makes WS_2 more appropriate for optoelectronic applications involving the higher energies of photons, like light-emitting diodes and lasers.¹³ Apart from these characteristics, WS_2 has a greater spin–orbit coupling and field-effect mobility than MoS_2 , both of which are beneficial for spintronic and high-speed electronics. Conversely, MoS_2 has a high photoluminescence efficiency in the visible range and would thus be preferable in applications such as optical sensing and light emission.

Both MoS_2 and WS_2 were dispersed to create colloidal inks, which were then used in the Ultrasonic Spray Coating (USC) process. Isopropanol was chosen as the solvent due to its ability to effectively disperse TMDC nanoparticles and its compatibility with the USC process. IPA possesses various benefits: it has a comparatively low boiling point of around 82.5 °C, making it suitable for fast evaporation of the solvent during deposition and smooth and uniform thin-film formation. IPA is also less harmful compared to most other organic solvents, has good wetting characteristics on different substrates, and offers adequate volatility to avoid ink pooling or coffee-ring effects upon

drying. The prepared inks were characterized to ensure proper dispersion and stability, which are crucial for achieving uniform and defect-free thin films.¹⁴

By understanding the intrinsic properties of MoS₂ and WS₂, and utilizing high-quality materials, the research aims to develop thin films with optimal performance for advanced technological applications.¹⁵

Impurities in the starting materials can introduce defects into the thin films, adversely affecting their electrical and optical properties.¹⁶ To ensure the highest quality films, MoS₂ and WS₂ were carefully handled and stored in a controlled environment to prevent contamination. Additionally, the dispersion process involved ultrasonic treatment to achieve a homogeneous suspension of nanoparticles in the solvent.¹⁷

1.3 Evolution of Thin Film Deposition

Thin films have always been of prime interest for different technological applications where adjusted properties are vital for the progress of several industries such as electronics, optoelectronics, and energy conversion devices. Traditional techniques for the deposition of thin films, like chemical vapor deposition and physical vapor deposition, remain limited in terms of uniformity, scalability, and compatibility with a wide range of materials.¹⁸ In the last few years, alternative deposition techniques like spray coating, spin coating, and inkjet printing have emerged, potentially holding the promise for solving these challenges due to their advantages of higher material utilization, scalability to large-area substrates, and exact control over the film properties.¹⁹ The following hypotheses are the foundation of the research: it will have immense effects on the morphology, thickness, and uniformity of the thin films produced from MoS₂ and WS₂ colloidal inks by varying the USC parameters; optimized settings for USC will be able to make thin films with improved properties for both photovoltaics and (photo)electrocatalytic applications²⁰; the difference in film quality and performance arising from the varied deposition parameters will be permitted by UV-Vis spectroscopy, Raman spectroscopy, and advanced characterization techniques²¹. The experimental technique will involve the systematic variation of the USC parameters to observe their effect on the properties of thin films²¹ produced with the MoS₂ and WS₂ colloidal inks. All the prepared samples will undergo UV-Vis spectroscopy to ascertain their optical properties and the uniformity of the films. The films will be characterized by using advanced techniques, which include Raman spectroscopy, SEM, and photoluminescence, to investigate their structural, morphological, and functional properties.

This work involves a comprehensive and systematic route to the optimization and evaluation of the process of USC-produced thin films. It includes the preparation of colloidal inks of MoS₂ and WS₂ in water and isopropanol, followed by preliminary experiments designed to establish baseline performance for USC-produced films. Key USC parameters are varied in a systematic manner to analyze their impact on the properties of the resulting films. The assessment of film quality and functionality is carried out through UV-Vis spectroscopy, Raman spectroscopy, and other advanced characterization techniques. By comparing the results with thin films produced by traditional methods, the advantages and limitations of the USC process can be effectively highlighted.

The expected outcomes of this research include the identification of optimum USC parameters to obtain high-quality thin films from MoS₂ and WS₂ colloidal inks, along with a thorough characterization of these films in terms of morphology, structural integrity, and functional properties. Furthermore, the study aims to compare the films produced via USC with those obtained through conventional deposition techniques, highlighting both the benefits and the possible limitations of the USC approach. Finally, this work proposes themes for further research and explores potential industrial applications based on the results, opening up new possibilities for the broader use of USC in thin film production.¹⁸

Thin film deposition techniques have shown continuous searching for scalable and inexpensive processes that could yield highly qualitative films. Among them, great interest has been focused on USC, which allows the deposition of uniform thin films with full control of the thickness and morphology of the films. USC is based on the principle of atomization of liquid precursors into fine aerosol droplets with the aid of ultrasonic energy. These droplets are then propelled toward the substrate, where they deposit, forming a thin, uniform film layer.^{23,24} Ultrasonic spray coating (USC) has vast potential for use where there are complex geometries and colloidal suspension is employed, mostly because of its fine control over properties like thickness, uniformity, and surface topography of films.²⁵

The development of thin film deposition methods has continuously evolved throughout history, driven by the demand for improved film quality, performance, and functionality. Spray coating techniques were initially developed for large coatings.²⁶ Later on, some more precise methods of spray coating, like ultrasonic spray coating, evolved.

Chemical vapor deposition (CVD) is a technique whereby gaseous precursor molecules react to deposit solid materials onto a substrate. It gives very good control of the composition and thickness of the film but may sometimes be limited by uniformity over large areas.^{20,22,23,26} On the other hand, there are the physical vapor deposition (PVD) techniques, such as sputtering and thermal evaporation. In these cases, deposition occurs from a source due to physical procedures, for example, bombardment with ions or atoms. While PVD offers relatively high purity levels and control over thin-film properties.²⁸ In the process of spin coating, a small volume of liquid precursor is deposited onto a substrate that subsequently is spun at desired speeds to spread the material in a uniform thin film. This process is very useful in producing uniform films.²⁹ One of the reasons for the huge attention that has been paid to inkjet printing is because it is capable of depositing patterns of functional materials onto substrates. This technique gives flexibility in material choice and deposition accuracy but may require an optimization route to achieve homogeneous thin films over large areas.³⁰

Such colloidal inks, comprising bi-dimensional materials and dispersed in solvents like water and isopropanol, are promising for several thin film applications. These materials show unique electronic, optical, and catalytic properties due to their crystal structure being made of layers and having a large surface area that makes them suitable for applications such as photovoltaics, electrocatalysis, sensors, and flexible electronics, where thin films could eventually improve device performance and durability.³²

In photovoltaic applications, these tunable-bandgap colloidal nanomaterial inks would be applied in creating thin film solar cells of high photoconversion efficiencies. The unique benefits of USC are in uniform and conformal depositions of active layers, which in turn enhance device performance and stability.³³ Likewise, thin films manufactured from colloidal inks find applications in electrocatalysts for energy conversion and storage devices. Ultrasonic spray coating enables rigorous control of both the composition and morphology of the films, ensuring that catalytic activity and durability are maximized under very aggressive operating conditions.³⁴

One of the promising techniques for the deposition of thin films is ultrasonic spray coating, which enables the preparation of homogeneous coatings with controlled thickness and morphology. To fully harness these advantages, it is essential to carefully optimize the process parameters to ensure reproducibility and suitability for specific applications.

Key parameters in Ultra Spray Coating, such as spray pressure, solution concentration, substrate temperature, and nozzle-to-substrate distance, affect thin film deposition during the process. Having a systematic variation of these parameters is necessary to enhance film quality, adhesion, and functional performance³⁵. Adjusting the spray pressure is essential for controlling droplet size and distribution on the substrate; higher pressures generally produce finer droplets, leading to a more uniform film, while lower pressures may result in larger droplets and potential agglomeration³⁶. The concentration of the colloidal solution affects the film's thickness and uniformity, and an optimal concentration ensures adequate coverage while avoiding issues such as excessive film thickness or sparse deposition³⁷. Maintaining the appropriate substrate temperature is critical for controlling the solvent evaporation rate and ensuring good adhesion of the coating; higher temperatures can enhance solvent evaporation, leading to quicker drying and better adhesion, while lower temperatures might cause incomplete evaporation and poor film quality. Finally, the distance between the nozzle and the substrate influences the droplet impact velocity and spreading; an optimal distance ensures that droplets spread evenly without splashing or bouncing, resulting in a smooth and consistent film³⁶. Systematic variation and optimization of these parameters are necessary to improve film quality, adhesion, and functional performance.

1.4 Overview of Spray Coating Techniques for 2D Materials

Spray coating, specifically using ultrasonic techniques, has gained prominence for its ability to uniformly deposit thin films of 2D materials. This technique allows for precise control over film thickness, composition, and morphology, making it ideal for creating high-quality 2D material coatings. The reviews of spray coating for 2D materials highlight that various spray coating methods, including ultrasonic spray coating and electrostatic spraying, have been employed to deposit 2D materials. Ultrasonic spray coating is noted for its fine mist generation and uniform deposition capability³⁶. Spray-coated 2D materials have been successfully used in electronics, such as flexible transistors; in optoelectronics, including photo detectors; and in energy applications like batteries and supercapacitors³⁵.

1.5 Significance of the Study

This research is significant as it pioneers the optimization of Ultrasonic Spray Coating (USC) to produce high-quality thin films from colloidal nanomaterial inks, a technique that has not been extensively explored before. The insights gained from this research are expected to advance USC as a viable and efficient method for creating thin films, potentially leading to improvements in the performance and efficiency of thin film-based devices across various technological domains. This work not only addresses a novel application but also sets a precedent for future investigations into the application of USC in advanced material processing.

1.6 Scope of the Study

The focus of this study is on the fabrication of USC using colloidal inks of bi-dimensional materials dispersed in non-toxic solvents, primarily water and isopropanol; the use of advanced characterization techniques such as Raman spectroscopy, SEM, UV-Vis spectroscopy, and photoluminescence for detailed analysis of the structure and morphology of thin films; and the evaluation of the potential of optimized thin films for efficient and durable photovoltaic and photocatalytic (photo)electrocatalytic applications.

Chapter 2: Methodology

2.1 Material and Substrate Preparation

Submerge the FTO (Fluorine-doped Tin Oxide) substrates in a Milli-Q water-free beaker that has been cleaned of contaminants with a little soap. Place the beaker into an ultrasonic bath for 20 minutes to remove surface impurities.

After this, transfer the substrates to a new clean jar containing isopropanol (IPA) and ultrasonicate for 20 minutes additional to remove organic residues. Dry substrates use clean air or a gentle flow of nitrogen.

Lastly, transfer substrates to a new clean jar containing acetone and ultrasonicate as before for 20 minutes. Carefully dry with clean air or nitrogen. Handle using clean gloves or tweezers to prevent recontamination.

The FTO substrates are now ready for further processing. Starting with the MoS₂ solution. Using the micropipette, we measure an equal volume of MoS₂ and isopropanol. For instance, if preparing 1 mL of solution, measure out 0.5 mL of MoS₂ and 0.5 mL of isopropanol. Place the MoS₂ into a clean container designed to handle chemical solutions, such as a vial or small bottle. Then, measure and add the isopropanol to the container with the MoS₂. Ensure that the isopropanol is added slowly and steadily to allow for proper mixing and to avoid any potential splashing or spillage. Once both components are in the container, gently swirl or mix the solution to ensure that the MoS₂ is fully dissolved or suspended in the isopropanol. The MoS₂ and isopropanol solution should now be homogeneous and ready for use in subsequent applications or experiments. Next, proceed with the WS₂ solution following a similar procedure as MoS₂.

