

**Synthesis and characterization of metal complexes
with organochalcogenophosphorus ligands,
single source precursors for new materials**

Houyem Trabelsi

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Cotutelle thesis

Synthesis and characterization of metal complexes with organochalcogenophosphorus ligands, single source precursors for new materials

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Abstract

Metal sulfide (MS) thin films have attracted significant attention due to their remarkable electrical and optical properties. Extensive research has focused on their synthesis through various precursors and deposition techniques. Among these, the use of transition metal complexes as single-source precursors (SSPs) offers a promising and efficient route for MS thin film processing. This approach integrates all required elements within a single molecular entity, simplifying the synthesis process, and enhancing control over growth parameters. Aerosol-assisted chemical vapor deposition (AACVD) is particularly well-suited for depositing films from SSPs, it operates under atmospheric pressure, accommodates non-volatile precursors, and provides excellent scalability for large-area applications.

Beyond their synthesis, the integration of nanostructured MS thin films into electronic devices, particularly gas microsensors, has gained increasing interest. Their high surface area, strong surface reactivity, and ability to function effectively at room temperature (RT) make them excellent candidates for gas sensing applications. These sensor devices hold great potential across diverse fields, including healthcare diagnostics, industrial process monitoring, food safety, agriculture, and air quality assessment.

Among MS-based gas sensors, Cu_xS and ZnS stand out as promising semiconductors with outstanding optoelectronic properties; however, their gas sensing behavior have been relatively underexplored, making them ideal target materials for this work. In this context, my thesis advances the state of the art by: (i) synthesizing a new copper SSP precursor, $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$, optimized for AACVD; (ii) developing novel AACVD routes for depositing Cu_2S thin films with particle- and flake-type nanostructures and (iii) establishing a new AACVD codeposition route for the growth of ZnS nanoleaves, with all depositions carried out at relatively low temperatures (below 500°C).

Furthermore, this thesis demonstrates the gas sensing capabilities of Cu_2S and ZnS thin films, representing a novel contribution to the field of gas sensor research. Cu_2S was found to be particularly suitable for chemoresistive gas sensing, operating effectively at RT under photoactivation and showing high selectivity toward NO_2 , while exhibiting negligible responses to ethanol, toluene, and hydrogen. In contrast, ZnS films were more appropriate for optical gas sensing, benefiting from their strong UV absorbance. ZnS

sensors displayed higher sensitivity to NO₂ and toluene, with measurable cross-sensitivity to ethanol, hydrogen, and carbon monoxide. The effect of humidity was significant for ZnS, leading to the formation of a ZnO overlayer, on its surface, whereas Cu₂S sensors maintained stable under humid conditions.

Key words

Single source Precursors (SSPs), metal sulfide thin films, AACVD, chemiresistive/optical gas sensor, NO₂, VOCs.

Resumen (Spanish)

Las películas delgadas de sulfuros metálicos (MS) son atractivas debido a sus propiedades eléctricas y ópticas notables. De ahí que numerosas investigaciones se centran en su síntesis mediante diversos precursores y técnicas de depósito. Entre ellas, el uso de complejos de metales de transición como precursores de fuente única (SSP, por sus siglas en inglés) ofrece una ruta prometedora y eficiente para el procesamiento de películas delgadas de MS. Este enfoque integra todos los elementos necesarios dentro de una sola entidad molecular, lo que simplifica el proceso de síntesis y mejora el control sobre los parámetros de crecimiento. La deposición química en fase vapor asistida por aerosol (AACVD) es especialmente adecuada para depositar películas a partir de SSP, opera a presión atmosférica, admite precursores no volátiles y ofrece una excelente escalabilidad para aplicaciones de gran área.

Más allá de su síntesis, la integración de películas delgadas nanoestructuradas de MS en dispositivos electrónicos, particularmente microsensores de gases, despierta un interés creciente. Su alta área superficial, fuerte reactividad superficial y capacidad para funcionar de manera eficaz a temperatura ambiente (RT) las convierten en excelentes candidatas para aplicaciones de detección de gases. Estos dispositivos sensores tienen un gran potencial en diversos campos, incluidos el diagnóstico en salud, la monitorización de procesos industriales, la seguridad alimentaria, la agricultura y la evaluación de la calidad del aire.

Entre los sensores de gas basados en MS, Cu_xS y ZnS destacan como semiconductores prometedores con excelentes propiedades optoelectrónicas; sin embargo, su comportamiento como sensores de gas es aún poco explorado, lo que los convierte en materiales objetivo ideales para este trabajo. En este contexto, mi tesis contribuye al estado del arte mediante: (i) la síntesis de un nuevo precursor SSP de cobre, $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$, optimizado para AACVD; (ii) el desarrollo de nuevas rutas AACVD para depositar películas delgadas de Cu_2S con nanoestructuras tipo partículas y láminas; y (iii) el establecimiento de una nueva ruta de codepósito por AACVD para el crecimiento de nanohojuelas de ZnS , con todos los depósitos realizados a temperaturas relativamente bajas (por debajo de 500 °C).

Además, esta tesis demuestra las capacidades de detección de gases de las películas delgadas de Cu_2S y ZnS , representando una contribución novedosa al campo de la investigación en sensores de gas. Se encontró que el Cu_2S es particularmente adecuado para la detección quimioresistiva de gases, operando eficazmente a RT bajo fotoactivación y mostrando alta selectividad hacia NO_2 , mientras que exhibe respuestas insignificantes al etanol, tolueno e hidrógeno. En contraste, las películas de ZnS fueron más apropiadas para la detección óptica de gases, beneficiándose de su fuerte absorbancia en UV. Los sensores de ZnS mostraron mayor sensibilidad hacia NO_2 y tolueno, con sensibilidad cruzada medible al etanol, hidrógeno y monóxido de carbono. El efecto de la humedad fue significativo para ZnS , llevando a la formación de una capa superficial de ZnO , mientras que los sensores de Cu_2S se mantuvieron estables en condiciones húmedas.

Palabras clave

Precusores de fuente única (SSP), capas delgadas de sulfuro metálico, AACVD, sensor de gas quimio resistivo/óptico, NO_2 , COV.

Resumen (Català)

Les pel·lícules fines de sulfurs metàl·lics (MS) són atractives per les seves propietats elèctriques i òptiques notables. Es per això que nombroses investigacions es centren en la seva síntesi mitjançant diversos precursors i tècniques de dipòsit. Entre elles, l'ús de complexos de metalls de transició com a precursors de font única (SSP, per les seves sigles en anglès) ofereix una ruta prometedora i eficient per al processament de pel·lícules fines de MS. Aquest enfocament integra tots els elements necessaris dins d'una sola entitat molecular, el que simplifica el procés de síntesi i millora el control sobre els paràmetres de creixement. La deposició química en fase vapor assistida per aerosol (AACVD) és especialment adequada per dipositar pel·lícules a partir de SSP, opera a pressió atmosfèrica, admet precursors no volàtils i ofereix una excel·lent escalabilitat per a aplicacions de gran àrea.

Més allà de la seva síntesi, la integració de pel·lícules fines nanoestructurades de MS en dispositius electrònics, particularment microsensores de gasos, desperta un interès creixent. La seva alta àrea superficial, forta reactivitat superficial i capacitat per funcionar de manera eficaç a temperatura ambient (RT) es converteixen en excel·lents candidates per a aplicacions de detecció de gasos. Aquests dispositius sensors tenen un gran potencial en diversos camps, inclòs el diagnòstic en salut, la monitorització de processos industrials, la seguretat alimentària, l'agricultura i l'avaluació de la qualitat de l'aire.

Entre els sensors de gas basats en MS, Cu_xS i ZnS destaquen com a semiconductors prometedors amb excel·lents propietats optoelectròniques; però, el seu comportament com a sensors de gas és encara poc explorat, el que els converteix en materials objectius ideals per a aquest treball. En aquest context, la meua tesi contribueix a l'estat de l'art mitjançant: (i) la síntesi d'un nou precursor SSP de coure, $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$, optimitzat per a AACVD; (ii) el desenvolupament de noves rutes AACVD per dipositar pel·lícules fines de Cu_2S amb nanoestructures tipus partícules i làmines; i (iii) l'establiment d'una nova ruta de codepòsit per AACVD per al creixement de nanofulles de ZnS , amb tots els dipòsits realitzats a temperatures relativament baixes (per baix de 500 °C).

A més, aquesta tesis demostra les capacitats de detecció de gasos de les pel·lícules fines de Cu_2S i ZnS , representant una contribució nova al camp de la investigació en sensors de gasos. Es va trobar que el Cu_2S és especialment adequat per a la detecció quimiorresistiva de gasos, funcionant eficaçment a RT sota fotoactivació i mostrant alta

selectivitat cap a NO_2 , mentre que mostra respostes insignificants a l'etanol, el toluè i l'hidrogen. En contrast, les pel·lícules de ZnS van ser més apropiades per a la detecció òptica de gasos, beneficiant-se de la seva forta absorència en UV. Els sensors de ZnS van mostrar major sensibilitat cap a NO_2 i toluè, amb sensibilitat creuada mesurable a l'etanol, hidrogen i monòxid de carboni. L'efecte de la humitat va ser significatiu per a ZnS, portant a la formació d'una capa superficial de ZnO, mentre que els sensors de Cu_2S es mantenen estables en condicions humides.

Paraules clau

Precursors de font única (SSP), capes primes de sulfur metàl·lic, AACVD, sensor de gas químic resistiu/òptic, NO_2 , COV.

Declaration

I hereby declare that this doctoral dissertation is my original work, carried out under the supervision of Pr. Khaled Alouani and Dr. Stella Vallejos Vargas, and with the tutoring of Pr. Montserrat Nafria Maqueda. To the best of my knowledge, the work presented herein has not been submitted for any other degree or qualification at this or any other institution.

I have duly acknowledged all the sources of information which have been used in the thesis.

Date: 06/12/2025, Barcelona

Author's signature

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List of abbreviations

AACVD	Aerosol assisted chemical vapor deposition
CV	Crystal violet
Cu ₂ S	Copper sulfide
CVD	Chemical vapor deposition
EDL	Electron depletion layer
Et	Ethyle
Fs	Flakes
HAL	Hole accumulation layer
LEDs	light-emitting diodes
LOD	Limit of detection
MB	Methylene blue
MEMS	Micro electro mechanical systems
MOX	Metal oxides
MS	Metal sulfide
NDIR	Non dispersive infra red
NPs	Nanoparticles
OP	Organophosphorus
PVD	Physical vapor deposition
QCM	Quartz crystal microbalance
RhB	Rhodamine B
SAW	Surface acoustic wave
SSPs	Single source precursors
TMCs	Transition metal chalcogenides
RT	Room temperature
VOCs	Volatile Organic Compounds
ZnS	Zinc sulfide

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Introduction

Motivation

Transition metal complexes are essential compounds in industry and everyday life, forming the foundation of everything from medicines to electronic devices [1–3]. These compounds, formed by the coordination of metal ions with various ligands, exhibit remarkable reactivity and stability. Synthesizing new metal complexes is worthwhile as it enables the development of advanced materials, efficient catalysts, and innovative medical treatments, each contributing significantly to scientific progress and practical applications across various fields. In this context, a novel approach has gained attention within the field of nanoscience, involving the use of metal complexes as single-source precursors (SSPs) for the synthesis of nanomaterials [4]. These precursors provide several key advantages, such as precise control over composition and deposition parameters [5], reduced processing time and cost, and the elimination of additional toxic reagents that could otherwise contaminate the final material. The synthesis and deposition of (SSPs) derived materials are often carried out using aerosol-assisted chemical vapor deposition (AACVD), a technique well-suited for non-volatile molecular precursors. AACVD operates under atmospheric pressure, offers excellent scalability [6], and enables the controlled fabrication of high-quality thin films, making it an ideal method for producing advanced nanostructured materials.

Among the most extensively studied materials are metal sulfides derived from SSPs, such as SnS [7], MoS₂ [8], ZnS [9] and Cu_xS [10], which exhibit exceptional electrical and optical properties, making them promising candidates for a wide range of applications, including solar cells, biomedical, and photocatalysis [11]. In addition to these applications, the use of (MS) materials have recently attracted growing attention as high performance sensing materials for detecting hazardous gases and VOCs [12]. This interest stems from their optoelectronic properties [13,14] and their ability to operate effectively at room temperature [15], which significantly reduces energy consumption [16], a critical requirement in the advancement of modern gas-sensing technologies.

The demand for these sensing devices has grown considerably in recent years due to their need in different fields such as industrial safety, environmental monitoring, food safety, medical diagnostics, and agricultural technologies [17–19]. The operating principle of these sensors relies on the interaction between target gas molecules and the (MS) sensitive layer, which initiates surface chemical reactions that result in measurable changes in the material's properties, specifically, its electrical resistance in the case of chemiresistive sensors, or its optical characteristics (such as absorbance, transmittance, or luminescence) for optical gas sensors. As a result, sensor performance such as sensitivity, selectivity and response/recovery time are highly dependent on the composition, morphology, crystalline structure and surface activity of the (MS) material employed.

Therefore, this thesis focused on developing MS-based gas sensors using SSPs for room-temperature detection of low-concentration analytes.

Objectives of the thesis

The main objective of this thesis is to synthesize metal complexes based on organochalcogenophosphorus ligands as single-source precursors (SSPs) for the aerosol-assisted chemical vapor deposition (AACVD) of metal sulfide thin films and their evaluation as gas sensing materials.