Both solutions—MoS₂ and WS₂—prepared at a 1:1 ratio with isopropanol, should be handled with care.

2.2 Spray Coating Method

The spray coating method employed in this research is an essential technique for the deposition of thin films of TMDCs onto substrates. This process, specifically Ultrasonic Spray Coating (USC), involves several critical parameters and steps to ensure the uniformity and quality of the deposited films.

The USC process begins with the preparation of colloidal inks containing the TMDCs, which are atomized using an ultrasonic nozzle. This nozzle generates high-frequency vibrations that break the liquid ink into fine droplets, which are then sprayed onto the substrate. The primary goal is to achieve a uniform distribution of these droplets across the substrate surface, forming a thin film of the desired thickness and quality.



Figure 1: Spray Coater

Key parameters of the USC process include spray pressure, nozzle-to-substrate distance, and deposition time. At lower pressures, larger droplets are formed, leading to uneven film thickness, while higher pressures produce finer droplets that contribute to a more uniform film.

The deposition process involves multiple runs with a time gap of approximately 30/60 seconds between each run. This allows the solvent to evaporate, reducing the risk of film defects and ensuring that each layer adheres properly to the substrate. During the process, the substrate is moved or rotated to ensure even coverage. The USC method is monitored and controlled through specialized software that manages the ultrasonic nozzle's operation and the

substrate's movement. This software allows for precise adjustments to the coating parameters, ensuring reproducibility and consistency in film production.

Reflectance Spectrum Measurement

After performing the spray coating, our next step was to measure the reflectance spectrum of the thin films using the **Jasco V-770 spectrophotometer** [Fig 2]. We began by turning on the spectrophotometer and allowing it to warm up for about 15-30 minutes to ensure stable operation. Once the instrument was ready,



Figure 2: Jasco V-770 spectrophotometer

We first measured the reflectance of a reference standard (BASELINE), set the wavelength range in the software from 300 nm to 700 nm, and recorded the baseline reflectance of the standard. This baseline was crucial for comparing and accurately assessing the reflectance of our thin film samples.

Next, we replaced the reference standard with our thin film sample. We carefully aligned the sample to ensure it was flat and properly positioned in the holder. After

closing the sample compartment to eliminate any external light interference, we initiated the measurement process through the software. The spectrophotometer scanned through the selected wavelength range, capturing the amount of light reflected at each wavelength by the thin film.

Finally, we reviewed the reflectance spectrum displayed by the software, which provided a detailed view of the intensity of light reflected at different wavelengths. This data revealed important optical properties of the thin film, such as its colour and thickness.

2.3 Characterization Techniques

The characterization techniques employed in this research are essential for a comprehensive understanding of the properties and performance of the thin films produced through Ultrasonic Spray Coating (USC). These methods provide crucial insights into the films' structural, morphological, and optical characteristics, which are vital for their applications in photovoltaic and (photo)electrocatalytic technologies.

SEM Scanning Electron Microscopy (SEM) is a surface-imaging method based on scanning with a focused beam of electrons across the surface of a specimen. As these electrons interact with the surface atoms, they produce signals—like secondary electrons and backscattered electrons—that are detected to create high-resolution images. SEM offers very precise information regarding the topography and morphology of the surface of the sample. The morphology of the samples was examined using field emission scanning electron microscopy (FESEM) with a Zeiss Merlin equipped with a Gemini-II column.

Raman Spectroscopy provides a non-destructive method for analyzing the vibrational modes of the materials within thin films. This technique is particularly useful for studying the crystalline structure of the Transition Metal Dichalcogenides (TMDCs) such as MoS₂ and WS₂. Raman spectroscopy can differentiate between different phases of the materials and detect any structural defects or distortions in the crystal lattice. The intensity and position of the Raman peaks are indicative of the material's quality, phase purity, and presence of defects. For example, shifts in the peak positions or changes in peak intensities can indicate strain, doping, or variations in crystal quality. Raman spectroscopy also helps in understanding the electronic properties of the materials by providing insights into their phonon modes and electronic band structure.⁴¹

A Renishaw InVia Raman microscope was employed to collect Raman spectra of the samples in backscattering configuration, using a 5x objective, a 514.5 nm excitation wavelength, and a 0.5 mW laser power. The RT Raman spectra were obtained averaging several spectra acquired in different regions of each sample, each one collected with a total exposure time of 225 s.

Photoluminescence (PL) is used to probe the electronic structure and optical properties of thin films. This technique involves exciting the film with light and measuring the emitted luminescence to gain insights into the material's electronic states and recombination processes. PL spectra provide information about the bandgap energy, defect states, and carrier recombination dynamics within the film. The intensity and wavelength of the emitted light can reveal details about the film's quality, such as the presence of non-radiative recombination centers or the efficiency of charge carrier transport. PL is particularly useful for assessing the performance of films in optoelectronic applications, where the efficiency of light emission and charge carrier dynamics play a critical role.⁴²

These characterization techniques collectively offer a thorough evaluation of the thin films produced by the USC process. By providing detailed information on surface morphology, structural integrity, optical properties, and spatial uniformity, these methods ensure that the films meet the required specifications for their intended applications. Each technique contributes

valuable data that helps in optimizing the deposition process and improving the performance of the films in various technological applications. In this work, PL spectra were measured using the Jasco V-770 spectrophotometer in the wavelength range of 340–650 nm. The excitation was performed using the instrument's internal broadband light source, and the measurements were carried out under steady-state conditions.

2.4 Energy Conversion Analysis

Energy conversion analysis involves evaluating how effectively thin films convert energy from one form to another, which is essential for applications in photovoltaic and electrocatalytic technologies. The analysis begins with understanding the efficiency of energy conversion mechanisms within the films, focusing particularly on their bandgap properties and overall performance in practical device applications.

The bandgap of a material is a fundamental property that dictates its ability to absorb and convert light into electrical energy. The bandgap of the nano-colloids was calculated using the Tauc plot equation (Equation (1)):

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

where α is the absorption coefficient, h is the Planck constant, ν is the frequency, E_g is the bandgap energy, and n is 2.⁴³ Thin films' bandgap is typically determined using UV-Vis's spectroscopy. By analyzing the absorption spectra, we calculate the bandgap energy of the material using methods such as the Tauc plot.

Chapter 3: Results and Discussions

This chapter presents the results of the experimental work carried out on Molybdenum Disulfide (MoS_2) and Tungsten Disulfide (WS_2) thin films. The focus is on understanding how various deposition parameters influence the material properties, with an emphasis on UV-Vis spectroscopy, Raman spectroscopy, and heatmap analysis. These results are crucial for optimizing the performance and applications of MoS_2 and WS_2 in various technological fields.

The importance of deposition parameters cannot be overstated. Temperature plays a significant role in enhancing the crystallinity and optical properties of the film. However, excessive temperatures or prolonged exposure can lead to degradation and reduced quality. Adequate volume is crucial for ensuring sufficient material deposition, resulting in a uniform film. There is an optimal range for volume, as deviations can negatively impact film quality. Additionally, deposition time affects particle interaction and film formation. Optimal deposition time is essential; too short may not allow sufficient film development, while too long can cause degradation.

Spray coating is a versatile technique employed to deposit thin films of different materials onto substrates. The quality and uniformity of MoS_2 and WS_2 thin films are significantly influenced by several parameters, including temperature, layer number, and spray duration.

Temperature is a critical factor in the deposition process, impacting film formation and crystallinity. A comparison between samples processed at 150°C and 200°C shows that higher temperatures generally enhance film formation and crystallinity. For instance, the sample processed at 200°C (200C_50L_30S) exhibits higher absorbance compared to the sample processed at 150°C (150C_50L_30S). This increase in absorbance suggests that elevated temperatures contribute to improved film quality and enhanced structural properties.

The number of layers directly influences the thickness and optical properties of thin films. A comparison between samples with 20 layers and 50 layers shows that samples with a higher number of layers often exhibit distinct absorbance features. For example, the sample 200C_50L_30S shows increased absorbance compared to 150C_20L_30S. This indicates that thicker films or higher concentrations of nanomaterials enhance the film's optical properties and overall performance. In a direct comparison between the sample 200C_50L_30S and 150C_20L_30S, the thicker film (200C_50L_30S) exhibits higher absorbance, suggesting that increasing the number of layers improves the film's optical and structural quality.

Spray duration affects the uniformity and thickness of the deposited film. A comparison between samples with spray durations of 30 seconds and 60 seconds shows that longer spray durations generally lead to higher absorbance, as evidenced by the increased absorbance in the sample 200C_20L_60S compared to 150C_20L_30S. This implies that extended spray durations contribute to thicker and more uniform films, enhancing the film's optical and physical properties. In a direct comparison between the sample 200C_20L_60S and 150C_20L_30S, the longer spray

duration results in greater absorbance, indicating better film uniformity and improved material quality.

We conducted a series of experiments on six thin film samples by spraying MoS₂ (Molybdenum disulfide) onto substrates. For each sample we varied critical parameters such as deposition temperature, duration of spraying, and the number of layers applied. The aim was to systematically investigate how these variables influence the optical and structural properties of thin films.

3.1 Effect of Parameters on MoS₂ Thin Film Quality

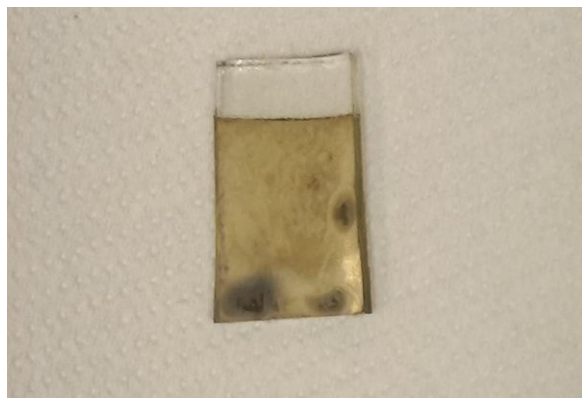


Figure 3a: MoS₂ film after ultrasonic spray coating (150 °C, 20L, 30S)

The sample **150C_20L_30S (1.64 eV)** [Fig 3a] was processed under the conditions of a temperature of 150°C, a volume of 20L, and a time of 30S. This sample demonstrates a moderate Tauc plot value. The moderate temperature combined with low volume and short deposition time results in a film with decent optical properties. The film quality is reasonable, but further optimization may be required to improve optical performance.



Figure 3b: MoS₂ film after ultrasonic spray coating (200 °C, 20L, 60S)

The sample **200C_20L_60S (1.65 eV)** [Fig 3b] was processed under the conditions of a temperature of 200°C, a volume of 20L, and a time of 60S. This sample shows a slightly higher Tauc plot value. The higher temperature and extended deposition time likely improve the film's crystallinity and uniformity, enhancing the optical properties. This suggests that increasing temperature and deposition time can lead to better film quality.

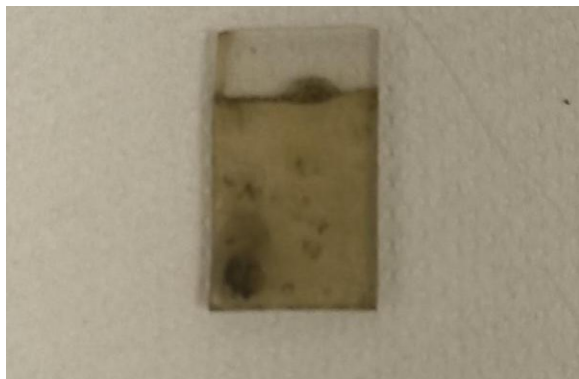


Figure 3c: MoS₂ film after ultrasonic spray coating (150 °C, 20L, 60S)

The sample **150C_20L_60S (1.63 eV)** [Fig 3c] was processed under the conditions of a temperature of 150°C, a volume of 20L, and a time of 60S. The Tauc plot value is lower compared to the 200°C samples. The extended deposition time at a moderate temperature might have caused some degradation or non-uniformity in the film, slightly reducing its optical quality. This indicates that longer deposition times at lower temperatures may not be as effective.