To achieve the main objective, the thesis is structured around the following specific objectives:

1. Synthesis and characterization of metal complexes based on organochalcogenophosphorus ligands, serving as single source precursors for the elaboration of metal sulfide films.
2. Synthesis of metal sulfide thin films via AACVD technique, followed by detailed structural, compositional, and morphological characterization.
3. Integration of the synthesized metal sulfide thin films into microsensor platforms and evaluation of their sensing performance toward target gases and volatile organic compounds (VOCs).

Scientific contribution

This work represents a significant advancement beyond the current state of the art through several key innovations. First, it investigates the use of a novel copper complex,

[Cu(Et₄P₂S₂)Cl]₂, as a SSPs for the AACVD of Cu₂S; this includes the establishment of specific routes for nanostructured Cu₂S films. Secondly, it studies a new co-deposition approach based on two reactants, Et₄P₂S₂ and ZnCl₂, for the AACVD synthesis of nanostructured ZnS thin films. Additionally, the thesis contributes with detailed analysis of the Cu₂S and ZnS nanostructured films, offering insight into their physico chemical properties and morphology control. Finally, this study reports the photoactivated and optical gas sensing properties of the Cu₂S and ZnS films, respectively, going beyond the state-of-the-art on the use of these materials in gas sensing.

Structure of the thesis

The thesis is divided into four chapters, described as follows:

Chapter 1: presents a comprehensive overview of the state of the art in the use of metal complexes as single-source precursors (SSPs) for the synthesis of metal sulfide materials, with a specific focus on copper and zinc sulfide thin films and their structural, optical, and electronic properties. In addition, it reviews the deposition methods employed to synthesize these materials, highlighting commonly used physical and chemical techniques, with particular emphasis on aerosol-assisted chemical vapor deposition (AACVD). Finally, chapter 1 outlines the diverse applications of Cu_xS and ZnS, with particular emphasis on their use in gas sensors. This section describes the architectures of chemiresistive and optical sensor devices and explains their sensing mechanisms.

Chapter 2: describes the experimental aspects of this study. It is structured into three main parts: the first describes the synthetic procedures employed to prepare the metal complexes based on organochalcogenophosphorus ligands, along with the analytical techniques used to confirm their molecular structures. The second part describes the AACVD of Cu_xS and ZnS, their direct integration into the sensor platforms, and the characterization methods applied to investigate their morphological, structural, and compositional properties. Finally, the chapter provides a detailed description of the gas sensing setup, including the architecture and operational parameters of sensor platforms employed in this study.

Chapter 3: is divided into two main sections. The first presents the results of the synthesis and characterization of the SSPs. The second details the AACVD of Cu_xS and ZnS thin

films from $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$ SSPs and a mixture of the ligand $\text{Et}_4\text{P}_2\text{S}_2$ and ZnCl_2 , respectively. The evaluation of the structural, morphological, and compositional properties of the AACVD is also discussed in this section. Particular emphasis is placed on the influence of the annealing process, examining how thermal treatment affects the film characteristics.

Chapter 4: Chapter 4 is devoted to the gas sensing performance of the AACVD films. Specifically, it presents and discusses the electrical response of Cu_xS to NO_2 , alongside the optical response of ZnS toward a range of gases and VOCs, all evaluated at room temperature.

The results of this research have been published in a specialized journal, two international conference proceedings, and one national conference proceeding. Other oral and poster presentations have also been presented during the thesis in various student workshops (e.g., machine learning in nanoscience in Mons, Belgium, JPhD at ICMAB, and YRD at IMB-CNM). Below the list and details of the indexed publications.

Journal article 1. Aerosol-assisted chemical vapor deposited Cu_2S structured films with photo activated NO_2 sensing properties, Trabelsi, H., Gracia, I., Alouani, K., & Vallejos, S. (2025), *Ceramics International*, 51(2), 1949-1957, doi: 10.1016/j.ceramint.2024.11.169.

Conference proceeding 1. gas sensing based on ZnS nanostructures for ethanol detection at room temperature, H. Trabelsi, I. Gràcia, K. Alouani, C. Cané, S. Vallejos, *Optical Proceeding of the Eurosensors XXXVI*, September 2025, doi: 10.5162/EUROSENSORS2025/MP31

Conference proceeding 2. Fabrication and characterization of Cu_2S -based gas microsensors with sensitivity to NO_2 , H. Trabelsi, I. Gràcia, K. Alouani, C. Cané, S. Vallejos, *15th Spanish Conference on Electron Devices*, January 2025, doi: 10.1109/CDE66381.2025.11038855

Conference proceeding 3. Aerosol Assisted Chemical Vapor Deposition of Copper Sulfide films with sensitivity to NO_2 , H. Trabelsi, I. Gràcia, K. Alouani, S. Vallejos, *Proceedings of the GAMS 2024 International Conference*, June 2024, doi: 10.26799/cp-gams-2024.

Further, a new journal article submission is under review.

Journal article 2. Aerosol-assisted chemical vapor deposition of ZnS nanoleaves with optical sensitivity to gases, Trabelsi, H., Gracia, I., Alouani, K., & Vallejos, S. (2025)., Submitted to Materials Science in Semiconductor Processing (Elsevier).

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Chapter I

State of the art

I.1. Introduction

Thin films are essential components in the development of advanced devices, due to their unique physicochemical properties and their use in wide range of applications. The deposition of thin films, which typically have thicknesses ranging from several nanometers to a few micrometers, are commonly applied onto solid surfaces such as glass, silicon wafers, and alumina substrates. They have widely spread applications in microelectronics, particularly as sensitive layer in gas sensors [1,2], solar cells [3], as well as in energy conversion and storage devices [4]. Thin films based on nanoparticles or nanostructured materials exhibit a high surface-to-volume ratio [5], enhanced optical and electrical properties, and versatile integration with rigid as well as flexible substrates [6]. The overall performance of these films is strongly influenced by key parameters including chemical composition, crystallinity, thickness, morphology, and deposition technique.

Among the various families of thin films, transition metal chalcogenides (TMCs) have garnered increasing attention owing due to their structural diversity and exceptional electronic, optical and catalytic properties [7]. These materials are composed of a transition metal (such as Mo, Cu, Zn, or Sn) bonded with a chalcogen element (S, Se, or Te), and can form binary, ternary, or quaternary compounds in either amorphous or crystalline phases. One of their key features is the wide range of their band gap, and their notable environmental stability. Owing to these advantageous properties, thin films based on transition metal chalcogenides (TMCs) are increasingly being used in a variety of applications, such as solar cells, gas sensing, photocatalysis, and light-emitting diodes (LEDs), among others [8–10], as illustrated in Figure I.1

The development of high-quality TMC thin films remains a major challenge in the field of functional materials. The electrical, optical and structural performance of devices incorporating these materials is strongly influenced by the intrinsic properties of the thin films, which primarily are determined by the choice of precursors and deposition method.

With regard to precursor selection, a novel synthetic route has been developed using metal complexes as single-source precursors (SSPs). Their advantages and key aspects of this approach are discussed in this chapter.

As for the deposition method, a wide range of techniques has been established and can be broadly categorized into two main groups: physical and chemical deposition methods. Among the most widespread are chemical vapor deposition (CVD) and physical vapor deposition (PVD). These approaches produce thin films of good quality, with well-controlled thickness and good adhesion to the substrate. Furthermore, they offer great flexibility in terms of choice of materials and operating conditions, making them particularly well suited to the synthesis of TMCs for advanced applications.

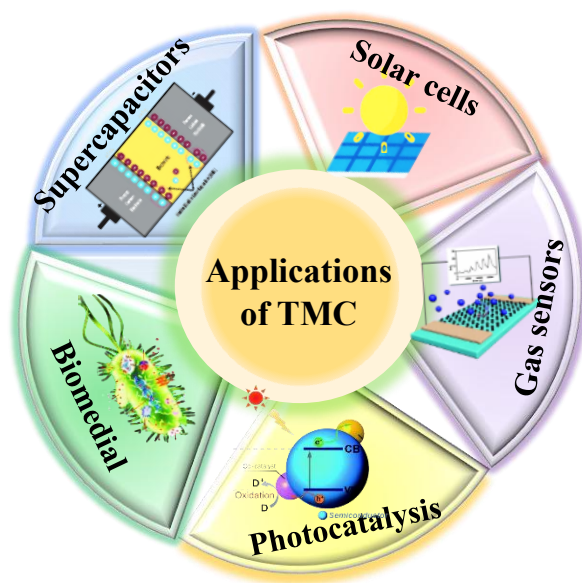


Figure I. 1. Transition metal chalcogenide applications in advanced technologies.

In this context, this chapter provides in a first part a comprehensive bibliographic review on metallic complexes based on organochalcogenophosphorus ligands and their uses as single-source precursors (SSPs) to elaborate metal chalcogenide thin films, particularly copper sulfide (Cu_xS) and zinc sulfide (ZnS); the two materials studied deeply in this thesis. The second part provides an overview on the attributes of Cu_xS and ZnS , including their optical, electrical, and thermal properties, while emphasizing their comparative advantages over traditional metal oxide-based compounds. In the third part, different physical and chemical deposition techniques utilized in the synthesis of Cu_xS and ZnS thin films are presented, with special emphasis placed on aerosol-assisted chemical vapor deposition (AACVD). Finally, the chapter concludes with an exploration of the diverse application fields of these materials, with a specific focus on their use in gas sensing devices.

I.2. Transition metal complexes based on organophosphorus (OP) ligands

Metal complexes are neutral or ionic species in which a central metal ion or atom is coordinated by surrounding molecules or ions known as ligands [11]. In recent years, transition metal complexes have attracted considerable attention due to their diverse and potential biological activities including antibacterial, antioxidant, and antitumor properties [12–14] as well as their unique physical characteristics, such as magnetic behavior and catalytic efficiency [15,16]. These attributes render them invaluable across a broad spectrum of applications, like medicine, industrial catalysis, and environment.

Importantly, the functional properties of these complexes are profoundly influenced by the nature and physicochemical characteristics of their coordinating ligands. Ligands enables the complex's stability, reactivity, solubility, and electronic structure, allowing for targeted performance in specific applications [17]. Among the most versatile and widely studied ligand classes are phosphines, particularly tertiary phosphines, which feature a lone pair of electrons on the phosphorus atom that act as both nucleophilic and basic character [18], enabling them to form robust coordination bonds not only with transition metals but also with chalcogens (S, Se, Te), carbon, and nitrogen [19]. Organophosphorus ligands (OP) are classified based on the number of donor atoms they use to bind to the metal center and can be monodentate (binding through one donor atom), bidentate (two donor atoms), or multidentate (three or more donor atoms), as illustrated in Figure I.2.

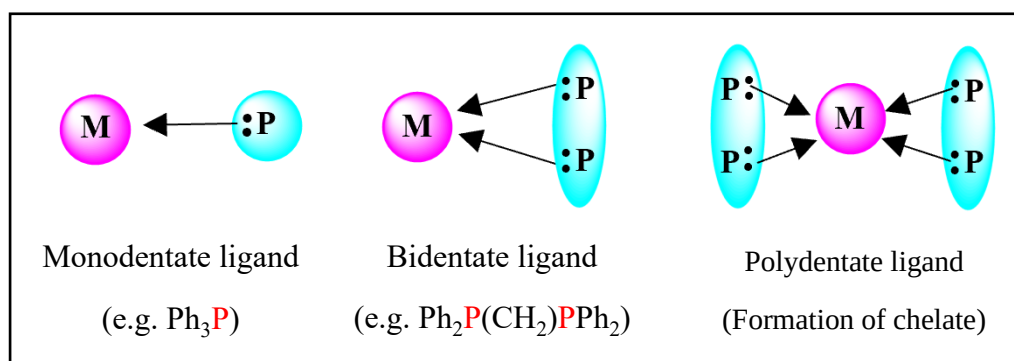


Figure I. 2. Common classes of organophosphorus ligands in coordination chemistry.

Recently, metal complexes based on (OP) ligands coordinated to chalcogen atoms (S, Se, Te) have been used as single-source precursors for nanomaterials synthesis [20,21]. Their precisely defined stoichiometry, tunable reactivity, and controlled thermal decomposition enable the deposition of metal chalcogenide thin films for next-generation functional nanoscale devices.

I.2.1. Metal complexes as single source precursors (SSPs)

The use of metal complexes as SSPs often have numerous advantages over conventional precursors [22] for the preparation of metal chalcogenide thin films. Firstly, they considerably simplify synthesis processes by integrating the necessary elements into a single chemical entity, thereby reducing the complexity of reactions and facilitating control of experimental parameters such as temperature, pressure or choice of solvent [23]. This simplification helps ensure consistent quality and better reproducibility of material properties, which is essential to meet the requirements of advanced applications. In addition, SSPs reduce production costs and time by limiting the number of components required and shortening manufacturing steps. Moreover, their use avoids the use of additional reagents that may be toxic or introduce impurities into the final material, thus improving the purity and safety of the synthesis process [24,25]. Furthermore, in some precursors, the phase of the deposited material can be controlled by the core structure of the precursor molecule [26]. Among the most widely studied metal complexes featuring phosphine chalcogenide ligands, the family of $[M((EPR_2)_2N)_3]$ and $[M((EPR_2)_2N)_2]$ (where M represents a transition metal, R denotes an alkyl or phenyl group, and E = S, Se, or Te). Paul O'Brien and his research group are among those who have used these complexes as single-source precursors in chemical vapor deposition (CVD), successfully synthesizing a broad range of binary and ternary chalcogenide materials, achieving diverse morphologies and crystalline phases. A summary of their key achievements is presented in the table below.

Table I. 1. Summary of metal chalcogenides deposited from single-source precursors (SSPs) using chemical vapor deposition (CVD) method.