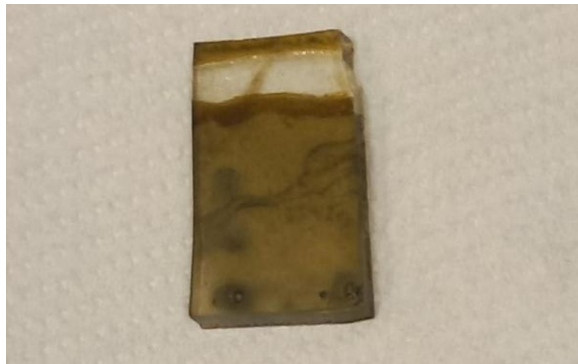
Figure 3d: MoS₂ film after ultrasonic spray coating (150 °C, 50L, 30S)

The sample **150C_50L_30S (1.63 eV)** [Fig 3d] was processed under the conditions of a temperature of 150°C, a volume of 50L, and a time of 30S. Increasing the volume while maintaining the same temperature and deposition time did not significantly change the Tauc plot value. This suggests that volume alone may not have a substantial impact on the optical properties unless combined with other optimized parameters.



Figure 3e: MoS₂ film after ultrasonic spray coating (200 °C, 50L, 30S)

The sample **200C_50L_30S (1.69 eV)** [Fig 3e] was processed under the conditions of a temperature of 200°C, a volume of 50L, and a time of 30S. This sample has the highest Tauc plot value, indicating the best optical properties. The high temperature combined with a larger volume and short deposition time creates a film with optimal crystalline and uniformity, leading to enhanced optical quality. This suggests that higher temperatures and volumes are beneficial for achieving high-quality films.



The sample **200C_25L_30S (1.58 eV)** [Fig 3f] was processed under the conditions of a temperature of 200°C, a volume of 25L, and a time of 30S. This sample shows the lowest Tauc plot value, despite the high temperature. The moderate volume appears insufficient to achieve optimal film quality, indicating that there is an optimal volume threshold needed to maximize the optical properties of the film.

Figure 3f: MoS₂ film after ultrasonic spray coating (200 °C, 25L, 30S)

3.2 Band Gap and Optical Transitions in MoS₂ Thin Films

Tauc plots were utilized to determine the optical band gaps of the MoS₂ thin films. The optical band gaps varied depending on the temperature, layer thickness, and spray duration. For instance, a sample subjected to low temperature (150°C), with a thin layer (20L) and short duration (30S), exhibited a Tauc plot value of 1.64 eV, suggesting moderate crystallinity and potential defects. In contrast, another sample under the same low temperature but with a longer duration (60S) showed a slightly lower band gap of 1.63 eV, indicating improved crystal quality due to the extended spray duration. A thicker layer (50L) with a short duration at the same temperature resulted in a similar band gap of 1.63 eV, pointing to enhanced crystallinity with the increased thickness. On the other hand, a higher temperature (200°C) with a medium layer thickness (25L) and short duration yielded a band gap of 1.58 eV, reflecting better crystallization due to the elevated temperature. The highest band gap of 1.69 eV was observed in a sample with a higher temperature, thicker layer (50L), and short duration, which implies improved film quality but also the introduction of stress due to the thicker layers. Another sample subjected to a higher temperature, with a thin layer and longer duration, had a band gap of 1.65 eV, indicating good crystallinity.

SAMPLE	TAUC PLOT VALUE (eV)
150C_20L_30S	1.64
150C_20L_60S	1.63
150C_50L_30S	1.63
200C_25L_30S	1.58
200C_50L_30S	1.69
200C_20L_60S	1.65

Table 1: Tauc plot values (optical band gaps)

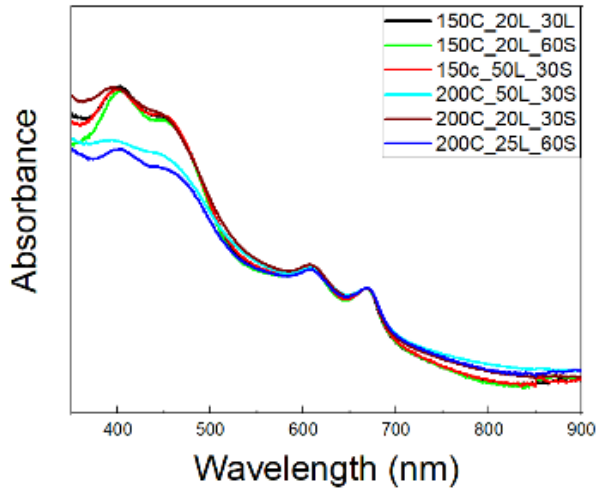


Figure 4a: UV-Vis absorption spectra of exfoliated MoS₂

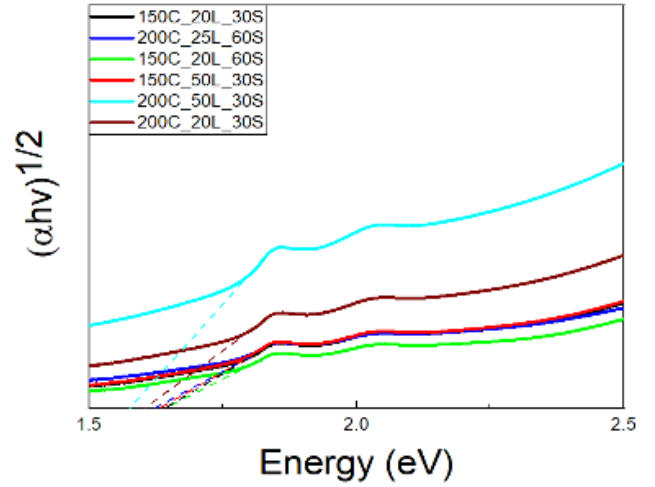


Figure 4b: UV-Vis Tauc plots of exfoliated MoS₂

The UV-Vis spectroscopy of the MoS₂ thin films revealed distinct absorbance peaks [Fig 4b] corresponding to the material's optical transitions. These absorbance levels varied according to the film quality and thickness, which were influenced by different deposition conditions [Fig 4a]. The results indicated that higher temperatures, increased layers, and longer spray durations generally enhanced absorbance, suggesting improved film quality and better electronic properties.

3.3 Evaluation of Surface Uniformity in MoS₂

MoS₂: 200°C_50L-30S

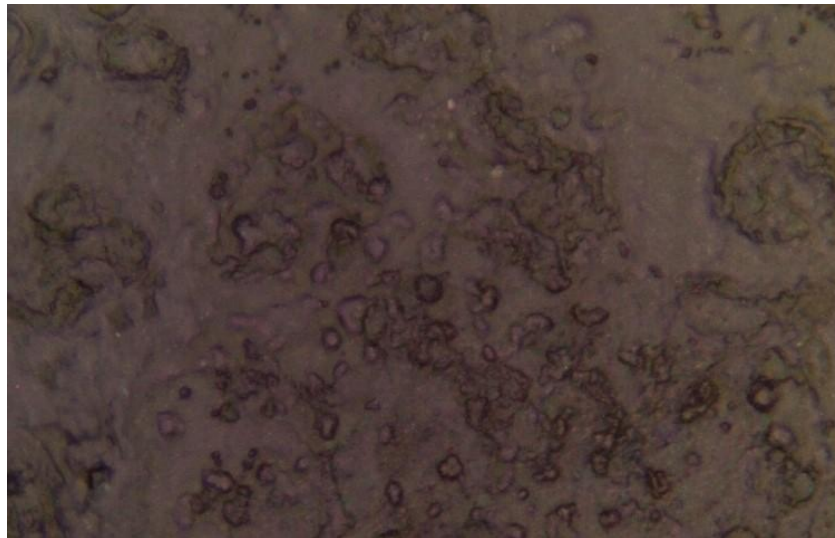


Figure 5: Optical micrograph of MoS₂ thin film (200 °C, 50L, 30S)

POSITION	DIFFERENCE
1	24.91
2	24.86
29	24.87
124	24.87

Table 2: Measurements showing minimal variation across positions

Due to the larger surface area under examination, we perform four distinct measurements to ensure that any variations are captured accurately. These measurements are taken from different sections of the area to check for potential discrepancies. After thorough analysis, we observe that all four measurements in **Table 2** exhibit a high degree of similarity, with minimal variation between them. This consistency suggests that the surface area is uniform and that the conditions affecting the measurements are stable across the entire area.

POSITION 1

The difference of peak 1 and peak 2 is 24.91

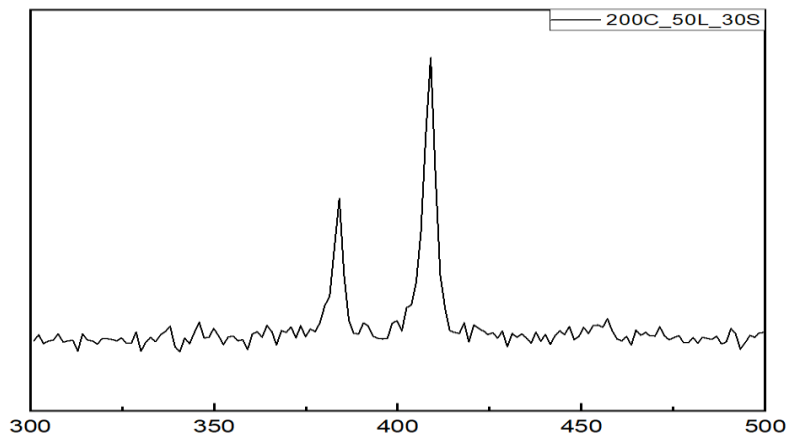


Figure 5a: Difference between peak 1 and peak 2 at Position 1, with a value of 24.91.