SSPs	TMC	Technique	Tdep (°C)	Morphology	Phase	Reference
[Pb((SP ⁱ Pr ₂) ₂ N) ₂]	PbS	LP-MOCVD	450	Rods	Cubic	[27]
[Pb((SeP ⁱ Pr ₂) ₂ N) ₂]	PbSe			Particles	Cubic	
[Bi((SP ⁱ Pr ₂) ₂ N) ₃]	Bi ₂ S ₃	LP-MOCVD	450	Irregular platelets	Orthorhombic	[28]
[Bi((SeP ⁱ Pr ₂) ₂ N) ₃]	Bi ₂ Se ₃	AACVD	475	Polygonal grains	Rrhombohedral	
[Cu((SeP ⁱ Pr ₂) ₂ N) ₃] + [In((SeP ⁱ Pr ₂) ₂ N) ₂ Cl]]	CuInSe ₂	AA-MOCVD	450	Plate-like particles	Tetragonal	[29]
[Zn((SePiPr ₂) ₂ N) ₂]	ZnSe	AACVD	525	Fibrous	Cubic	[30]
[Ni((SePiPr ₂) ₂ N) ₂] [Co((SePiPr ₂) ₂ N) ₂]	NiSe ₂ CoSe ₂	AA-MOCVD	500 525	Wires Flakes	Cubic orthorhombic	[31]

Among the synthesized metal chalcogenides films, binary metal sulfides, such as SnS, ZnS, MoS₂ and Cu_xS, etc. constitute an important class of materials composed of a transition metal bonded to sulfur, generally represented by the formula M_xE_y (M: transition metal, E = S and 1 < x, y < 2). Their exceptional optoelectronic [32,33] and thermal properties [34,35] make them particularly suitable for a wide range of technological applications [36]. Moreover, certain metal sulfide thin films, such as MoS₂ nanowires, exhibit exceptional structural flexibility, making them highly suitable for integration into flexible electronic devices [37].

I.3. Binary metal sulfides

The use of metal sulfide thin films has become widespread in recent years due to the many advantages they offer over metal oxides, particularly in terms of electrical conductivity and optical properties. In fact, their excellent visible light transparency make them highly

suitable for applications in optical devices and solar cells, this is the case for instance for ZnS, SnS and CdS [38]. Furthermore, their manufacture is often simpler and less costly, as they can be deposited at relatively low temperatures using techniques such as sputtering or chemical vapor deposition, unlike metal oxides, which sometimes require more stringent manufacturing conditions [39].

Among these materials, Cu_xS and ZnS stand out for their valuable semiconductor properties, their non-toxic nature and their varied applications [38]. They play an essential role in the development of key areas such as optoelectronics, nanotechnology and renewable energy technologies. However, their potential remains unexplored in the field of gas detection, offering new opportunities and representing a promising challenge for their integration as innovative materials in gas sensing devices.

I.3.1. Copper sulfide (Cu_xS)

Copper sulfide (Cu_xS) is an industrially important Group I-VI p-type semiconductor with several crystallographic phases at room temperature, depending on its copper content. Copper-rich phases include chalcocite (Cu_2S), djurleite ($\text{Cu}_{1.94}\text{S}$), digenite (Cu_9S_5 or $\text{Cu}_{1.8}\text{S}$), spionkopite ($\text{Cu}_{1.4}\text{S}$) and anilite ($\text{Cu}_{1.75}\text{S}$). In contrast, copper-poor phases include covellite (CuS) and villamaninite (CuS_2) [40]. These different structures influence the material's electronic, optical and structural properties, making it particularly interesting for a variety of applications.

I.3.1.1. Optical properties

Copper sulfide (Cu_xS) has several crystalline phases that significantly influence its optical properties. The two main phases of Cu_xS are covellite (CuS) and chalcocite (Cu_2S). The covellite phase, which is the most stable, has a bandgap between 2.2 and 2.8 eV [41], enabling it to absorb light efficiently in the visible and near infrared [42]. This characteristic makes it particularly attractive for applications in optoelectronic devices, such as low-cost solar cells and photodetectors. In contrast, the chalcocite (Cu_2S) phase of copper sulfide has a bandgap of around 1.2 eV [43], which is lower than that of the covellite (CuS) phase. This difference in bandgap significantly influences the material's optical absorption properties, with the covellite phase exhibiting higher absorbance in both the visible and near-infrared regions compared to the chalcocite phase [43]. As a

result, the chalcocite phase is less suitable for optoelectronic applications that require broad-spectrum light absorption.

I.3.1.2. Electrical properties

Thin films of (Cu_xS) exhibit electrical properties that are highly dependent on its crystalline phase and the annealing conditions applied after its synthesis. The crystalline structure of Cu_xS plays a key role in its electrical conductivity. For example, the covellite (CuS) phase has a higher intrinsic conductivity than other phases such as chalcocite (Cu_2S), due to the presence of copper vacancies favoring charge carrier transport. Studies have shown that the transition between these phases can modify the carrier density and influence the electrical resistivity of the material [44].

Furthermore, the annealing temperature has a considerable influence on the electrical properties of Cu_xS , improving its crystallinity and reducing structural defects [45]. In fact, Aghad et al. demonstrated that annealing induces a phase transition from covellite (CuS) to chalcocite (Cu_2S) and subsequently to djurleite ($\text{Cu}_{1.95}\text{S}$) at 250 °C and 300 °C, respectively. They showed that this phase evolution leads to a marked decrease in electrical conductivity from $286.62 \Omega^{-1} \text{cm}^{-1}$ for covellite to $178.01 \Omega^{-1} \text{cm}^{-1}$ for chalcocite, and further down to $23.53 \Omega^{-1} \text{cm}^{-1}$ for djurleite [46].

I.3.1.3. Thermal properties

Few studies have been conducted on the thermal properties of copper sulfides (Cu_xS), despite their remarkable composition and temperature dependent behavior. For instance, Yong et al. show that Cu_2S undergoes phase transitions at elevated temperatures, significantly modifying its thermal behavior. Thermal conductivity drops from $1.60 \text{ W.m}^{-1}.\text{K}^{-1}$ for the β phase at 400 K to $0.68 \text{ W.m}^{-1}.\text{K}^{-1}$ for the α phase at 700 K [47]. These thermal characteristics underline the potential of Cu_xS -based materials for a variety of applications, for instance, in thermoelectric devices and photothermal systems.

In addition, Zhao et al. demonstrated that the difference between the crystalline phases of Cu_xS can influence thermal conductivity. Indeed, they observed a decrease in thermal conductivity from $0.5 \text{ W.m}^{-1}.\text{K}^{-1}$ for $\text{Cu}_{1.97}\text{S}$ to $0.3 \text{ W.m}^{-1}.\text{K}^{-1}$ for Cu_2S , in a temperature range between 600 and 700 K [48].

I.3.2. Zinc sulfide (ZnS)

Zinc sulfide (ZnS) is an n-type semiconductor belonging to group II-VI, with a gap energy of 3.54 eV for the cubic zinc blende (ZB) phase and 3.91 eV for the hexagonal wurtzite (WZ) phase. It offers numerous advantages, such as non-toxicity and the abundance of its elements (Zn and S). These characteristics make ZnS a particularly suitable material for optical and electrical applications.

I.3.2.1. Optical properties

ZnS has a direct bandgap of around 3.72 eV in its cubic phase and 3.77 eV in the hexagonal phase [49], enabling it to absorb and emit efficiently in the ultraviolet region and near-infrared regions [50]. These outstanding optical characteristics facilitate its integration into a variety of applications, including transparent electronic devices and optical coatings.

The optical properties of ZnS thin films are strongly influenced by deposition parameters. For instance, Hathot et al. demonstrated that increasing the deposition time during spray pyrolysis leads to a rise in film thickness from 109 nm to 150 nm resulting in a corresponding decrease in optical transmittance, from 74 % to 61 % [51].

Studies by F. Göde have demonstrated that the annealing temperature ranging from 100 °C to 500 °C significantly influences the optical properties of ZnS thin films, showing a decrease in the bandgap energy from 4.01 eV in the as-deposited films to 3.82 eV after annealing at 500 °C [52].

I.3.2.2. Electrical properties

Zinc sulfide (ZnS) is a semiconductor with n-type conductivity [53]. Recent studies have considerably improved our understanding of the electrical properties of zinc sulfide (ZnS), highlighting its potential in a variety of applications.

A study by Koaib et al. investigated the influence of annealing temperature on the electrical and dielectric properties of ZnS thin films. The results showed that the electrical conductivity increased after annealing at 350 °C, but decreased when the annealing temperature was raised further to 450 °C, which may be attributed to a decrease in defect states, which enhances carrier mobility and energy gap [54]. Similarly, other research groups have studied the effect of annealing on the resistivity of ZnS. Before annealing,

ZnS has a resistivity of $5.15 \times 10^3 \Omega\cdot\text{cm}$, which changes with annealing temperature: it increases to $6.51 \times 10^3 \Omega\cdot\text{cm}$ at 300 °C, then gradually decreases to $3.62 \times 10^3 \Omega\cdot\text{cm}$ and $1.79 \times 10^3 \Omega\cdot\text{cm}$ after annealing at 400 °C and 500 °C, respectively [55].

Furthermore, a study by Othman et al. revealed that Mn-doped ZnS nanoparticles exhibit higher dielectric constant values ($\epsilon_r = 160$) than undoped ZnS nanoparticles ($\epsilon_r = 70$), thus indicating an increase in grain boundary depletion potential [56]. Other research groups have demonstrated that varying the Cu/S molar concentration ratio within the range of 0.40 to 0.45 M significantly influences film resistivity, reporting an increase from approximately 10^{-4} to $5 \times 10^{-4} \Omega\cdot\text{cm}$ [57].

I.3.2.3. Thermal properties

A few studies address the thermal properties of ZnS, including one by Mandal et al., which examines the thermal conductivities of pure ZnS and core/shell ZnS/CdS nanowires as a function of temperature. The results show that the thermal conductivity of pure ZnS and core/shell nanowires decreases slightly with increasing temperature (300-700 K), which is in line with the expected reduction in average phonon free length at higher temperatures. In addition, core/shell ZnS/CdS nanowires exhibit lower thermal conductivity than pure ZnS nanowires over the entire temperature range [35].

I.4. Metal sulfide thin films deposition methods

Metal chalcogenide thin films have been prepared by a variety of physical and chemical methods, including pyrolysis spray [58,59], electrochemical deposition [60,61], chemical bath deposition [62,63], vapor deposition [64,65], hydrothermal method [66,67], sputtering [68,69] and atomic layer deposition [70,71]. Figure I.3 provides a schematic illustration of all these techniques.

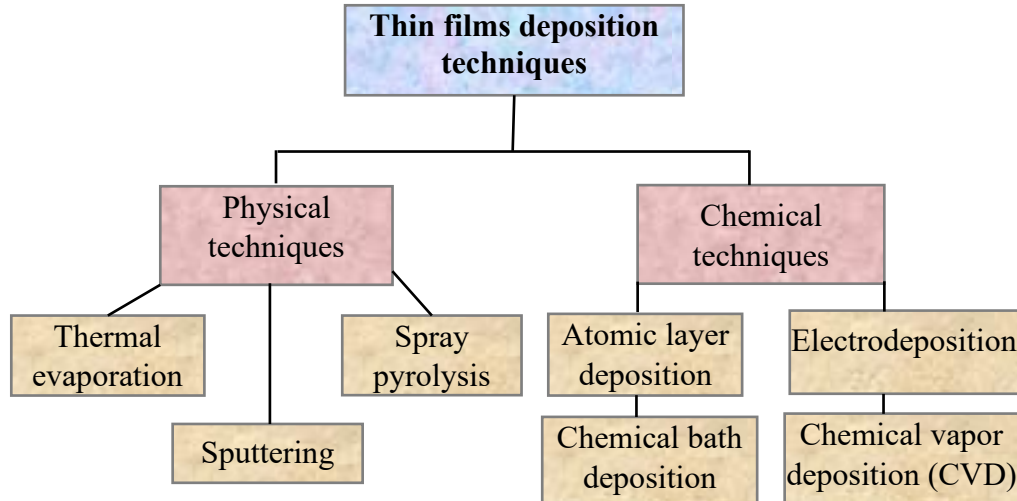


Figure I. 3. Classification diagram of deposition methods used for synthesizing metal chalcogenide thin films.

The following section focuses on deposition techniques for Cu_xS and ZnS , along with the critical process parameters that govern the characteristics of the resulting thin films.

I.4.1. Copper sulfide (Cu_xS) deposition techniques

I.4.1.1. Spray pyrolysis

Spray pyrolysis is a widely used technique for depositing copper sulfides. The process involves atomizing a precursor solution into fine droplets, which are then sprayed onto a heated substrate. This method is prized for its simplicity, low cost and scalability, making it ideal for the manufacture of a wide range of materials, such as semiconductors, oxides and other functional thin films used in solar cells, sensors, and catalysts.

The quality of the resulting film can be influenced by a number of factors, such as the precursor concentration. Pradeepa et al. have successfully deposited CuS thin films from a mixture of copper sulfate (Cu precursor) and thiourea (S precursor). They studied the effect of varying the concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.05 M, 0.1 M, 0.15 M, 0.2 M) versus a fixed concentration of thiourea (0.1 M) on the morphology and optical properties of CuS [58]. Another factor to take into account includes the substrate temperature. Previously, the research group of Firat et al. studied the effect of glass substrate temperature on the crystalline phase, crystallite size and surface uniformity of thin films. They observed that an increase in substrate temperature led to a decrease in crystallite size, from 11.92 nm to 9.60 nm. In addition, a phase change was observed: at 240 °C, the film consisted of the hexagonal CuS phase, while at 280 °C, it exhibited the cubic $\text{Cu}_{1.765}\text{S}$

phase. When the substrate temperature reached 320 °C, the copper sulfide thin film revealed a polycrystalline structure composed of mixture of cubic $\text{Cu}_{1.76}\text{S}$ and hexagonal Cu_2S phases [72].

I.4.1.2. Electrodeposition

Copper sulfide electrodeposition (Cu_xS) is an electrochemical process in which a film of copper sulfide is deposited on a conductive surface from an electrolytic solution containing copper ions and sulfide compounds. This process requires the application of an electric current in an electrochemical cell, where specific conditions must be met to promote Cu_xS formation. Among these conditions, the concentration of copper and sulfide ions in the electrolyte, as well as the temperature and pH of the solution, play a crucial role. Precise control of these parameters results in Cu_xS films with targeted properties, used in a variety of applications such as solar cells, sensors and optoelectronic devices.

Numerous studies have successfully synthesized (Cu_xS) thin films using this method, highlighting the impact of different parameters on the properties of the films obtained. Among them, Yang and Hu studied the effect of bath temperature on the crystallinity of the copper sulfide (CuS) formed. They reported that nanoparticles produced at room temperature were weakly crystalline, whereas an increase in temperature to 80 °C resulted in the formation of well-structured crystalline particles [73].

Furthermore, Dhasade et al. investigated the effect of deposition time on the growth of CuS nanorods at room temperature by the electrodeposition method and demonstrated its influence on the optical bandgap energy of the resulting films, which increased from 2.05 eV to 2.49 eV as deposition time varied from 15 min to 30 min [74].

I.4.1.3. Atomic layer deposition (ALD)

Thin copper sulfide films can be deposited efficiently using the atomic layer deposition (ALD) technique, which allows precise control of film thickness and composition. The ALD principle is based on the sequential introduction of precursor chemicals into a reaction chamber. Each precursor is introduced separately and reacts only with the substrate surface, saturating it to form a monolayer. After each step, an inert gas is used to remove unreacted molecules and by-products, ensuring precise thickness control. This cycle is repeated until the desired thickness is reached, enabling layer-by-layer growth.

Schneider et al. used this technique to deposit Cu_xS thin films, using copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$) and hydrogen sulfide (H_2S) as precursors for copper and sulfur. Deposition was carried out over a temperature range from 130 to 300 °C. The properties of the films obtained are highly dependent on the number of deposition cycles, particularly in terms of thickness and chemical composition. Depending on the conditions, it is possible to obtain either multiphase compounds consisting of digenite ($\text{Cu}_{1.8}\text{S}$), chalcocite (Cu_2S), djurleite ($\text{Cu}_{31}\text{S}_{16}$) and covellite (CuS), or single-phase digenite ($\text{Cu}_{1.8}\text{S}$) films. This process is based on a growth mechanism involving in situ reduction of copper and loss of sulfur by evaporation [75].

Other copper precursors, such as CuCl [76], copper di-sec-butylacetamidinate [$\text{Cu}(\text{sBu-amd})_2$] [77] and copper bis-tetramethylheptanedionate [$\text{Cu}(\text{thd})_2$] [78], have been used to produce copper sulfide thin films.

I.4.1.4. Chemical bath deposition (CBD)

Chemical bath deposition of copper sulfide (Cu_xS) is a widely used solution synthesis technique for the manufacture of thin films, thanks to its simplicity, efficiency and low cost. The process is based on the controlled precipitation of Cu_xS from a solution containing copper ions (Cu^{2+}) and sulfur sources (such as thiourea or sodium sulfide) in an aqueous medium. Film formation relies on the nucleation and progressive growth of Cu_xS particles on an immersed substrate, under the influence of key parameters such as temperature, pH, precursor concentration, and deposition time. By adjusting these parameters, it is possible to control the thickness, morphology and crystallinity of the films obtained.

Gracia et al. deposited Cu_xS thin films using the chemical bath deposition (CBD) method, varying the bath temperature from 25 to 70 °C [79]. They showed that increasing the bath temperature up to 70 °C significantly improved the crystallinity and morphology of the films. Optical properties were also affected: a higher density of free carriers was observed, leading to a decrease in near-infrared transmittance due to absorption by these carriers. Finally, they found that an increase in temperature caused a sharp decrease in resistivity, with values ranging from 10^6 to $10^{-2} \Omega\cdot\text{cm}$.

Other research groups have studied the effect of precursor concentration and bath pH on the thickness and crystallinity of CuS films. They reported that increasing the CuSO_4

concentration from 0.1 M to 0.15 M led to a decrease in film thickness from 148 nm to 136 nm, while improving CuS crystallinity. In addition, increasing bath pH leads to faster film growth, resulting in an increase in film thickness [80].

I.4.1.5. Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is a widely used technique for manufacturing thin films of materials on solid substrates. It is based on the chemical reaction of gaseous precursors, which decompose or react on the surface of the heated substrate to form a solid film. Depending on the nature of the precursors and the operating conditions (temperature, pressure, gas flow), different process variants can be used, such as low-pressure CVD (LPCVD), metal-organic chemical vapor deposition (MO-CVD) or aerosol-assisted chemical vapor deposition (AACVD).

Meester et al. synthesized Cu_xS nanoparticles in the size range 100-500 nm by low-pressure chemical vapor deposition (LP-CVD) at temperatures ranging from 127 °C to 505 °C. They demonstrated that films deposited at temperatures below 230 °C are composed of pure CuS, while the phase composition begins to evolve towards a mixture of CuS and Cu_9S_5 above 230°C. Pure Cu_9S_5 was obtained at deposition temperatures between 285 °C and 315 °C [81].

Nomura et al. deposited CuS particles at 400 °C and $\text{Cu}_{1.96}\text{S}$ sheet-like structures at 450 °C using the chemical vapor deposition from metal-organic precursors (MO-CVD) technique, using the copper(I) bis(diethyldithiocarbamate) complex, $\text{Cu}(\text{dtcEt}_2)_2$, as a single-source precursor [82].

The O'Brien group has investigated the use of copper complexes as single-source precursors for the synthesis of various copper sulfide phases (Cu_xS) via the AACVD method. For example, copper(II) dithiocarbonates complexes $[\text{Cu}(\text{S}_2\text{CNR}_2)_2]_2$ and bis(piperidinedithiocarbamate)copper(II) $[\text{Cu}(\text{Ppdtc})_2]_2$, have been used to produce slabs of digenite ($\text{Cu}_{1.8}\text{S}$) at 450 °C [83] and djurleite ($\text{Cu}_{1.94}\text{S}$) at 350, 400 and 450 °C, respectively [84]. Similarly, a copper(II) thiobiuret complex, $[\text{Cu}(\text{SON}(\text{CNiPr}_2)_2)_2]$, yielded chalcocite (Cu_2S) with scalable morphologies, including spheres, grains, and plates, as a function of deposition temperatures (280-400 °C) [85].

In another study, copper xanthate complexes such as $[\text{Cu}(\text{SCSOCH}_2\text{CH}(\text{CH}_3)_2)_2]$ were used to synthesize Cu_2S nanoparticles. By varying solvents and deposition temperatures

between 175 °C and 250 °C, spherical, flower-shaped or flake-like nanostructures were obtained [86].

I.4.2. Zinc sulfide (ZnS) deposition techniques

I.4.2.1. Electrodeposition

Ghezali et al. studied the electrodeposition of zinc sulfide thin films, highlighting the effect of applied potential on the properties of the films obtained. AFM and SEM studies revealed that increasing the deposition potential from -1 V to -1.3 V had a strong influence on film morphology, shape, crystallite size and thickness. In addition, X-ray diffraction analyses showed that the crystallinity of ZnS thin films improved with increasing deposition potential, indicating better structural organization at higher potentials [87].

Another research group investigated the influence of the complexing agent, triethanolamine (TEA), concentration on film morphology, increasing it from 1% to 4% in the deposition bath. They observed a marked improvement in film quality, characterized by higher density and more complete surface coverage of the substrate. Additionally, the same group demonstrated that raising the pH of the electrolyte bath from 3.5 to 5 significantly reduced the size of the ZnS nanoparticles from approximately 160 nm to 40 nm accompanied by a corresponding decrease in the optical bandgap energy from 3.98 eV to 3.74 eV [88].

I.4.2.2. Hydrothermal deposition

Previous studies have demonstrated the synthesis of zinc sulfide (ZnS) films by the hydrothermal method, revealing varied morphologies influenced by deposition conditions, such as the choice of precursors, autoclave temperature and time, and the use of surfactants. Notably, Ibupoto et al. reported the formation of ZnS nanoclusters composed of nanowires using zinc acetate dihydrate and thiourea as precursors for Zn^{2+} and S^{2-} , respectively. Their work highlighted the significant impact of the concentration of the cationic surfactant cetyltrimethylammonium bromide (CTAB) on the growth, length, and thickness of ZnS nanowires [89].

Other research groups have demonstrated a wide variety of ZnS morphologies using different surfactants that promote crystal growth along specific directions. This surfactant-mediated control not only enables precise tuning of particle shape but also

effectively prevent agglomeration. For example, ZnS microspheres and hollow nanospheres have been synthesized using acrylamide as a surfactant [90], or the polymer polyvinylpyrrolidone (PVP) [91] and polyvinylidene fluoride (PVDF) to obtain ZnS nanowires [92].

I.4.2.3. Atomic Layer Deposition (ALD)

The deposition of ZnS thin films using the atomic layer deposition (ALD) technique has also been widely explored, highlighting the use of specific precursors to ensure precise control of film thickness and composition. Commonly employed precursors include zinc diethyl (DEZn) in combination with hydrogen sulfide (H_2S), used in a temperature range from 200 to 350 °C [93]. Other studies have explored alternative precursors, such as organometallic compounds containing sulfide ligands, to improve the structural and optical properties of the resulting films [94,95]. In addition, the influence of deposition parameters, notably the number of ALD cycles and temperature, has been studied to optimize the morphology, crystallinity, and transmittance of ZnS films [96,97].

I.4.2.4. Chemical bath deposition (CBD)

Several studies have reported the deposition of ZnS thin films by the chemical bath method, highlighting the influence of various parameters on the structural and optical properties of the resulting ZnS thin films [98]. These parameters include bath temperature, precursor concentration, solution pH, deposition time, and the effect of annealing on film characteristics. For example, Abdullah et al. examined the impact of deposition time on the properties of the films formed. They showed that an increase in deposition time from 18 h to 39 h resulted in a significant increase in film thickness, as well as a growth in grain size from 37 nm to 56 nm. In addition, an increase in bandgap energy was observed, from 2.45 eV to 3.53 eV [99].

The work of Mohammed et al. demonstrated that the bandgap energy of narcissus-like ZnS nanostructures is tunable via CBD parameters. Their results indicated that an increase in deposition time (5–60 min), pH (9–11.5), bath temperature (40–75 °C), or precursors concentration (0.05–0.3 M) resulted in a decrease in the bandgap energy from 4.0 eV to 3.9 eV [100].

I.4.2.5. Chemical vapor deposition (CVD)

The deposition of ZnS thin films has been achieved also through a variety of chemical vapor deposition methods like atmospheric-pressure (AP-CVD), metal-organic (MO-CVD), and low-pressure (LP-CVD).

Researchers have synthesized polycrystalline ZnS films by the CVD technique, using high temperatures ranging from 590-630 °C to 700-800 °C. They then studied the optical properties of the films obtained, demonstrating a high transmittance of around 75 % [101,102]. In addition, other investigations show the synthesis of ZnS using the metal-organic chemical vapor deposition (MO-CVD) technique. The results show significant differences in the properties of the films obtained, depending on the deposition temperature. For example, Kumar et al. optimized the growth of ZnS nanowires on GaAs substrates over a temperature range from 400 to 550 °C [103], using zinc diethyl (DEZn) as the zinc source and di-tert-butyl sulfide (DTBS) as the sulfur source. Similarly, Melhem et al. deposited a single-crystal layer of ZnS-WZ (wurtzite) at a temperature of 360 °C [103,104] using the same precursors. Few studies have also been reported on the use of low-pressure CVD (LP-CVD) for the deposition of ZnS films [105].

Recently, a new approach to elaborating zinc sulfide using single-source precursors (SSPs) has attracted growing interest, in particular thanks to the aerosol-assisted CVD (AACVD) technique. This method has been the subject of numerous studies due to its significant advantages, including simplification of the synthesis process, improved film quality, and a reduction in the number of precursors, thus limiting the risk of deposit contamination.

Various metal complexes have been synthesized and used as SSPs for the AACVD deposition of ZnS thin films. These include zinc thiosemicarbazones, deposited at temperatures between 400 and 500 °C [106], and zinc(II) thioureides ($S=C=N-R$; $R = iPr$, Cy , tBu , $C_6Me_3H_2$) deposited at temperatures ranging from 150 to 300 °C [107]. In addition, other studies have explored the use of zinc(II) dithiobiuret complexes bearing different alkyl substituents ($R = ethyl$, $methyl$, $butyl$) and have demonstrated the influence of the R radical on the morphology of the ZnS films obtained [108,109].

I.4.3. AACVD technique and its advantages

Aerosol-Assisted Chemical Vapor Deposition (AACVD) is a thin-film deposition technique based on the atomization of a precursor solution into fine droplets in the form of an aerosol, which is then transported by a carrier gas (such as nitrogen) to a heated substrate. Upon arrival on the substrate, the solvent evaporates, leaving the precursor to thermally decompose or chemically react to form the desired material in the form of a homogeneous thin film.

Figure I.4 illustrates the surface reactions involved in the growth of material, transported in aerosol form, within the aerosol-assisted chemical vapor deposition (AACVD) chamber.