POSITION 2

The difference of peak 1 and peak 2 is 24.86

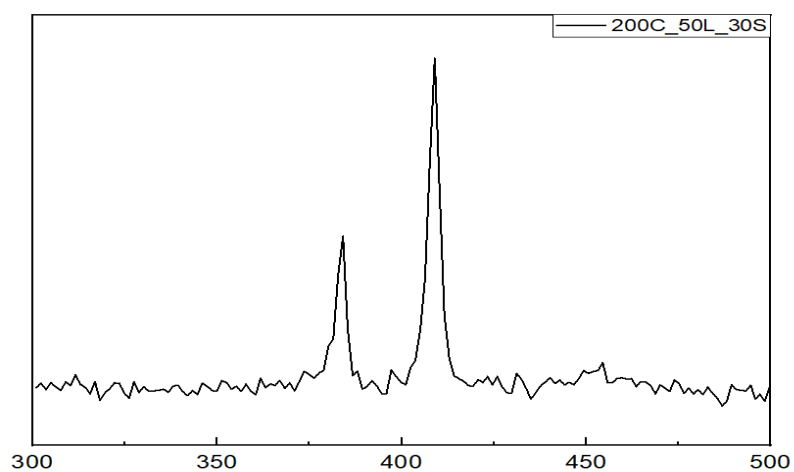


Figure 5b: Difference between peak 1 and peak 2 at Position 2, with a value of 24.86

POSITION 3

The difference of peak 1 and peak 2 is 24.87

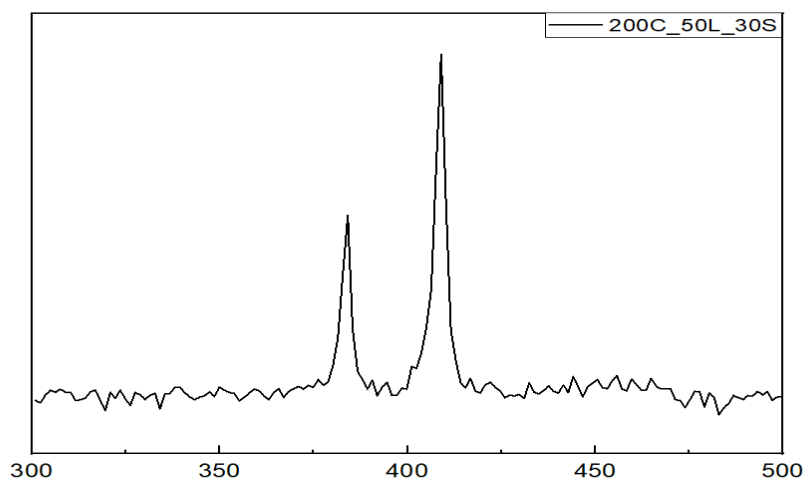


Figure 5c: Difference between peak 1 and peak 2 at Position 3, with a value of 24.87

POSITION 4

The difference of peak 1 and peak 2 is 24.87

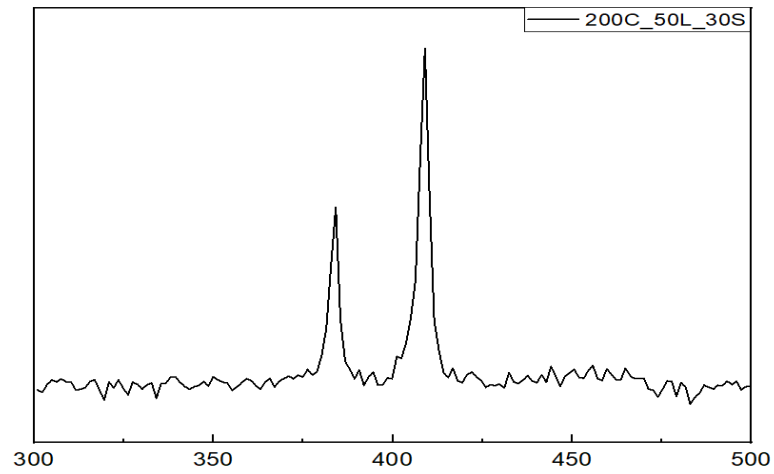


Figure 5d: Difference between peak 1 and peak 2 at Position 4, with a value of 24.87

MoS₂: 150C_50L_30S



Figure 6: Optical micrograph of MoS₂ thin film (150 °C, 50L, 30S)

POSITION	DIFFERENCE
1	25.99
2	24.98
29	23.89
124	24.80

Table 3: Measurements showing minimal variation across positions

For the MoS₂ sample at 150°C with 50L and 30S conditions, we conducted four distinct measurements present in **Table 3** across different sections of the surface to capture any potential variations. The results consistently showed minimal discrepancies, indicating a high degree of uniformity across the surface. This consistency suggests that the measurement conditions are stable and that the surface area does not introduce significant variability. As a result, we can confidently rely on the findings, knowing that the extensive area does not impact the accuracy of our data.

POSITION 1

The difference of peak 1 and peak 2 is 25.99

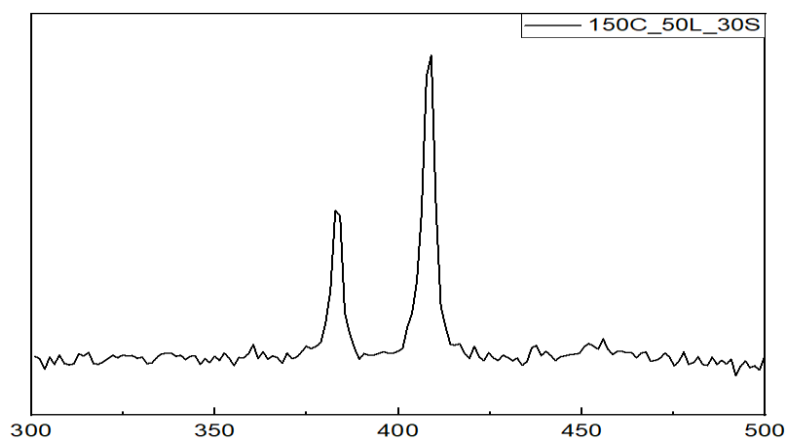


Figure 6a: Difference between peak 1 and peak 2 at Position 1, with a value of 25.99

POSITION 2

The difference of peak 1 and peak 2 is 24.98

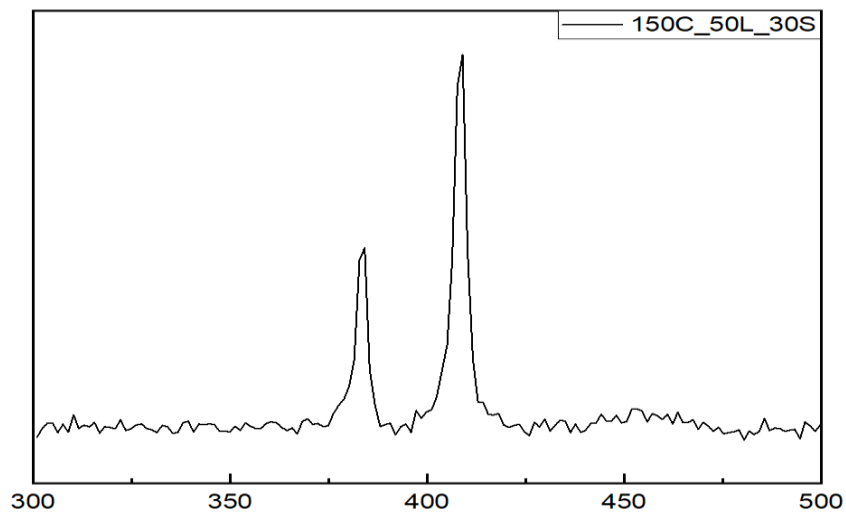


Figure 6b: Difference between peak 1 and peak 2 at Position 2, with a value of 24.98

POSITION 3

The difference of peak 1 and peak 2 is 24.89

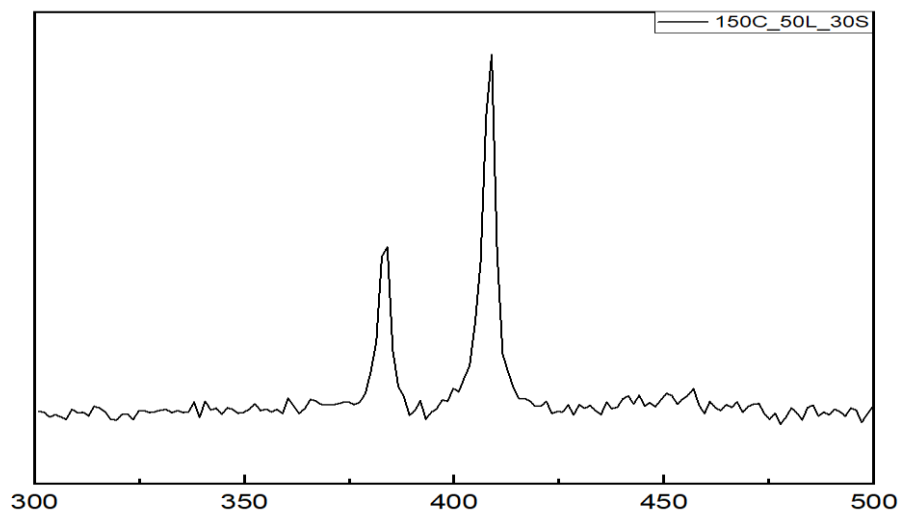


Figure 6c: Difference between peak 1 and peak 2 at Position 3, with a value of 24.89

POSITION 4

The difference of peak 1 and peak 2 is 25.80

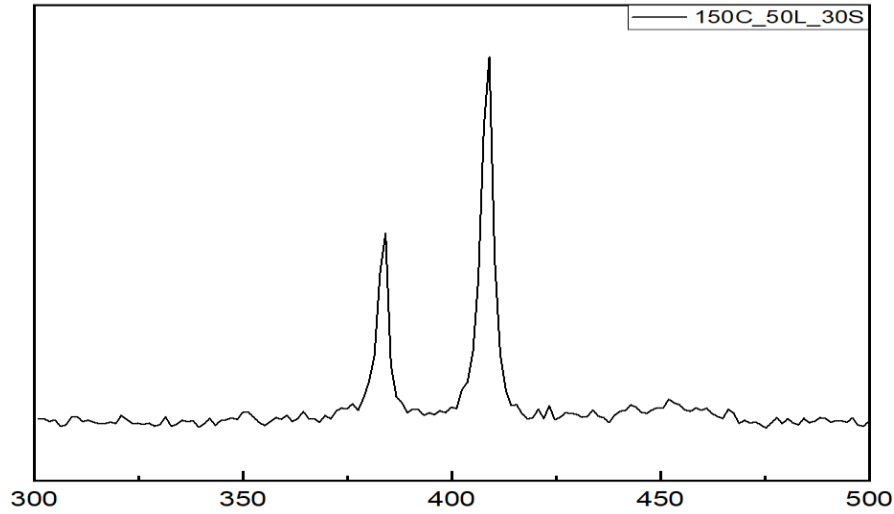


Figure 6d: Difference between peak 1 and peak 2 at Position 4, with a value of 25.80

3.4 Raman and SEM Analysis of MoS₂ Thin Films

Raman spectroscopy was employed to analyze the vibrational modes of the MoS₂ thin films. The Raman spectra displayed characteristic peaks corresponding to the E_{2g} and A_{1g} modes, with the intensity and position of these peaks providing insights into the film's structural and electronic properties. Variations in temperature, layer number, and spray duration were found to affect the Raman peaks, reflecting changes in film quality and structural characteristics.

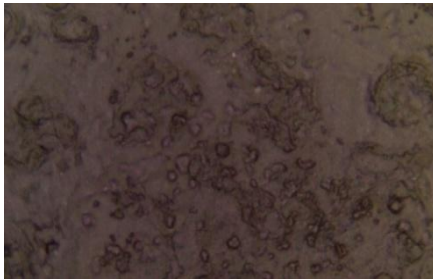


Figure 7a: Optical microscopy image of MoS₂ thin film surface morphology.