Typically, two types of reaction can occur when the aerosol enters the chamber:

- Heterogeneous reaction in AACVD thin films deposition

During aerosol-assisted chemical vapor deposition (AACVD) process, precursor molecules (metal complexes) in the gaseous state are directed towards a heated substrate surface (e.g., silicon). When they come into contact with the surface, these species undergo adsorption, i.e. they attach themselves to the surface by physical or chemical bonds. After this initial interaction, adsorbed molecules can diffuse along the surface, exploring energetically favorable positions to organize themselves structurally.

A limited number of atoms or molecules form a regular crystal lattice. These are the preferred sites for the subsequent accumulation of matter, enabling progressive growth. As new species from the precursors reach these sites, the crystal lattice expands, eventually leading to the formation of a continuous, uniform thin film.

The quality and morphology of the resulting film are highly dependent on process parameters such as substrate temperature, surface energy and precursor decomposition, which together influence adsorption, diffusion and nucleation kinetics [110,111].

- Homogeneous reaction in the AACVD thin films deposition

In a homogeneous reaction during aerosol-assisted chemical vapor deposition (AACVD), precursor decomposition can occur prematurely in the vapor phase. This premature decomposition can lead to the formation of by-products in the form of fine vapor phase particles. This phenomenon is mainly due to the high temperature applied, but is also

influenced by other parameters such as transport time, carrier gas flow rate, and the solvent used during deposition. If these fine particles are adsorbed onto the substrate surface, they may undergo subsequent heterogeneous reactions. This secondary reaction mechanism often leads to the formation of porous films, which can affect the morphology and quality of the deposited material [110,111].

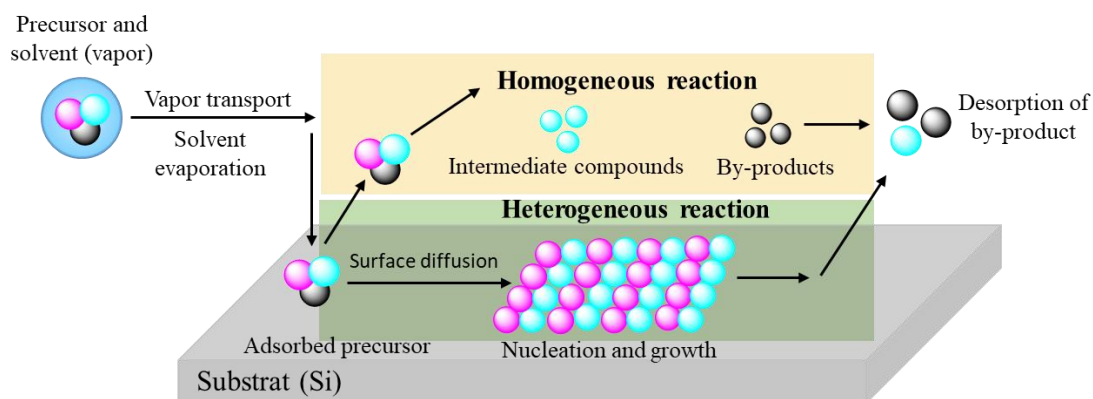


Figure I. 4. Schematic illustration of surface reactions and material growth in AACVD.

Compared with other conventional CVD methods, AACVD (Aerosol Assisted Chemical Vapor Deposition) offers several notable advantages for depositing thin films [112,113]:

- Operates at atmospheric pressure, simplifying equipment and reducing costs.
- Allows the use of non-volatile precursors, as precursor solubility is more important, broadening the range of materials that can be used.
- Unlike CVD, which can require temperatures as high as 1000 °C for certain materials, this method operates effectively at much lower temperatures. For example, ZnS can be deposited via AACVD at 200–300 °C [114], compared to 590–630 °C using conventional CVD [115].

Like other deposition techniques, Aerosol-Assisted Chemical Vapor Deposition (AACVD) involves several tunable parameters that critically influence the quality of the resulting thin films. These parameters govern the nature of surface reactions whether heterogeneous or homogeneous and directly affect the structural, morphological, and functional properties of the deposited films. The key parameters include [116]:

- Choice of precursor: This is one of the most critical factors in AACVD. To achieve precise control over film composition and quality, we employ metal complexes as single-source precursors. These precursors offer tailored solubility and well-defined

thermal decomposition profiles, enabling the reproducible deposition of high-quality thin films.

- Substrate temperature: Temperature plays a pivotal role in determining reaction kinetics, film crystallinity, and adhesion to the substrate.
- Carrier gas flow rate: This parameter influences precursor transport in the reaction zone, and ultimately the uniformity and thickness of the deposited film.
- Solvent: The choice of solvent plays a crucial role in AACVD, as its physicochemical properties particularly boiling point, heat of combustion, and density significantly influence the morphology of the resulting thin films [117].
- Aerosol droplet size: Controlled using an ultrasonic atomizer to produce droplets of optimal size for efficient delivery into the AACVD reactor. Finer droplets facilitate more complete precursor vaporization resulting in more uniform and higher-quality thin films [118].

I.5. Application areas for Cu_xS and ZnS thin films

The remarkable electronic and optical properties of copper sulfide (Cu_xS) and zinc sulfide (ZnS) make them particularly attractive materials for a wide variety of applications, both industrially and in materials science research. Figure I.5 illustrates the various fields of application for these compounds, with concrete examples. The technological importance of these semiconductors will be explored in greater depth in the following sections.

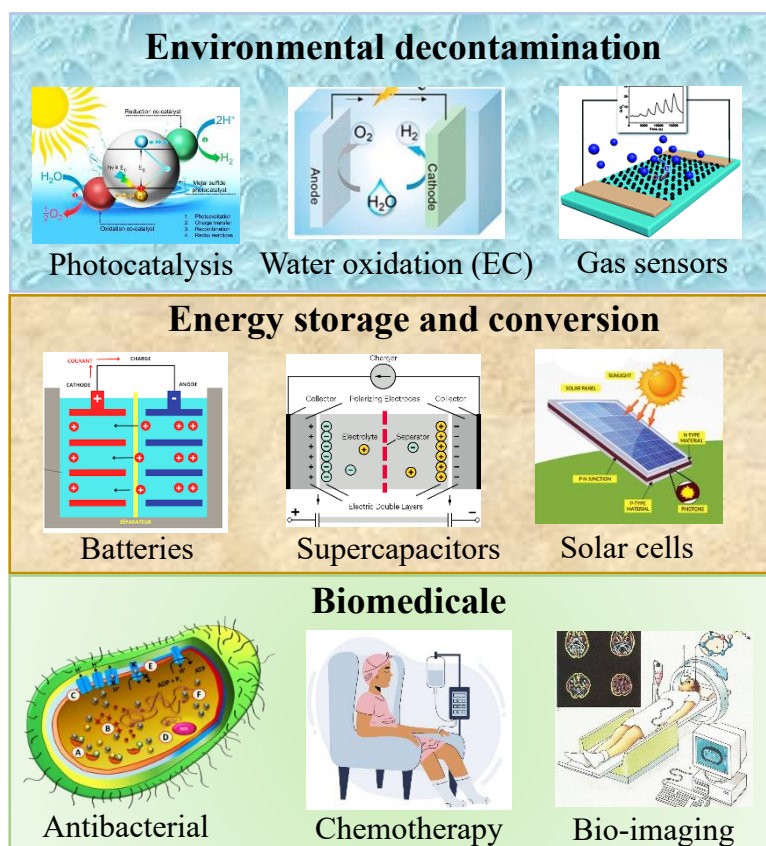


Figure I. 5. Applications fields of copper and zinc sulfide thin films.

I.5.1. Copper sulfide (Cu_xS) application fields

I.5.1.1. Solar cells: Photovoltaics

Copper sulfide (Cu_xS) thin films, particularly p-type, have been widely exploited in solar cell applications thanks to their high efficiency, outstanding optical and electrical properties, and low production cost. These materials are characterized by high light absorption coefficients, enabling them to efficiently capture sunlight even in the form of thin films, an essential factor in optimizing energy conversion efficiency.

In this context, Kamazani et al. studied the influence of Cu_2S morphology ranging from nanospheres and nano-flowers to quantum dots and bulk films on solar cell efficiency. Their results demonstrated that quantum dots achieved the highest energy conversion efficiency (37 %), followed by nanoflowers and microspheres, while bulk films showed the lowest performance. This study highlights the importance of controlling material morphology to improve the performance of photovoltaic devices [119].

Hamed et al. demonstrated that incorporating 3 % copper sulfide (CuS) as a dopant into the P3HT:PC₆₁BM active layer of a bulk heterojunction photovoltaic cell structured as

glass/ITO/PEDOT: PSS/P3HT:PC₆₁BM: CuS/LiF/Al significantly enhances the device's power conversion efficiency energy conversion efficiency, with an increase of up to 69 % compared to undoped devices. Optimum performance was achieved with an energy conversion efficiency (PCE) of 5.04 % under ambient conditions [120].

Other studies have focused on the heterostructures formed by various metal sulfides combined with Cu_xS, demonstrating that the addition of copper sulfide significantly improves the energy conversion efficiency of solar cells. For example, in the case of PbS/Cu_{2-x}S-based devices, an energy conversion efficiency of up to 8.07 % was achieved, compared with just 2.36 % for a PbS-based device of the same thickness. Similarly, CdS/Cu₂S heterostructures, where Cu₂S thin films have a greater thickness than CdS, have also shown a marked improvement in performance, with efficiencies of up to 8.5 % [121]. In addition, other photovoltaic devices based on CuS/WS₂ and CuS/MoS₂ heterostructures deposited by sputtering and chemical vapor deposition have been reported by the group of Husain et al. showing energy conversion efficiencies of 8.21 % and 7.12 %, respectively [122]. This work illustrates the interest of Cu_xS in improving photovoltaic devices.

I.5.1.2. Energy storage

Energy storage has become a fundamental element of modern technological progress, playing a crucial role in meeting the world's growing demand for sustainable and efficient energy solutions. In this context, advanced materials with exceptional properties are essential for developing high-performance energy storage devices. Among these materials, copper sulfide (Cu_xS) stands out as a promising candidate thanks to its unique combination of properties, including high electrical conductivity, excellent redox activity and structural adaptability. These characteristics make Cu_xS particularly suitable for applications in lithium-ion batteries, sodium-ion batteries, and supercapacitors [123].

Several research groups have explored the use of Cu_xS copper sulfide as a promising electrode material for rechargeable metal-ion batteries, including lithium (Li), magnesium (Mg), sodium (Na) and aluminum (Al) batteries [124–127]. These studies highlight the potential of Cu_xS thanks to its outstanding electrochemical properties, such as high charge storage capacity, cyclic stability and electrical conductivity, which make it a key candidate for efficient and sustainable energy storage systems.

Wu et al. reported the use of CuS nanoparticles as high-performance cathode materials for magnesium secondary batteries. These materials feature a high reversible capacity of 175 mA h g⁻¹ at a current density of 50 mA g⁻¹. In addition, the cathode shows excellent high-speed performance maintenance, with a capacity of 90 mA h g⁻¹ at a current density of 1000 mA g⁻¹, as well as exceptional long-term stability, retaining its performance over more than 350 cycles [128].

In addition, copper sulfide thin films (Cu_xS) have been widely used as materials for electrochemical supercapacitors, thanks to their remarkable electrochemical properties, including high charge storage capacity and cyclic stability [129–131]. These characteristics enable Cu_xS-based supercapacitors to offer high energy density, fast charging time and long lifetime [132], making them ideal candidates for applications requiring fast, reliable energy supply, thus meeting the growing demands of modern technologies.

I.5.1.3. Biomedical field

Copper sulfide (Cu_xS) has been used for biological applications, both in vitro and in vivo, due to its non-toxic nature and unique properties. In in vitro applications, CuS nanoparticles are widely used as biosensors for DNA detection, food analysis and bioreactor monitoring [133]. In addition, copper sulfide nanoparticles (Cu_xS) have proven to be a versatile and promising material in the medical field. They feature excellent biocompatibility, remarkable photothermal conversion efficiency due to their ability to absorb near-infrared (NIR) light and convert it into heat, and suitability as drug carriers. These features have paved the way for a wide range of applications, notably in cancer therapy, where they are used for photoacoustic imaging, photothermal therapy and transdermal drug delivery systems [134,135].

I.5.1.4. Photocatalysis

Copper sulfide is currently being extensively explored as a photocatalyst due to its many advantageous properties. It is environmentally friendly, economical and non-toxic, while exhibiting excellent chemical stability as well as unique optical and electrical characteristics [136,137]. These properties increase its effectiveness in removing dyes from wastewater. In addition, copper sulfide shows an impressive ability to efficiently capture solar energy, generating electron-hole pairs that play a crucial role in the redox reactions essential to photocatalytic processes.

Ajibade et al. demonstrated significant percentage degradation of certain pollutants using CuS nanoparticles synthesized from a single precursor, Cu(II) dithiocarbamate. These nanoparticles achieved an impressive 85 % degradation of crystal violet (CV), 100 % degradation of methylene blue (MB) and 81 % degradation of rhodamine B (RhB) over 120 min. In addition, the nanoparticles were able to degrade a ternary mixture of all three dyes (CV/MB/RhB), highlighting their potential for treating systems contaminated with complex dyes [138].

Another research group has shown that CuS microflowers (3D) decompose rhodamine B very rapidly under visible light. They achieved 64 % degradation in 3 minutes and almost complete degradation (99 %) in 12 minutes [139]. Other Cu_xS morphologies have been used as photocatalysts for the degradation of RhB and MB. These morphologies include, among others, microspheres [140], nanotubes [141], and flower-like structures [142] and others [143,144]. Their degradation efficiency ranges from 70 % to 100 % under visible light.

I.5.1.5. Gas sensors

A limited number of studies have explored the use of copper sulfide thin films (Cu_xS) as gas sensors. For instance, Cu_xS-based sensor was developed by Galdikas et al. for the detection of ammonia (NH₃) at room temperature [145]. Sagade and Sharma subsequently extended this work by exploring different Cu_xS stoichiometries (where x = 1, 1.4 and 2), demonstrating the influence of material composition on sensor performance [146].

Wang et al. studied hydrothermally deposited CuS flower-shaped nanostructures for ethanol sensing. In this study, they demonstrated that the sensor exhibits high sensitivity to ethanol at an operating temperature of 260 °C, with a response that increases proportionally with ethanol concentration. In addition, a comparison of CuS sensitivity at 170 °C to 100 ppm of other volatile organic compounds (VOCs), such as methanol, benzene, dichloromethane and hexane, revealed a significantly higher response to ethanol, with an R_g/R_a ratio of 5.22, higher than that obtained for the other gases. These results underline the excellent selectivity and performance of CuS for the specific detection of ethanol [147].

I.5.2. Zinc sulfide (ZnS) application fields

I.5.2.1. Solar cells: Photovoltaics

ZnS thin films have attracted considerable interest as next-generation materials for various types of solar cells, including dye-sensitized solar cells (DSSCs), quantum dot-sensitized solar cells (QDSCs), Cu(In,Ga)Se₂-based thin-film solar cells (CIGS), as well as organic-inorganic hybrid solar cells [148].

Sánchez et al. have demonstrated that the use of ZnS quantum dots (QDs) synthesized in the presence of the polymer polyvinylpyrrolidone (PVP) as a stabilizing agent significantly improves solar cell performance. Specifically, the efficiency of commercial polycrystalline solar cells increased by 6.1 % after the deposition of ZnS (QDs) synthesized with a concentration of 0.10 mM PVP, underlining the importance of this polymer in optimizing photovoltaic properties [149].

Other studies have explored heterojunctions of ZnS with other metal sulfides with the aim of improving the performance of photovoltaic cells. Notable examples include ZnS/MoS₂ [150], ZnS/SnS [151], ZnS/CdS [152], and ZnS/PbS [153] heterojunctions. In addition, double heterojunctions, such as ZnS/ZnSe/CdTe [153], have also been investigated for their potential to optimize the efficiency of photovoltaic devices by promoting better charge separation and transport.

I.5.2.2. Energy storage

Zinc sulfide (ZnS) is attracting growing interest as an electrode material for supercapacitors due to its low cost, high conductivity and eco-friendliness. Various ZnS nanostructures have been developed to enhance electrochemical performance, including ZnS nanosheets with a high specific capacitance of 347.3 F.g⁻¹ and excellent cyclic stability [154], hydrothermally synthesized ZnS nanoflakes achieving a remarkable specific capacitance of 650 C.g⁻¹ [155], and solvothermally prepared graphene nanocomposites decorated with ZnS nanoparticles, offering 197.1 F.g⁻¹ [156]. These advances underline the potential of ZnS for high-performance energy storage.

In addition, ZnS films are being widely studied as a promising anode material for batteries. In 2016, Su et al. demonstrate ZnS's high sodium (Na) ion storage performance [157]. Subsequently, other studies have explored the use of ZnS in different morphologies as an anode material in sodium, lithium, and potassium batteries [158–161].

I.5.2.3. Optoelectronics

Zinc sulfide (ZnS), as an n-type semiconductor, is one of the most widely recognized materials for its outstanding optical properties. It has excellent transparency in the visible and infrared regions (>60 %) [162], making it particularly suitable for advanced optoelectronic applications. These include coatings, photodetectors and sensors, where its ability to efficiently convert light into electrical signals plays a crucial role.

In this context, several research groups have developed ZnS thin films using various deposition techniques such as spray pyrolysis, sequential ion adsorption reaction (SILAR) and thermal evaporation, and investigated their performance as photodetectors in the UV region. These studies have demonstrated ZnS remarkable stability over time, as well as excellent sensitivity [163–165].

Due et al. studied the optoelectronic properties of ZnS nanowires synthesized by thermal chemical vapor deposition and demonstrated their suitability for use in light detection devices under ultraviolet B (UVB) irradiation. The device showed a photocurrent gain of 0.572, a responsivity of 2.761 mW/cm², a response time of 3.2 s and a recovery time of 3.6 s, underlining its potential for efficient UVB detection [166].

I.5.2.4. Photocatalysis

Zinc sulfide (ZnS) thin films also show promising photocatalytic properties, attributed to their strongly negative reduction potential for excited electrons and their ability to rapidly generate excitons under light irradiation. These characteristics make them particularly effective for the degradation of various pollutants. Notably, Baran et al. demonstrated the enhanced photocatalytic activity of ZnS functionalized with ruthenium nanoparticles for CO₂ reduction, underlining its potential in pollution control applications [167].

Several studies have investigated the degradation of (RhB) using different ZnS morphologies. Among these, ZnS nanoparticles synthesized by hydrothermal methods achieved a degradation rate of 87 % under solar irradiation [168], while ZnS quantum dots obtained by thermolysis showed an efficiency of 71.46% under visible light [169]. In addition, nanobats achieved maximum photocatalytic degradation of 93 % after 60 minute of exposure to sunlight [170], and hydrothermally synthesized ZnS nanospheres showed promising photocatalytic activity under UV irradiation [171].

I.5.2.5. Gas sensors

Different ZnS nanostructures with varying morphologies have demonstrated potential for detecting various volatile gases [172]. Specifically, ZnS nanospheres and nanoparticles have been used to detect formaldehyde (CH_2O) at room temperature and 295 °C [173]. ZnS nanowires showed efficiency in detecting acetone ($\text{C}_3\text{H}_6\text{O}$) and ethanol ($\text{C}_2\text{H}_6\text{O}$) at 320 °C [174], while ZnS nanobands revealed sensitivity to oxygen [175] and hydrogen (H_2) [176]. These distinct performances can be attributed to the specific structural and electronic properties induced by each morphology, which directly influence the adsorption and desorption mechanisms of gaseous molecules on the material surface.

Recent studies have explored the functionalization of ZnS thin films with gold (Au) nanoparticles, resulting in improved sensitivity to other gases, notably NO_2 under photoactivation [177], as well as to several volatile organic compounds (VOCs) at 260 °C [178].

In addition, other research has investigated the doping of ZnS-based sensors with various metals to improve their performance. Among these studies, Jeyad and Abbas examined ZnS thin films doped with different concentrations of tin (Sn), ranging from 10 % to 25 %. Their results showed that ZnS films doped with 25 % Sn exhibited significantly improved crystallinity, resulting in increased sensor sensitivity as well as faster response times compared with undoped ZnS [179].

I.6. Solid-state Gas sensors

A gas sensor is a device capable of detecting the presence and concentration of gases in a given environment. It works by converting a chemical or physical interaction between the target gas and a sensitive material into a measurable electrical (e.g., resistance, frequency, current, or voltage) [180] and/or optical (e.g., absorbance, luminescence) signals.

In pursuit of facilitating the measurement of these signals, a variety of gas-sensing transducing platforms may be employed, based on bulk or micro-electro-mechanical systems (MEMS)-based substrates, opaque or transparent substrates, or rigid and flexible substrates [181]. Thus, the choice of the transducing platforms is linked to the sensing principle to be applied (e.g., resistive, optical, acoustic, magnetic, etc.).

For instance, optical sensors demand substrates with high transparency in the operational wavelength range (e.g., glass for visible/NIR detection), while chemiresistive sensors often rely on thermally insulating, micromachined MEMS platforms to minimize power consumption during high-temperature operation. Similarly, acoustic wave devices (e.g., SAW (Surface Acoustic Wave) or QCM (Quartz Crystal Microbalance) sensors) require piezoelectric substrates that can efficiently generate and detect mechanical vibrations. Additionally, the platform must also support environmental stability and scalable fabrication.

Overall, the performance of the sensor is assessed based on several key functional parameters, including sensitivity, selectivity, precision, limit of detection (LOD), reversibility, and response and recovery times.

- Sensitivity: is the ability of a gas sensor to detect the lowest concentration of a target gas. It can be defined as the slope of its calibration curve, representing the change in sensor response per unit change in the concentration of the target gas [182], and can be expressed as:

$$S = \frac{\Delta \text{Response}}{\Delta \text{Concentration}}$$

- Selectivity: is the ability of gas sensor to determine a specific gas in the presence of other components [183]. The selectivity factor/coefficient (K) of the target gas to another gas is defined as:

$$K = \frac{S_1}{S_2}$$

Where S1 and S2 represent the sensitivities of the sensor to a target gas and another gas, respectively.

- Response time: is defined as the time a sensor takes to reach 90 % of its of its fully deviated value, while recovery time refers to the time required for the sensor to return to its baseline or initial state after the gas is removed.
- Stability: may be defined as the ability of a gas sensor to produce reliable measurements for fixed interval of time or to varying environmental conditions.
- Limit of detection (LOD): is the lowest concentration of a detectable analyte that the sensor can reliably distinguish from background noise or a blank sample.

LOD formulas is based on the use of linear regression models. When the signal is three times greater than the noise, the theoretical LOD can be estimates using the slope of the linear region of the response curve (commonly referred to as the sensitivity) and the root-mean-square (RMS) deviation at the baseline [184].

$$\text{LOD} = \frac{3 \text{ RMS noise}}{\text{Slope}}$$

where RMS noise is the noise level in the absence of the analyte gas and it can be calculated using the following equation [185]:

$$\text{RMS noise} = \sqrt{\frac{\sum \text{Rx}^2}{N}} ; \text{Rx}^2 = \sum (y_i - y)^2$$

- Precision: refers to the consistency and repeatability of a gas sensor's measurements when exposed to the same gas concentration under the same environmental conditions [186].

I.6.1. Chemiresistive gas sensors

Chemiresistive sensors are a widely adopted class of gas sensors, operating on the fundamental principle that the electrical resistance of the sensing material changes in response to chemical reactions occurring on its surface. The direction of this resistance changes increases or decreases depending on both the semiconductor type (p-type or n-type) and the nature of the target gas (oxidizing or reducing). Among electrical sensing platforms, MEMS-based implementations stand out for their miniaturized footprint, compatibility with standard microfabrication processes, and cost-effective scalability, as well as low power consumption compared to bulk platforms [187,188].

I.6.1.1. MEMS-based gas sensors architecture

In MEMS-based gas sensors, a sensing material like Cu₂S is deposited onto the electrodes, with a micro-heater integrated beneath the structure. A dielectric layer consisting of Si₃N₄/SiO₂ provides electrical insulation between the heater and the sensing element. The sensor can be activated thermally and/or through light excitation (photoactivation) using a light-emitting diode (LED).

Figure I.6 shows a cross-sectional illustration of a MEMS-type gas sensor. The device is fabricated on a silicon substrate and integrates three key components: a microheaters, interdigitated electrodes, and a sensitive material. A spiral-shaped micro-heater typically made of doped polysilicon, to control the temperature of the sensing material, heating it to an optimal range that promotes chemisorption of target gas molecules. In MEMS-based designs, the microheaters are integrated in an optimal way, minimizes heat loss to the substrate and then improves power consumption compared to conventional bulk sensors. The sensitive material, commonly made of metal oxides (MOX), metal sulfides (MS), or other materials, is directly deposited over the interdigitated electrodes. These electrodes serve as transducers, converting the chemical interaction between the sensing film and the target gas into a measurable electrical signal, most often a change in electrical resistance. Alternatively, the MEMS gas sensor can be activated optically by eliminating the microheater entirely and replacing thermal activation with photoexcitation. In this approach, light delivered either from an integrated source or an external emitter is used to photoexcite the sensing material, generating electron–hole pairs that enhance surface reactivity. This photoinduced process effectively promotes the chemisorption of gas molecules without the need for resistive heating.

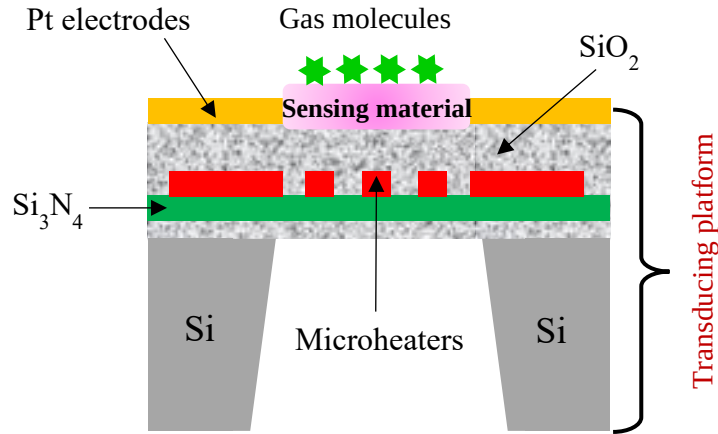


Figure I. 6. Schematic cross-sectional illustration of a MEMS gas sensor [189].

I.6.1.2. Sensing mechanism via thermal/photoactivation

The gas-sensing mechanism of resistive sensors is primarily governed by sulfur vacancies (SVs) in metal sulfide (MS) thin films. These sulfur vacancies act as single-electron acceptors and play a pivotal role in the sensing process [190].

The typical gas-sensing mechanism can be described as follows:

In air, oxygen molecules adsorb onto the sensor surface and onto sulfur vacancy sites, where they capture free electrons from the conduction band to form chemisorbed oxygen species. At temperatures above 150 °C, the dominant species at the surface involve chemically active O^- and O^{2-} species, with the relative concentration of O^{2-} likely increasing as temperature rises [191]. The adsorption of this species (at both the surface and sulfur vacancy sites) depletes charge carriers near the surface: in n-type semiconductors, where it reduces the concentration of free electrons. (e.g., ZnS), it results in the formation of an electron depletion layer (EDL), whereas in p-type materials (e.g., Cu_2S), it leads to a hole accumulation layer (HAL).