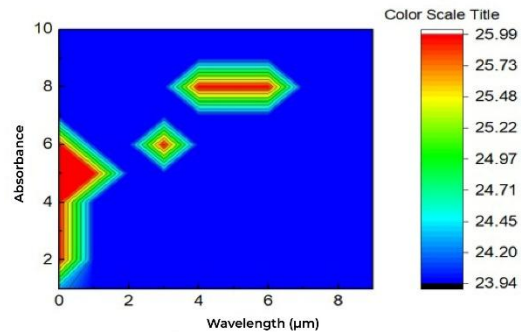
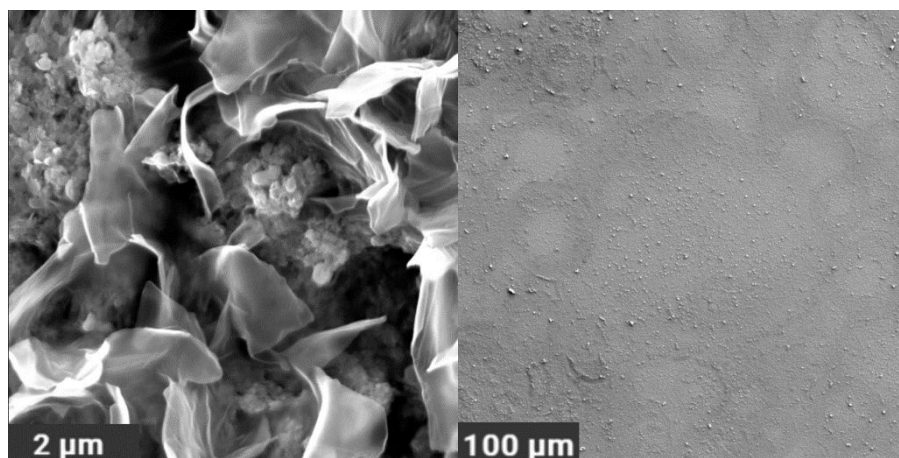


Figure 7b: Raman spectroscopy data showing absorbance versus wavelength for MoS₂ thin film.

[Fig 7b]: The x-axis represents the Wavelength (in nm), likely corresponding to the range of light or wavelengths used to probe the thin film sample. The y-axis shows Absorbance, measuring how much light the sample absorbs at each wavelength. The color scale on the right depicts the intensity, with red indicating the highest absorbance and blue representing the lowest. This 2D mapping helps visualize how different regions of the thin film respond to light. High absorbance could signify denser material accumulation, while lower absorbance may suggest thinner or less material deposition. The color variations across the plot reflect differences in film thickness or composition, allowing for the identification of non-uniformities. Regions with higher absorbance could be thicker or have more concentrated nanomaterials, providing valuable insight for film optimization.



SEM images of MoS₂ showing a flaky structure **(8a)** at 2 μm and a smooth surface with particles **(8b)** at 100 μm.

SEM measurements were performed on selected MoS₂ samples to characterize the morphology of the exfoliated nanosheets in detail.

This **[Figure 8a]** was captured at a scale of 2 μm, whereas the field of view equaled 10.5 μm, giving a highly magnified view of the surface morphology of the sample. The structure observed appears complicated, flaky, and layered. Such an intricate texture may be interpreted to mean that there are thin, sheet-like materials, possibly indicative of substances.

[Figure 8b] was captured at a lower magnification of 100 μm, representing a wider spread of the sample. This image, however, shows a rather smooth and flat surface texture with smaller, well-dispersed particles or granules on the surface. These particles could represent surface impurities, particulate inclusions, or heterogeneities within the material.

Now after this we conducted a series of experiments on six thin film samples by spraying WS₂ (Tungsten disulfide) onto substrates. For each sample, we varied critical parameters which we have also used in MoS₂ such as deposition temperature, duration of spraying, and the number of layers

applied. The aim was to systematically investigate how these variables influence the optical and structural properties of thin films.

3.5 Effect of Parameters on WS₂ Thin Film Quality

The analysis of the various samples indicates a clear relationship between the Tauc plot values and the conditions under which the films were produced.

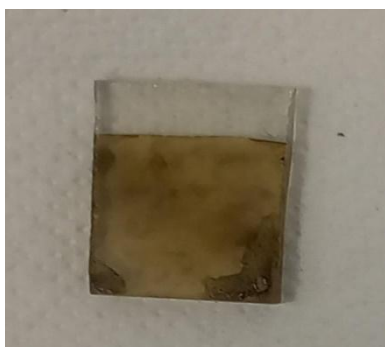


Figure 9a: WS₂ film after ultrasonic spray coating (150°C, 20L, 30S)

Sample **150C_20L_30S** [Fig 9a], exhibits a lower Tauc plot value of 1.70 eV, which reflects the effects of moderate temperature and low volume on film quality. These conditions suggest reasonable but not optimal optical properties, indicating that further optimization is necessary.

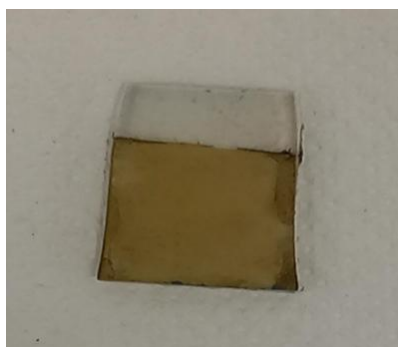


Figure 9b: WS₂ film after ultrasonic spray coating (150°C, 20L, 60S)

Sample **150C_20L_60S** [Fig 9b], This sample has the highest Tauc plot value of 1.76eV, indicating the best optical properties. The moderate temperature combined with a lower volume and higher deposition time creates a film with optimal crystallinity and uniformity, leading to enhanced optical quality.

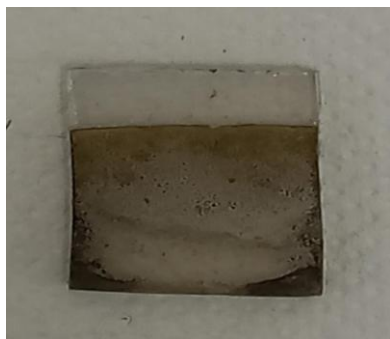


Figure 9c: WS₂ film after ultrasonic spray coating (150°C, 50L, 30S)

Sample **150C_50L_30S** [Fig 9c], the Tauc plot value rises to 1.75 eV. This outcome suggests that a larger volume contributes positively to film quality and optical properties, potentially compensating for the moderate temperature.

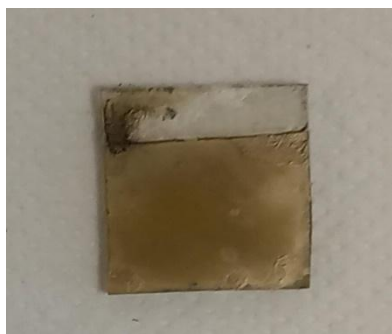


Figure 9d: WS₂ film after ultrasonic spray coating (200°C, 25L, 30S)

In Sample **200C_25L_30S** [Fig 9d], Tauc plot value is 1.74, despite the high temperature. The moderate volume appears insufficient to achieve optimal film quality, indicating that there is an optimal volume threshold needed to maximize the optical properties of the film.



Figure 9e: WS₂ film after ultrasonic spray coating (200°C, 50L, 30S)

The lowest Tauc plot value of 1.70 eV is observed in Sample **200C_50L_30S** [Fig 9e], despite the high temperature. The high volume appears insufficient to achieve optimal film quality, indicating that there is an optimal volume threshold needed to maximize the optical properties of the film.

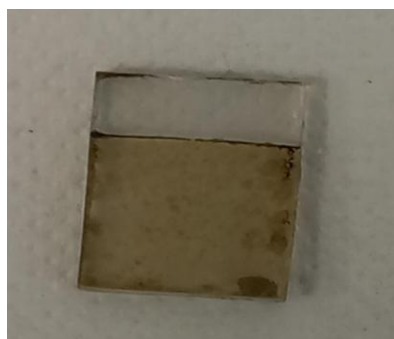


Figure 9f: WS₂ film after ultrasonic spray coating (200°C, 20L, 60S)

In contrast, sample **200C_20L_60S** [Fig 9f], with a higher temperature of 200°C and a longer deposition time of 60 seconds, shows a moderate Tauc plot value of 1.73 eV. This improvement can be attributed to better film crystal clearness under these conditions, resulting in enhanced optical performance.

3.6 Band Gap and Optical Transitions in WS₂ Thin Films

The analysis of the samples reveals distinct relationships between the processing conditions and the resulting Tauc plot values, which correlate with the films' crystalline and potential defects.

Sample 1 (150C_20L_30S) shows a Tauc plot value of 1.70 eV under conditions of low temperature (150°C), thin layer (20L), and short duration (30S). This band gap suggests lower crystalline with some potential defects, possibly due to the combination of low temperature and short deposition time.

Sample 2 (150C_20L_60S), where the deposition duration is extended to 60 seconds at the same low temperature and thin layer conditions, the Tauc plot value increases to 1.76 eV. This higher band gap indicates an improvement in crystal quality, likely due to the longer deposition time allowing for better film formation.

Sample 3 (150C_50L_30S) maintains a low temperature but increases the layer thickness to 50L while keeping the duration short at 30 seconds. The resulting Tauc plot value of 1.75 eV suggests better crystallinity due to the thicker layer, which may have contributed to a more uniform film structure.

SAMPLE	TAUC PLOT VALUE (eV)
150C_20L_30S	1.70
150C_20L_60S	1.76
150C_50L_30S	1.75
200C_25L_30S	1.74
200C_50L_30S	1.70
200C_20L_60S	1.73

Table 4: Tauc plot values (optical band gaps)

Sample 4 (200C_25L_30S), the temperature is raised to 200°C, with a medium layer thickness of 25L and a short duration of 30 seconds. This combination results in a Tauc plot value of 1.74 eV, reflecting improved crystallization at the higher temperature, which enhances the optical properties of the film.

Sample 5 (200C_50L_30S) uses the same high temperature but with a thicker layer (50L) and short duration (30S). The Tauc plot value here is 1.70 eV, indicating that while the higher temperature improves film quality, the thicker layer may introduce stress, leading to a slightly lower band gap.

Finally, **Sample 6** (200C_20L_60S) combines high temperature (200°C) with a thin layer (20L) and longer deposition time (60S), resulting in a Tauc plot value of 1.73 eV. This band gap suggests good crystalline, with the higher temperature and extended duration working together to produce a film with enhanced optical properties. Overall, the Tauc plot values present in **Table 4** reflect the impact of temperature, layer thickness, and deposition time on film quality. Higher temperatures generally improve crystallinity, while the balance between layer thickness and deposition time is crucial for achieving optimal optical performance.

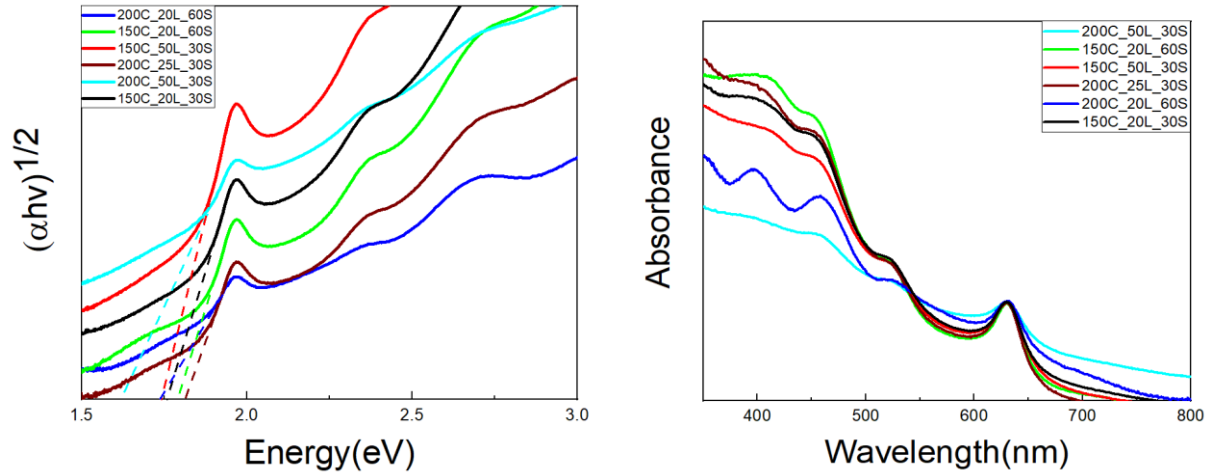


Figure 10a: UV-Vis Tauc plots and **Figure 10b** corresponding absorption spectra [10b] of exfoliated WS₂

The UV-Vis analysis of WS₂ thin films reveals key absorbance characteristics that are indicative of the material's optical transitions [Fig 10b]. The UV-Vis spectra for these films shows absorbance peaks, which offer valuable insights into how the films interact with light. These variations in absorbance are directly influenced by the deposition parameters used during film preparation, such as temperature, layer number, and spray duration.