Upon exposure to an oxidizing gas, the EDL in n-type semiconductors widens due to additional electron withdrawal, causing a measurable increase in electrical resistance. Conversely, exposure to a reducing gas donates electrons back to the conduction band, narrowing the EDL and decreasing resistance. A complementary response occurs in p-type semiconductors, where changes in the HAL modulate conductivity in the opposite direction [192].

When the sensor is reintroduced to air, the target gas molecules desorb, and the surface oxygen species are re-established, allowing the electrical resistance to return to its baseline value.

A similar mechanism occurs when the microheater is replaced by UV illumination at room temperature. Under UV light, electron ($e^-_{(hv)}$) hole ($h^+_{(hv)}$) pairs are photogenerated in the semiconductor. The photogenerated electrons promote the adsorption and ionization of oxygen (O_2), leading predominantly to the formation of $O_2^- (hv)$ ions, where $O_2^- (hv)$ is the dominant adsorbed oxygen species at lower temperatures, including room temperature [193,194]. The sensing mechanism including both types of sensor activation, is schematically illustrated in Figure I.7.

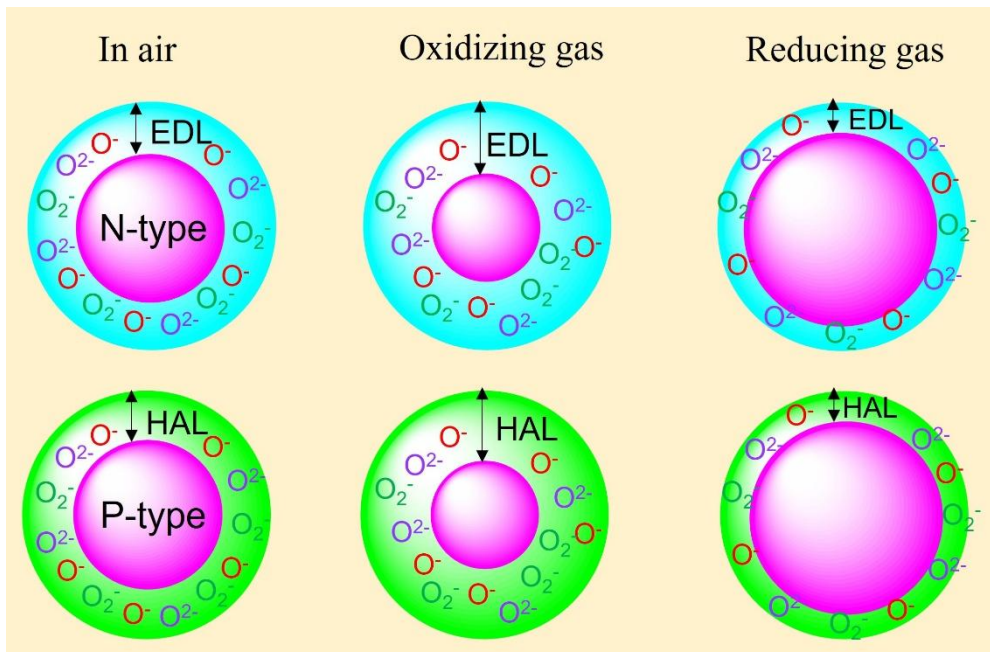


Figure I. 7. Schematic representations of the thermal and photo-activated gas-sensing mechanisms of metal sulfide-based sensors upon exposure to oxidizing or reducing gases, involving various oxygen species (O_2^- , O^- and O^{2-}).

I.6.2. Optical gas sensors

An optical gas sensor is a device that detects the presence and quantifies the concentration of specific gases by measuring changes in the optical properties such as absorbance, transmittance or reflectance of a sensing material at room temperature during gas exposure [195,196]. A wide range of optical sensor have been developed to address different application needs. For instance, nondispersive infrared (NDIR) sensors exploit the characteristic infrared absorption fingerprints of gases like CO_2 and CH_4 [197].

Photoionization detectors (PIDs) utilize ultraviolet (UV) light to ionize volatile organic compounds (VOCs), generating a measurable current proportional to concentration ideal for detecting low levels (ppb) of VOCs [198].

Among the various commercial platforms explored for optical gas sensing, glass substrates have remained relatively underexplored in the literature despite their significant potential.

I.6.2.1. Glass-based optical gas sensor architecture

The platform includes key elements that function together to achieve optical gas detection, as illustrated in Figure I.8. A standard glass slide, which offers several advantages: it is cost-effective, highly transparent across the visible and near-infrared spectral ranges. This broad optical transparency supports multiple detection including absorption, transmittance, reflectance, and luminescence, making glass an attractive substrate for economically optical sensors. Deposited onto this substrate a sensing material, often semi-transparent material such as zinc sulfide (ZnS), directly interacting with target gas molecules and transducing their presence into a measurable optical signal through reversible changes in its optical properties.

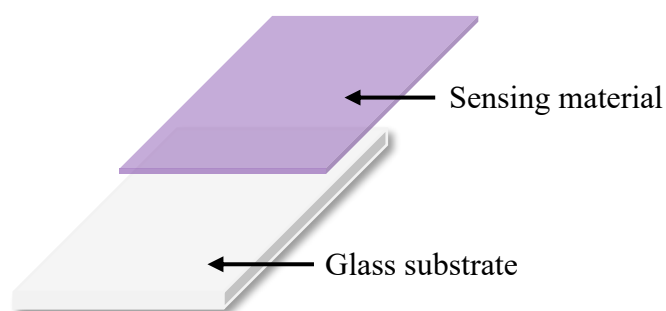


Figure I. 8. Schematic illustration of a Glass-based optical gas sensor.

I.6.2.2. Sensing mechanism of the optical sensor

The gas sensing mechanism of an optical sensor for metal sulfide like ZnS in the presence of sulfur vacancies, it can describe it as follow, with a schematic illustration in Figure I.9:

Under illumination in an oxygen containing environment, oxygen molecules (O_2) adsorb onto the vacancies sites and capture electrons, primarily from the sulfur vacancy level to form chemisorbed oxygen species, most likely O_2^- (ads) due to the RT operation [199,200]. This process leaves behind holes. Simultaneously, additional electrons from

the conduction band (CB) may also be captured, resulting in additional adsorbed oxygen species O_2^- (ads) at the surface of the MS.

When gas molecules approach the sensor surface, they capture electrons (in case of oxidizing gases) from the conduction band, becoming negatively charged (e.g., NO_2^-) and subsequently adsorbing onto the surface. Moreover, when sulfur vacancy states remain unoccupied, incoming gas molecules can extract electrons from these localized defect states, forming negatively charged complexes [201]. This electron transfer depletes the free charge carrier density in the film, thereby changing its optical properties (absorbance, transmittance or reflectance). This is in agreement with similar observation reported earlier in the literature [202].

The interaction of the film surface with reducing gases is expected to trigger a similar process, with the key difference being that the reducing molecules donate electrons to the conduction band and/or fill localized states associated with sulfur vacancies. This increases the free charge carrier density, thereby inducing measurable changes in the optical properties of the metal sulfide (MS) thin films.

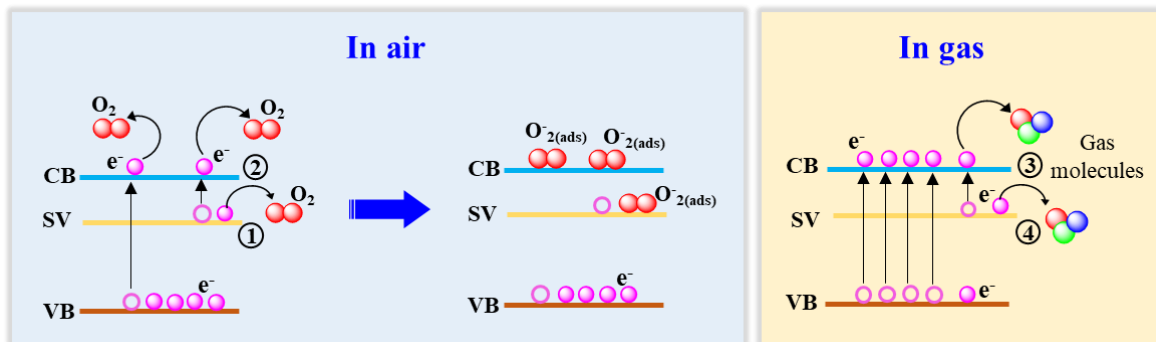


Figure I. 9. Schematic illustration of the optical gas-sensing mechanism in metal sulfide (MS) thin films.

I.6. Conclusion

The literature review highlighted the utility of metal complexes featuring organophosphorus chalcogen ligands as single-source precursors (SSPs) for the synthesis of metal sulfide thin films, with particular attention given to copper sulfide (Cu_xS) and zinc sulfide (ZnS), which were selected due to their promising optical and electrical properties, that allow their use in different applications, most notably in gas sensing technologies. From various deposition techniques available, AACVD stands out for its scalability and ability to produce high quality thin films under controlled conditions. The review further examined the architectural designs of both resistive and optical-based sensors employed in this context, their mode of activation and their sensing mechanisms.

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Chapter II

Thin films deposition using single-source
precursors (SSPs): Synthesis and
characterization techniques

II.1. Introduction

Coordination chemistry is a branch of inorganic chemistry that focuses on the study of coordination compounds, which are formed when metal ions bond to surrounding molecules or ions known as ligands. Their properties depend on both the metal center and the coordinated ligands, which can be varied to achieve the desired characteristics. These complexes play crucial roles in organic synthesis, biology, medicine, pollution removal, and the synthesis of nanoscale materials [1].

The study of metal cation complexation by organochalcogenophosphorus compounds synthesized in our laboratory has revealed their potential as single-source precursors (SSPs) for the deposition of M_xE_y -type thin films, where M represents a transition metal and E is a chalcogen (S, Se, or Te), with stoichiometric ratios typically ranging between $1 < x, y < 2$. Due to their unique properties, these thin films hold strong promise for incorporation into microelectronic devices, offering potential applications in gas sensing, photovoltaics, and transistor technologies areas that are critical to advancing future electronic systems. In this context, the choice of abundant and non-toxic materials such as Cu_2S and ZnS is particularly advantageous, enabling the development of eco-friendly and scalable electronic devices while maintaining desirable optoelectronic properties.

This chapter is structured into two main sections. The first part focuses on the synthesis of metal complexes, based particularly on copper, zinc, and cadmium metals, derived from organochalcogenophosphorus ligands, detailing the reaction pathways and methodologies employed. It also outlines the analytical techniques utilized to characterize and confirm the structural properties of the synthesized compounds. These include infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and thermogravimetric analysis (TGA).

In the second part of this chapter, the synthesized metal complexes are utilized as single-source precursors (SSPs) for the preparation of metal chalcogenide thin films with general formula M_xE_y . We describe the deposition technique employed (AACVD), along with the experimental parameters, placing particular emphasis on factors such as deposition temperature, substrate selection, concentration of the precursors, etc. Additionally, we outline the principles and applications of the various characterization techniques used to evaluate the structural, morphological, and compositional properties of the resulting

materials. These include X-ray diffraction (XRD), scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Finally, we present an overview of the setup and tests conditions employed for the gas sensing characterization of the AACVD films.

II.2. Single source precursors for the AACVD process

In this section, we present the metal complexes designed and prepared with the aim of serving as potential single-source precursors (SSPs) for the growth of metal sulfide thin films using the AACVD technique. These compounds were synthesized at the University of Tunis El Manar.

II.2.1. Synthesis of copper complex using Et₄P₂S₂ ligand

[Cu(Et₄P₂S₂)Cl]₂: Copper(II) chloride (0.40 g; 4.12 mmol) was dissolved in 5 ml of absolute ethanol. After 2 h, a stoichiometric amount of the ligand tetraethyldiphosphine disulphide (1 g; 4.12 mmol) dissolved in 5 ml of dichloromethane was added dropwise at room temperature. A red-brown colour appeared immediately in agreement with a previous report for [Cu(Et₄P₂S₂)Cl₂] [2]. Afterwards, this compound was rapidly reduced to a copper(I) complex displaying a pale yellow color with a white precipitate containing the dimeric complex [Cu(Et₄P₂S₂)Cl]₂ [3]. The precipitate was then washed with anhydrous diethyl ether and dried in vacuum. The resulting white powder displayed well dispersed and uniform crystal particles. Yield: 1.12 g (80 %).

II.2.2. Synthesis of zinc complex using Et₄P₂S₂ ligand

[Zn(Et₄P₂S₂)Cl₂]: Anhydrous zinc(II) chloride, ZnCl₂ (0.5 g; 3.66 mmol), was dissolved in 5 mL absolute ethanol and stirred for one hour. Afterwards, a stoichiometric amount (with a slight excess) of the commercially available ligand Et₄P₂S₂ (1 g; 3.66 mmol), previously dissolved in 5 mL dichloromethane, was added dropwise at room temperature. The resulting reaction mixture was stirred for additional three hours. Subsequently, diethyl ether was slowly added to induce precipitation, and the mixture was stored overnight in a freezer to promote crystallization. No crystal formation was observed in the solution, suggesting that the complexation reaction between zinc and the Et₄P₂S₂ ligand did not proceed effectively, likely due to weak metal–ligand interactions.

As a result, we opted to use a solution containing both precursors ZnCl_2 and $\text{Et}_4\text{P}_2\text{S}_2$ introduced directly into the AACVD system in an attempt to deposit the desired film. The AACVD protocol for the co-deposition of these reactants is described in detail in Section II.4 of this chapter.