The correlation between deposition parameters and absorbance highlights the importance of optimizing these conditions to achieve the desired film characteristics. By carefully controlling the temperature, layer number, and spray duration, it is possible to tailor the optical properties of WS₂ thin films to specific applications.

3.7 Evaluation of Surface Uniformity in WS₂

WS₂: 150C_20L_60S

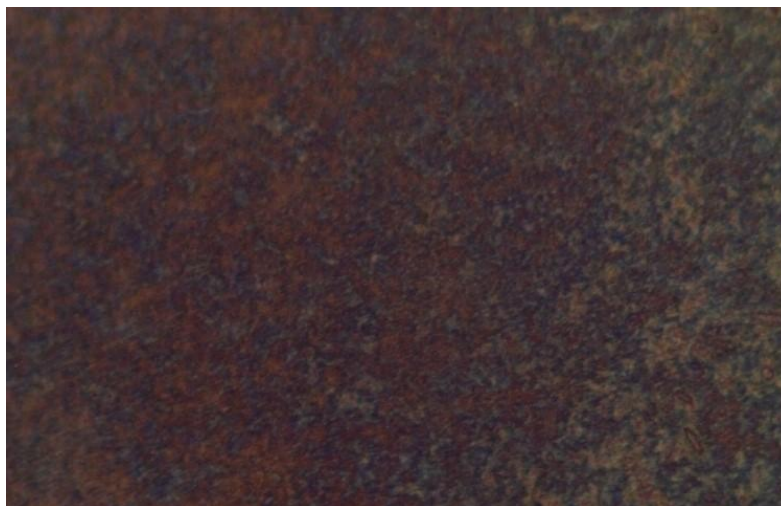


Figure 11: Optical micrograph of WS₂ thin film (150 °C, 20L, 60S)

SAMPLE	RATIO
SPECTRUM 0	2.668
SPECTRUM1	2.660
SPECTRUM2	2.592

Table 5: Measurements showing minimal variation across positions

We conduct three separate measurements present in **Table 5** across different sections of the larger surface area. This approach ensures that discrepancies are detected if present. Upon careful analysis, we find that all three measurements are remarkably consistent, with only minimal ratio observed. This consistency indicates that the surface area is uniform and that the conditions influencing the measurements remain stable throughout. The uniformity across the area strengthens our confidence in the reliability of our findings, confirming that the larger surface area does not introduce significant variability.

Spectrum 0

The ratio of peak 1 and peak 2 is 2.668

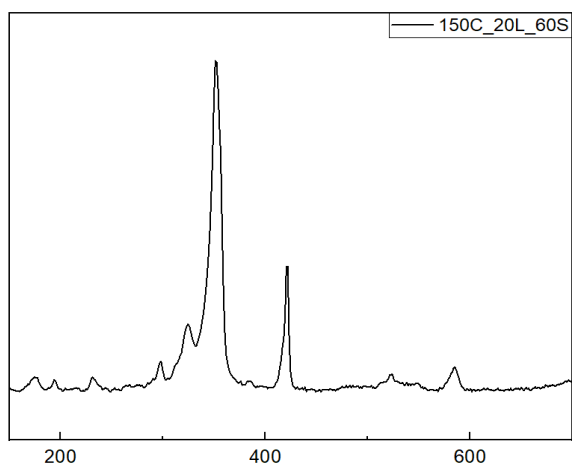


Figure 11a: Ratio of peak 1 and peak 2 at spectrum 0, with a value of 2.668

Spectrum 1

The ratio of peak 1 and peak 2 is 2.660

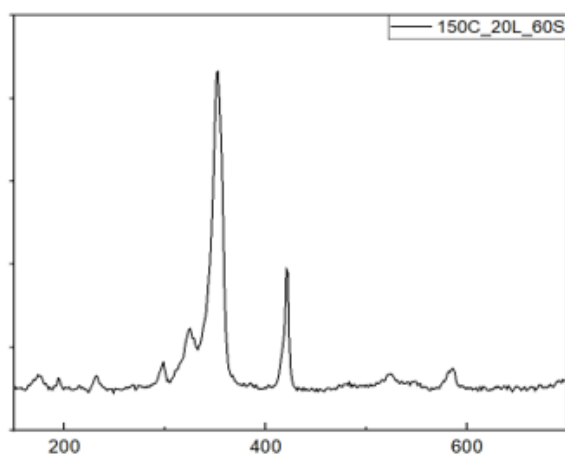


Figure 11b: Ratio of peak 1 and peak 2 at spectrum 1, with a value of 2.660

Spectrum 2

The ratio of peak 1 and peak 2 is 2.592

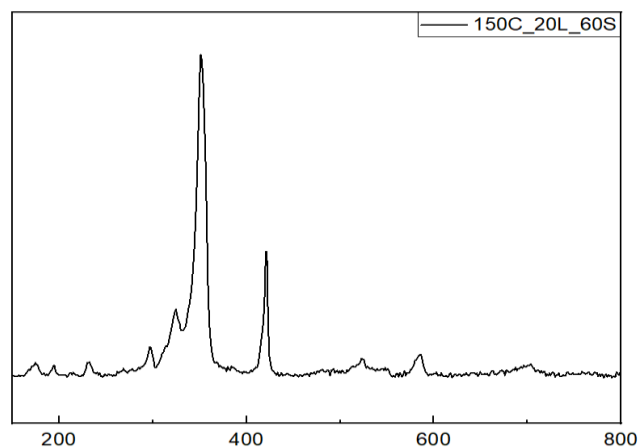


Figure 11c: Ratio of peak 1 and peak 2 at spectrum 2, with a value of 2.592

WS₂ 200C_25L_30S



Figure 12: Optical micrograph of WS₂ thin film (150 °C, 20L, 60S)

SAMPLE	RATIO
SPECTRUM0	2.433
SPECTRUM1	2.497
SPECTRUM2	2.743

Table 6: Measurements showing minimal variation across positions

To ensure the detection of any potential variations, we take three distinct measurements present in **Table 6** from various sections of the larger surface area. This method is designed to identify any discrepancies. After thorough analysis, we observe that all three measurements show a high level of consistency, with only minimal ratios detected. This consistency suggests that the surface area is uniform, and the conditions affecting the measurements are stable across the entire area. The uniformity and the reliability of our results, affirming that the larger surface area does not introduce significant variability.

Spectrum 0

The ratio of peak 1 and peak 2 is 2.433

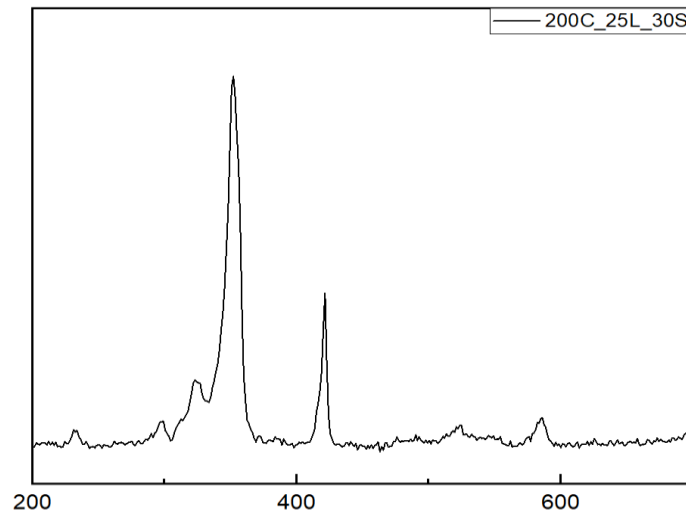


Figure 12a: Ratio of peak 1 and peak 2 at spectrum 0, with a value of 2.433

Spectrum1

The ratio of peak 1 and peak 2 is 2.497

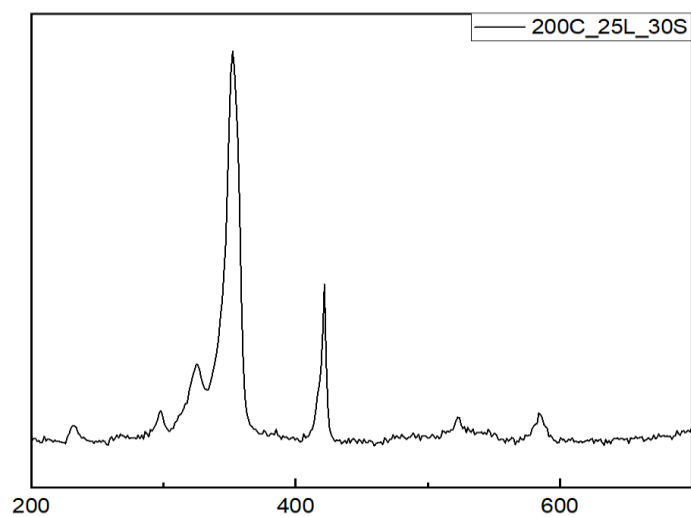


Figure 12b: Ratio of peak 1 and peak 2 at spectrum 1, with a value of 2.497

Spectrum 2

The ratio of peak 1 and peak 2 is 2.743

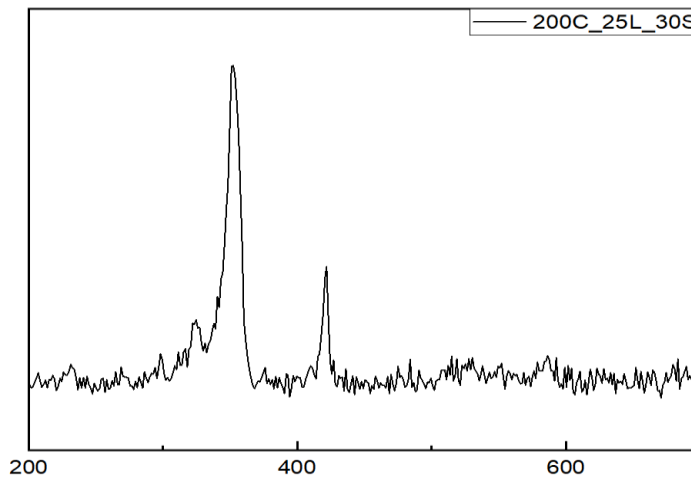


Figure 12c: Ratio of peak 1 and peak 2 at spectrum 2, with a value of 2.743

3.8 Raman and SEM Analysis of WS₂ Thin Films

The Raman analysis of WS₂ thin films focuses on identifying key peaks associated with the A₁g and E₂g modes, which are characteristic of the material's vibrational properties. These peaks in the Raman spectra provide crucial information about the film's structural and electronic properties. Variations in the intensity and position of these peaks serve as indicators of changes in the film's structure, such as crystallinity and layer thickness.

The effect of deposition parameters, including temperature, layer number, and spray duration, plays a significant role in influencing these Raman peaks. As observed with MoS₂, adjustments in these parameters lead to shifts in peak position and changes in intensity, reflecting the film's quality and any structural modifications that occur during deposition. The correlation between deposition conditions and Raman spectral features allows for a deeper understanding of the film's properties, enabling the optimization of WS₂ thin films for various applications.

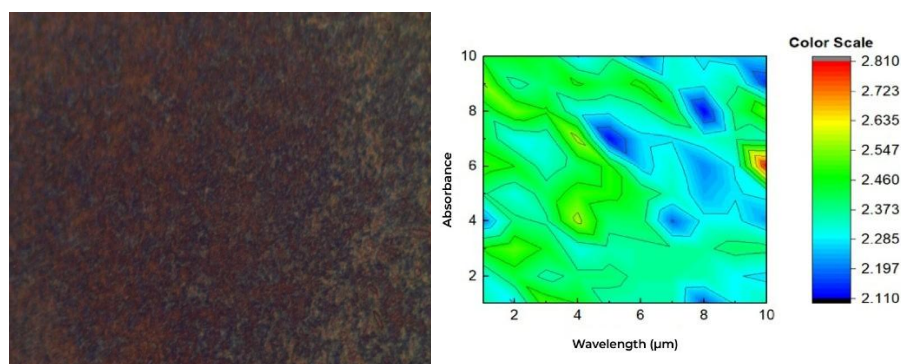


FIGURE 13a: Optical microscopy image of MoS₂ thin film surface morphology and **Figure 13b** Raman spectroscopy showing absorbance versus wavelength.

The analysis of the 2D mapping heatmap for WS₂ [Fig 13b] provided insights into the variation of a key material property. The heatmap illustrates how this specific property changed with factors such as temperature and substrate type. Contour lines on the heatmap depicted constant values of the property, while the color scale, ranging from blue (lower values) to red (higher values), indicated the range of these values. Unlike the smooth gradient observed for MoS₂, the WS₂ heatmap displayed more distinct and isolated regions with sharp transitions. This pattern suggested that the property underwent significant changes under certain conditions, revealing well-defined phases or states.

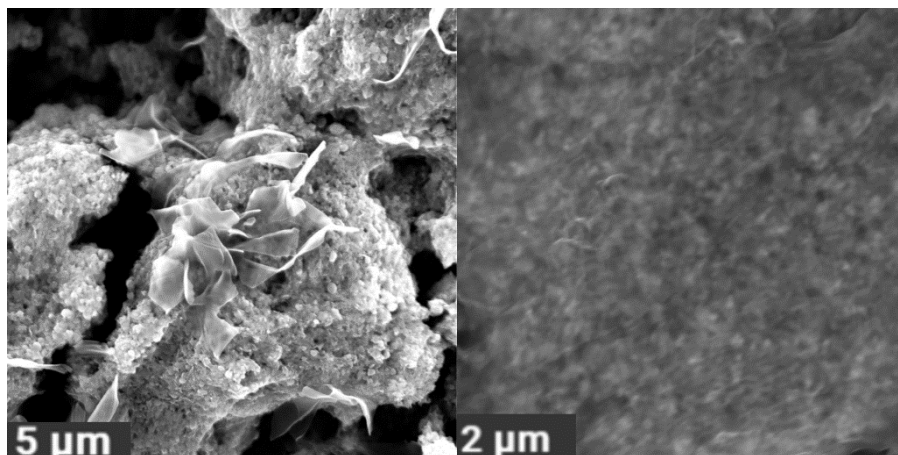


Figure 14a: SEM images of WS_2 showing a flaky structure at $5\mu\text{m}$ and **Figure 14b** shows smooth surface with particles at $2\mu\text{m}$.

The first image [**Figure 14a**] exhibits a rough, porous surface with the presence of flake-like features, which are characteristic of the exfoliated layers of WS_2 . On the other hand, the second image [**Figure 14b**] shows a smooth surface with uniform roughness, which points more toward a change in phase or process. The lack of distinct flakes in this region of the image might suggest a more compact or amorphous structure, therefore affecting the electrical or catalytic behavior of the material.

3.9 Photoluminescence Spectra of MoS_2 and WS_2 Thin Films

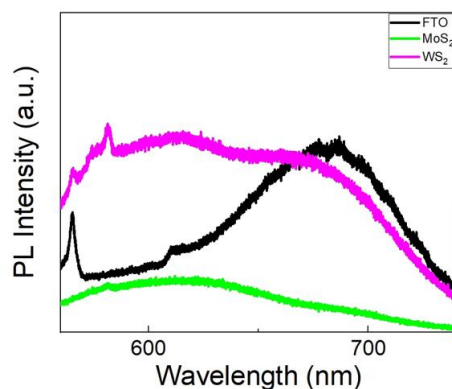


Figure 15: Photoluminescence spectra of FTO, MoS_2 , and WS_2 thin films showing PL intensity versus wavelength.

The image displays a photoluminescence (PL) [**Fig 15**] spectrum that characterizes thin films made from colloidal 2D materials, specifically MoS_2 and WS_2 . The graph plots PL intensity (in arbitrary

units, a.u.) against the wavelength (in nanometers, nm). The three curves represent the PL response of different materials: FTO (black curve), likely referring to a fluorine-doped tin oxide substrate used as a reference or baseline in the PL measurement; MoS₂ (green curve), showing the PL spectrum for a MoS₂ thin film, which exhibits a relatively low PL intensity across the measured wavelength range; and WS₂ (magenta curve), where the PL spectrum shows a significantly higher PL intensity, with a prominent peak around the 650–700 nm range. The differences in PL intensity and spectral features between the MoS₂ and WS₂ films indicate variations in their optical properties, likely due to differences in their bandgap energies and electronic structures. The PL spectra provide insights into the excitonic properties and quality of the thin films prepared from these 2D materials.

Chapter 4: Conclusion

This thesis provides a detailed examination of the optimization of thin film production using ultrasonic spray coating with colloidal nanomaterial inks, specifically focusing on MoS₂ and WS₂. The research aimed to optimize deposition parameters to produce high-quality thin films with potential applications in photovoltaic and photo electrocatalytic devices.

The volume of the spray and the number of layers applied were critical in determining the film's thickness and uniformity. An optimal spray volume, when applied in controlled layers, resulted in films that were uniform in thickness and consistent in their structural and electronic properties. The use of multiple layers was particularly effective in improving the homogeneity and stability of the films.

The duration of the spray also played a key role in the deposition process. While longer spray durations generally led to thicker films with better coverage, the study observed diminishing returns beyond a certain point. Excessive spray time could lead to non-uniformity and potential cracking, highlighting the need for careful balancing of spray duration with other parameters.

A comparative analysis of MoS₂ and WS₂ films revealed that while general optimization strategies could be applied to both materials, material-specific adjustments were necessary to achieve the best results. Comparing the two heatmaps provides valuable insights into the behavior of MoS₂ and WS₂ under similar experimental conditions. The MoS₂ heatmap exhibits a more complex and denser contour pattern, suggesting a continuous variation of the property with the experimental parameters. In contrast, the WS₂ heatmap shows distinct regions, indicating sharper transitions. Additionally, the property range for MoS₂ is narrower (23.94 to 25.99) compared to WS₂ (2.118 to 22.81), which might reflect differences in the sensitivity of the measured property to the experimental conditions. These differences highlight the unique characteristics of MoS₂ and WS₂, informing their selection and optimization for specific technological applications. The findings of this research make significant contributions to the field of thin film technology, offering valuable insights into the production of high-performance thin films using ultrasonic spray coating. The study's outcomes could influence the development of more efficient and cost-effective manufacturing processes for various applications, including solar cells, sensors, and catalytic devices.

While this thesis has advanced the understanding of optimizing thin film production, it also opens avenues for future research. Exploring other two-dimensional materials beyond MoS₂ and WS₂ could determine the broader applicability of the optimization strategies developed. Additionally, assessing the long-term stability and environmental impact of these films under operational conditions would provide crucial insights for practical applications.

The integration of these optimized films into actual devices, such as photovoltaic cells, represents another promising direction for future research. This step would validate the laboratory findings and identify any additional factors that need consideration during the transition from lab-scale production to commercial-scale manufacturing.

In conclusion, this thesis has successfully demonstrated the importance of optimizing deposition parameters in the production of high-quality thin films using ultrasonic spray coating. The systematic approach taken in this research has provided a robust framework for understanding and controlling the factors that influence film properties, paving the way for future advancements in thin film technology. The insights gained here not only enhance our understanding of this field but also hold the potential to drive innovation in various applications where these films are utilized.

REFERENCES

- (1) Rick, W.; Sampaio, V.; Linniker, P.; Serra, C.; Oliveira Dantas, N.; Ribeiro, R.; De Sousa, M.; Christine, A.; Silva, A. *Nanocomposites Thin Films: Manufacturing and Applications*. www.intechopen.com.
- (2) Chen, Y.; Sun, M. Two-Dimensional WS₂/MoS₂ heterostructures: Properties and Applications. *Nanoscale*. Royal Society of Chemistry March 21, 2021, pp 5594–5619. <https://doi.org/10.1039/d1nr00455g>.
- (3) Chen, Y.; Sun, M. Two-Dimensional WS₂/MoS₂ heterostructures: Properties and Applications. *Nanoscale*. Royal Society of Chemistry March 21, 2021, pp 5594–5619. <https://doi.org/10.1039/d1nr00455g>.
- (4) Peng, Q.; De, S. Outstanding Mechanical Properties of Monolayer MoS₂ and Its Application in Elastic Energy Storage. *Physical Chemistry Chemical Physics* 2013, 15 (44), 19427–19437. <https://doi.org/10.1039/c3cp52879k>.
- (5) Zhao, Y.; Liu, J.; Zhang, X.; Wang, C.; Zhao, X.; Li, J.; Jin, H. Convenient Synthesis of WS₂-MoS₂ Heterostructures with Enhanced Photocatalytic Performance. *Journal of Physical Chemistry C* 2019. <https://doi.org/10.1021/acs.jpcc.9b08101>.
- (6) Lei, W.; Xiao, J. L.; Liu, H. P.; Jia, Q. L.; Zhang, H. J. Tungsten Disulfide: Synthesis and Applications in Electrochemical Energy Storage and Conversion. *Tungsten*. Springer September 1, 2020, pp 217–239. <https://doi.org/10.1007/s42864-020-00054-6>.
- (7) Abbas, O. A.; Zeimpekis, I.; Wang, H.; Lewis, A. H.; Sessions, N. P.; Ebert, M.; Aspiotis, N.; Huang, C. C.; Hewak, D.; Mailis, S.; Sazio, P. Solution-Based Synthesis of Few-Layer WS₂ Large Area Continuous Films for Electronic Applications. *Sci Rep* 2020, 10 (1). <https://doi.org/10.1038/s41598-020-58694-0>.
- (8) Nath Upadhyay, S.; Akash Kumar Satrughna, J.; Pakhira, S. Recent Advancements of Two-Dimensional Transition Metal Dichalcogenides and Their Applications in Electrocatalysis and Energy Storage. <https://doi.org/10.1007/s42247-021-00241-2>/Published.
- (9) Nath Upadhyay, S.; Akash Kumar Satrughna, J.; Pakhira, S. Recent Advancements of Two-Dimensional Transition Metal Dichalcogenides and Their Applications in Electrocatalysis and Energy Storage. <https://doi.org/10.1007/s42247-021-00241-2>/Published.
- (10) Ferreira, P.; Abreu, B.; Freire, C.; Fernandes, D. M.; Marques, E. F.; Dell'era, A. Materials Nanocomposites Prepared from Carbon Nanotubes and the Transition Metal Dichalcogenides WS₂ and MoS₂ via Surfactant-Assisted Dispersions as Electrocatalysts for Oxygen Reactions. 2021. <https://doi.org/10.3390/ma>.
- (11) Luan, Q.; Yang, C. L.; Wang, M. S.; Ma, X. G. First-Principles Study on the Electronic and Optical Properties of WS₂ and MoS₂ Monolayers. *Chinese Journal of Physics* 2017, 55 (5), 1930–1937. <https://doi.org/10.1016/j.cjph.2017.08.011>.

- (12) Luan, Q.; Yang, C. L.; Wang, M. S.; Ma, X. G. First-Principles Study on the Electronic and Optical Properties of WS₂ and MoS₂ Monolayers. *Chinese Journal of Physics* 2017, 55 (5), 1930–1937. <https://doi.org/10.1016/j.cjph.2017.08.011>.
- (13) Kim, S. J.; Kim, D.; Min, B. K.; Yi, Y.; Mondal, S.; Nguyen, V. T.; Hwang, J.; Suh, D.; Cho, K.; Choi, C. G. Bandgap Tuned WS₂ Thin-Film Photodetector by Strain Gradient in van Der Waals Effective Homo Junctions. *Adv Opt Mater* 2021, 9 (22). <https://doi.org/10.1002/adom.202101310>.
- (14) Adilbekova, B.; Lin, Y.; Yengel, E.; Faber, H.; Harrison, G.; Firdaus, Y.; El-Labban, A.; Anjum, D. H.; Tung, V.; Anthopoulos, T. D. Liquid Phase Exfoliation of MoS₂ and WS₂ in Aqueous Ammonia and Their Application in Highly Efficient Organic Solar Cells. *J Mater Chem C Mater* 2020, 8 (15), 5259–5264. <https://doi.org/10.1039/d0tc00659a>.
- (15) Bertolazzi, S.; Gobbi, M.; Zhao, Y.; Backes, C.; Samorì, P. Molecular Chemistry Approaches for Tuning the Properties of Two-Dimensional Transition Metal Dichalcogenides. *Chemical Society Reviews*. Royal Society of Chemistry September 7, 2018, pp 6845–6888. <https://doi.org/10.1039/c8cs00169c>.
- (16) Mihai, C.; Simandan, I. D.; Sava, F.; Buruiana, A. T.; Bocirnea, A. E.; Tite, T.; Zaki, M. Y.; Velea, A. Synthesis of Wrinkled MoS₂ Thin Films Using a Two-Step Method Consisting of Magnetron Sputtering and Sulfurization in a Confined Space. *Sustainability (Switzerland)* 2024, 16 (9). <https://doi.org/10.3390/su16093819>.
- (17) Grayfer, E. D.; Kozlova, M. N.; Fedorov, V. E. Colloidal 2D Nanosheets of MoS₂ and Other Transition Metal Dichalcogenides through Liquid-Phase Exfoliation. *Advances in Colloid and Interface Science*. Elsevier B.V. July 1, 2017, pp 40–61. <https://doi.org/10.1016/j.cis.2017.04.014>.
- (18) Acosta, E. *Thin Films/Properties and Applications*. www.intechopen.com.
- (19) Chaudhary, K. T. *Thin Film Deposition: Solution Based Approach*. www.intechopen.com.
- (20) Butt, M. A. Thin-Film Coating Methods: A Successful Marriage of High-Quality and Cost-Effectiveness—A Brief Exploration. *Coatings*. MDPI August 1, 2022. <https://doi.org/10.3390/coatings12081115>.
- (21) Sesti, V.; D’Antonio, M.; Lucotti, A.; Moretti, P.; Castagna, R.; Bertarelli, C.; Tommasini, M. Combining UV-Vis and Resonance Raman Spectroscopy to Characterize Molecular Aggregation. *Crystals (Basel)* 2023, 13 (7). <https://doi.org/10.3390/cryst13071141>.
- (22) Grosso, D.; Boissière, C.; Faustini, M. Thin Film Deposition Techniques. In *The Sol-Gel Handbook*; Wiley Blackwell, 2015; Vol. 1–3, pp 277–316. <https://doi.org/10.1002/9783527670819.ch09>.
- (23) Perednis, D.; Gauckler, L. J. *Thin Film Deposition Using Spray Pyrolysis*; Springer Science + Business Media, Inc. Manufactured in The Netherlands, 2005; Vol. 14.
- (24) Zeng, C.; Pu, J.; Wang, H.; Zheng, S.; Chen, R. Influence of Microstructure on Tribological Properties and Corrosion Resistance of MoS₂/WS₂ Films. *Ceram Int* 2020, 46 (9), 13774–13783. <https://doi.org/10.1016/j.ceramint.2020.02.167>.

- (25) Singh, H.; Kumar, M.; Singh, R. An Overview of Various Applications of Cold Spray Coating Process. *Mater Today Proc* 2022, *56*, 2826–2830. <https://doi.org/10.1016/j.matpr.2021.10.160>.
- (26) Tejero-Martin, D.; Rezvani Rad, M.; McDonald, A.; Hussain, T. Beyond Traditional Coatings: A Review on Thermal-Sprayed Functional and Smart Coatings. *Journal of Thermal Spray Technology*. Springer New York LLC April 17, 2019, pp 598–644. <https://doi.org/10.1007/s11666-019-00857-1>.
- (27) Rahemi Ardekani, S.; Sabour Rouh Aghdam, A.; Nazari, M.; Bayat, A.; Yazdani, E.; Saievar-Iranizad, E. A Comprehensive Review on Ultrasonic Spray Pyrolysis Technique: Mechanism, Main Parameters and Applications in Condensed Matter. *Journal of Analytical and Applied Pyrolysis*. Elsevier B.V. August 1, 2019. <https://doi.org/10.1016/j.jaap.2019.104631>.
- (28) Shahidi, S.; Moazzenchi, B.; Ghoranneviss, M. A Review-Application of Physical Vapor Deposition (PVD) and Related Methods in the Textile Industry. *EPJ Applied Physics* 2015, *71* (3). <https://doi.org/10.1051/epjap/2015140439>.
- (29) Sahu, N.; Panigrahi, S. *Fundamental Understanding and Modeling of Spin Coating Process : A Review*; 2009; Vol. 83.
- (30) Shah, M. A.; Lee, D. G.; Lee, B. Y.; Hur, S. Classifications and Applications of Inkjet Printing Technology: A Review. *IEEE Access*. Institute of Electrical and Electronics Engineers Inc. 2021, pp 140079–140102. <https://doi.org/10.1109/ACCESS.2021.3119219>.
- (31) Hassan, K.; Nine, M. J.; Tung, T. T.; Stanley, N.; Yap, P. L.; Rastin, H.; Yu, L.; Losic, D. Functional Inks and Extrusion-Based 3D Printing of 2D Materials: A Review of Current Research and Applications. *Nanoscale*. Royal Society of Chemistry October 7, 2020, pp 19007–19042. <https://doi.org/10.1039/d0nr04933f>.
- (32) Luo, S.; Dong, S.; Lu, C.; Yu, C.; Ou, Y.; Luo, L.; Sun, J.; Sun, J. Rational and Green Synthesis of Novel Two-Dimensional WS₂/MoS₂ Heterojunction via Direct Exfoliation in Ethanol-Water Targeting Advanced Visible-Light-Responsive Photocatalytic Performance. *J Colloid Interface Sci* 2018, *513*, 389–399. <https://doi.org/10.1016/j.jcis.2017.11.044>.
- (33) Alaaeddin, M. H.; Sapuan, S. M.; Zuhri, M. Y. M.; Zainudin, E. S.; AL-Oqla, F. M. Photovoltaic Applications: Status and Manufacturing Prospects. *Renewable and Sustainable Energy Reviews*. Elsevier Ltd March 1, 2019, pp 318–332. <https://doi.org/10.1016/j.rser.2018.12.026>.
- (34) Zhang, Q.; Guan, J. Single-Atom Catalysts for Electrocatalytic Applications. *Advanced Functional Materials*. Wiley-VCH Verlag August 1, 2020. <https://doi.org/10.1002/adfm.202000768>.
- (35) Rahemi Ardekani, S.; Sabour Rouh Aghdam, A.; Nazari, M.; Bayat, A.; Yazdani, E.; Saievar-Iranizad, E. A Comprehensive Review on Ultrasonic Spray Pyrolysis Technique: Mechanism, Main Parameters and Applications in Condensed Matter. *Journal of Analytical and Applied Pyrolysis*. Elsevier B.V. August 1, 2019. <https://doi.org/10.1016/j.jaap.2019.104631>.
- (36) Abe, A.; Goss, J. A.; Zou, M. Exploring the Impact of Spray Process Parameters on Graphite Coatings: Morphology, Thickness, and Tribological Properties. *Coatings* 2024, *14* (6). <https://doi.org/10.3390/coatings14060714>.

- (37) Cai, Z.; Deng, S.; Liao, H.; Zeng, C.; Montavon, G. The Effect of Spray Distance and Scanning Step on the Coating Thickness Uniformity in Cold Spray Process. *Journal of Thermal Spray Technology* 2014, 23 (3), 354–362. <https://doi.org/10.1007/s11666-013-0002-0>.
- (38) Orts Mercadillo, V.; Chan, K. C.; Caironi, M.; Athanassiou, A.; Kinloch, I. A.; Bissett, M.; Cataldi, P. Electrically Conductive 2D Material Coatings for Flexible and Stretchable Electronics: A Comparative Review of Graphenes and MXenes. *Advanced Functional Materials*. John Wiley and Sons Inc September 1, 2022. <https://doi.org/10.1002/adfm.202204772>.
- (39) Zhu, C.; Fu, Y.; Yu, Y. Designed Nanoarchitectures by Electrostatic Spray Deposition for Energy Storage. *Advanced Materials*. Wiley-VCH Verlag January 4, 2019. <https://doi.org/10.1002/adma.201803408>.
- (40) Canepa, S.; Alam, S. B.; Ngo, D.-T.; Ross, F. M.; Mølhave, K. In Situ TEM Electrical Measurements. In *Controlled Atmosphere Transmission Electron Microscopy*; Springer International Publishing, 2016; pp 281–300. https://doi.org/10.1007/978-3-319-22988-1_10.
- (41) Andre Lyon, L.; King, C. D.; Fox, A. P.; Ba, B. E. *Raman Spectroscopy*; 1998.
- (42) Tebyetekerwa, M.; Zhang, J.; Xu, Z.; Truong, T. N.; Yin, Z.; Lu, Y.; Ramakrishna, S.; Macdonald, D.; Nguyen, H. T. Mechanisms and Applications of Steady-State Photoluminescence Spectroscopy in Two-Dimensional Transition-Metal Dichalcogenides. *ACS Nano*. American Chemical Society November 24, 2020, pp 14579–14604. <https://doi.org/10.1021/acsnano.0c08668>.
- (43) Pozzati, M.; Boll, F.; Crisci, M.; Domenici, S.; Smarsly, B.; Gatti, T.; Wang, M. Systematic Investigation on the Surfactant-Assisted Liquid-Phase Exfoliation of MoS₂ and WS₂ in Water for Sustainable 2D Material Inks. *Physica Status Solidi - Rapid Research Letters* 2024. <https://doi.org/10.1002/pssr.202400039>.