II.2.3. Synthesis of cadmium complex using L1 = $(\text{Me}_2\text{N})_3\text{PS}$ and L2 = $(\text{Me}_2\text{N})_3\text{PSe}$ ligands

Commercial organophosphorus ligand $(\text{Me}_2\text{N})_3\text{P}$ was used as starting points for the synthesis of their sulfur $(\text{Me}_2\text{N})_3\text{PS}$ and selenium $(\text{Me}_2\text{N})_3\text{PSe}$ derivatives, with the aim of promoting the formation of a metal-chalcogen (M-S/Se) bond within the cadmium complexes studied.

➤ Synthesis of tris(dimethylamino)phosphine chalcogenide ligand $(\text{Me}_2\text{N})_3\text{P}(\text{E})$ (E = S and Se)

A solution of tris(dimethylamino)phosphine $(\text{Me}_2\text{N})_3\text{P}$, 1.00 g, 6.12 mmol) in 100 mL toluene was prepared in a 250 mL round-bottom flask. The corresponding chalcogen (E = S: 0.19 g, 6.12 mmol; E = Se: 0.48 g, 6.12 mmol) was added in slight excess, and the reaction mixture was stirred at room temperature. Once the addition is complete, the reaction is kept under reflux for 3 to 4 hours, causing the solution to change from colorless to pale yellow. After this reflux time, the solution is concentrated under reduced pressure to isolate the product [4].

Yield $(\text{Me}_2\text{N})_3\text{P}(\text{S})$ = 92 %, ^{31}P NMR (121 MHz, reference 85 % H_3PO_4 in D_2O , solvent CDCl_3): $\delta^{31}\text{P}\{^1\text{H}\}$ = 81.80.

Yield $(\text{Me}_2\text{N})_3\text{P}(\text{Se})$ = 85 %, ^{31}P NMR (121 MHz, reference 85 % H_3PO_4 in D_2O , solvent CDCl_3): $\delta^{31}\text{P}\{^1\text{H}\}$ = 82.59.

➤ Synthesis of cadmium complexes $[\text{Cd}(\text{L1})_2](\text{NO}_3)_2$ and $[\text{Cd}(\text{L2})_2](\text{NO}_3)_2$

Hydrated cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (0.5 g, 1.62 mmol), was dissolved in 10 ml of absolute ethanol and stirred at room temperature for 30 minute. Subsequently, 7 ml of ethyl orthoformate was added dropwise and the reaction mixture was stirred for an additional hour at room temperature.

The reaction mixture is left to stir overnight at room temperature. The following day, a solution of ligand L1 (0.63 g, 3.24 mmol) or L2 (0.78 g, 3.24 mmol) in dichloromethane (5 mL) is added dropwise. Stirring is continued for additional 3 hours. The solvent is subsequently evaporated under reduced pressure, leaving behind a white solid. The residue is then thoroughly washed with diethyl ether and dried under vacuum to yield the final product [5].

[Cd(L1)₂](NO₃)₂: Yield = 75 %, white solid, ³¹P NMR (121 MHz, reference 85 % H₃PO₄ in D₂O, solvent CDCl₃): δ ³¹P{1H} = 74.03.

[Cd(L2)₂](NO₃)₂: Yield = 60 %, white solid, ³¹P NMR (121 MHz, reference 85 % H₃PO₄ in D₂O, solvent CDCl₃): δ ³¹P{1H} = 73.24.

II.3. Characterization methods for synthesized precursors

To study the chemical and physical characteristics of the complexes, various characterization methods, including IR, NMR and TGA were employed. The principles underlying these methods, as well as the experimental conditions applied in this study, are presented below.

II.3.1. IR spectroscopy

Infrared (IR) spectroscopy is an analytical technique that relies on the absorption of infrared radiation by molecules, which induces transitions between vibrational energy levels. Each type of chemical bond absorbs radiation at a characteristic frequency within the infrared range, producing a unique spectral fingerprint for the molecule [6].

In this study, IR spectroscopy was employed to identify key functional groups and to investigate the coordination environment in metal complexes by analyzing metal-ligand vibrational modes. Particular attention was given to the absorption bands associated with P=S bonds, typically observed in the range of 650 and 500 cm⁻¹. The presence of these bands supports the successful coordination of the ligand to the metal center.

➤ IR spectroscopy instrument

A Thermo Scientific Nicolet iS200 FTIR spectrometer, in the mid-infrared region (4000-400 cm^{-1}) at a resolution of 4 cm^{-1} (Figure II.1) was used to record Fourier-transform infrared (FTIR) spectra.



Figure II. 1. Photograph of a Thermo Scientific Nicolet iS200 FTIR Spectrometer.

II.3.2. Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy is a crucial analytical technique to confirm the formation of metal complexes by analyzing the chemical environment of atomic nuclei. In this study, NMR was employed to compare the spectra of the free ligands with those of their corresponding metal complexes, enabling the identification of structural and electronic changes resulting from coordination to the metal center. Notably, chemical shifts observed in ^{31}P NMR spectra offer insight into indication of the formation of the bond ligand–metal interactions, while the analysis of spin-spin couplings constants provides valuable information on the connectivity and spatial arrangement of atoms within the complex [7].

➤ NMR experimental conditions

Nuclear Magnetic Resonance (NMR) spectra were acquired using a Bruker Avance III-400 MHz spectrometer (Figure II.2). ^1H and ^{13}C NMR spectra were recorded in deuterium chloroform (CDCl_3), with chemical shifts (δ) reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal reference. ^{31}P NMR measurements, 85% phosphoric acid (H_3PO_4) was used as an external reference. All experiments were conducted at a constant temperature of 298 K. Spectral data were processed and analyzed

using TopSpin and MestReNova software to determine chemical shifts and spin-spin coupling constants.



Figure II. 2. 400 MHz BRUKER nuclear magnetic resonance (NMR) spectroscopy image [8].

II.3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to monitor the change in mass of a material as a function of temperature or time under a controlled atmosphere (such as air, nitrogen, or argon). Based on the principle of thermal decomposition, TGA provides critical insights into a material's thermal stability, compositional makeup, and the nature of its degradation products [9].

In the context of our study, TGA plays a pivotal role in understanding the thermal stability and decomposition behavior of the synthesized complexes. By analyzing the mass loss profiles, we can identify key decomposition events, such as the release of chalcogen atoms from the ligands and the breakdown of metal-ligand bonds. These observations are essential for determining the optimal conditions required for the deposition of high-quality materials via chemical vapor deposition methods as AACVD.

➤ TGA experimental conditions

Thermogravimetric analysis (TGA) was conducted using a NETZSCH STA 449F1 Jupiter instrument. The measurements were performed under a nitrogen atmosphere (N_2), with the temperature increasing from 20 to 600 °C, with a heating rate of 10 °C·min⁻¹. The samples were placed in a closed, perforated alumina (Al_2O_3) dish, enabling controlled outgassing of decomposition products during heating (Figure II.3).



Figure II. 3. Image of the STA 449 F1 Jupiter used for TGA analysis [10].

II.4. Elaboration of metal chalcogenide thin films by AACVD

The synthesized complexes or SSPs were used for the AACVD deposition of metal sulfides, employing various experimental conditions to tune properties such as the morphology, phase, and chemical composition of the resulting films. This section outlines the protocols for the AACVD process, including the type of the substrates employed, the surface cleaning steps, the deposition procedure and their direct integration into the sensing platforms. These processes were carried out at the Institute of Microelectronics of Barcelona (IMB-CNM, CSIC).

II.4.1. Substrates

The fabrication of uniform, high-quality materials require precise control over key experimental parameters. Substrate selection is especially critical, as it directly affects the nucleation, growth, and structural characteristics of the deposited material.

II.4.1.1. Choice of the substrate

The selection of an appropriate substrate for thin-film deposition is a critical step in the process. The substrate must be thermally stable under deposition conditions and compatible with subsequent material characterization techniques. In this study, the material was deposited on various substrates namely glass (1 cm × 1 cm), silicon (Si) (0.5 mm × 0.5 mm), and alumina (1 cm × 1 cm) tiles depending on the intended application and the type of analysis required. In the results section it is specified the type of substrate used for each study.

In addition, we employed gas sensor substrates (Figure II.4a) fabricated in the clean room facility of the IMB-CNM (CSIC) by micro-electro-mechanical systems (MEMS)

technology. These MEMS based substrates integrate four $\text{Si}_3\text{N}_4/\text{SiO}_2$ membranes (1×1 mm in size), with thickness of 300 nm and 500 nm, respectively, each incorporating a meander-shaped polysilicon resistive heater, covering an area of $400 \times 400 \mu\text{m}$ and having a thickness of 480 nm. Then membrane also integrates on the top interdigitated Ti/Pt electrodes with a $10 \mu\text{m}$ gap. Further information on the design, composition, and fabrication of these sensors can be found in the following references [11,12].

Commercially available indium-tin-oxide (ITO)-coated glass substrates were also employed as transduction platforms for gas sensing applications (Figure II.4b). Additional details regarding the substrate design can be found in the linked resource [13].

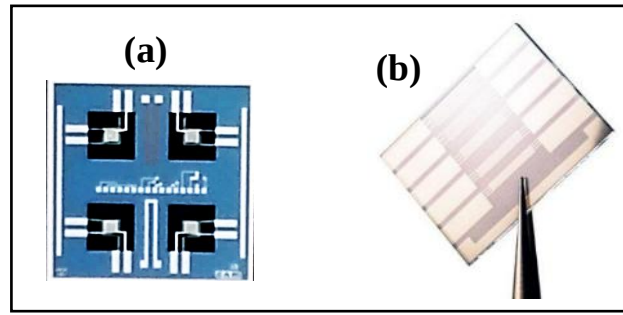


Figure II. 4. (a) MEMS based substrates and (b) Glass substrate containing indium tin oxide (ITO) patterned electrodes.

II.4.1.2. Substrate treatment

Effective substrate cleaning before thin-film deposition is critical to achieving strong adhesion, and uniform film morphology. Surface contaminants can lead to defects, poor coverage, and degradation of the film's structural and functional properties.

The following procedure was used to clean substrates such as glass, silicon, or alumina prior to deposition:

- Ultrasonic cleaning: Substrates are placed in a beaker containing isopropanol and subjected to ultrasonic cleaning for 10 minutes to remove surface contaminants.
- Rinsing: The substrates are then carefully rinsed with deionized (DI) water to eliminate residual isopropanol and other impurities.
- Drying: Excess water is removed by gently drying the substrates with a stream of nitrogen gas.

- Preheating in AACVD Reactor: Finally, the cleaned substrates are introduced into the AACVD reactor and allowed to equilibrate at the desired deposition temperature for 10 minutes before the deposition process begins.

II.4.2. Aerosol Assisted Chemical Vapor Deposition

The AACVD depositions were carried out in a customized reactor equipped with a reactor, heating elements to reach high temperatures ($\approx 900\text{ }^{\circ}\text{C}$), a temperature controller, and an ultrasonic atomizer (1.6 MHz).

Figure II.5 shows a schematic representation of the AACVD system [14] used for depositing thin films of copper, zinc, and cadmium sulfides.

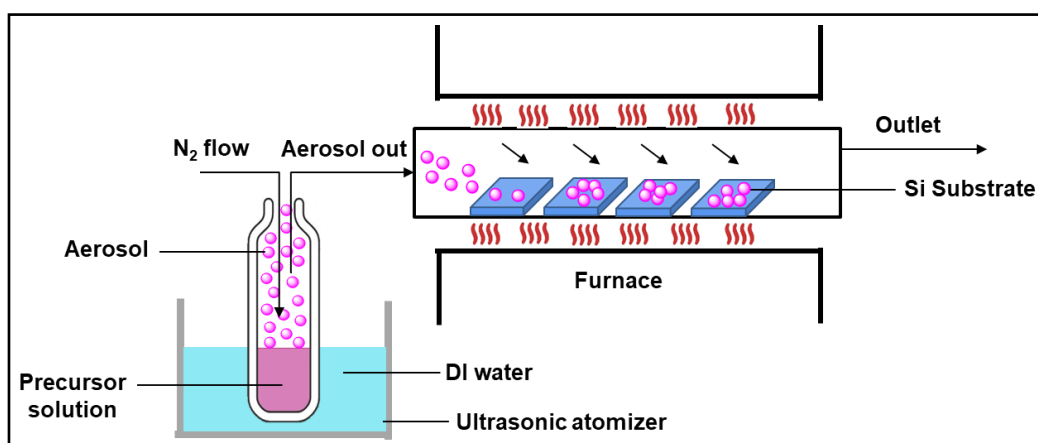


Figure II. 5. Illustrative schematic of the AACVD system.

Generally, a precursor solution was introduced into the system as fine aerosol droplets transported to the hot-wall reactor using a nitrogen flow (200 sccm). The optimization of AACVD parameters is strongly influenced by the choice were optimized for of the precursors studied, according to:

- Each precursor exhibits a unique thermal decomposition profile, which directly determines the minimum deposition temperature required to achieve the desired material.
- Their solubility, as each precursor often require specific solvents to ensure homogeneous solution preparation and stable aerosol generation due to of a precursor strongly influenced by its their unique chemical nature and molecular structure dictates the selection of an appropriate solvent. As a result, different

precursors often require specific solvents to ensure homogeneous solution preparation and stable aerosol generation.

Furthermore, the optimization of film deposition, also included systematic adjustment of other parameters such as solution concentration, droplet size, and aerosol flux to produce high quality films and precisely tailor the properties of the resulting films.

Deposition onto the bare substrates and sensor substrates followed the same steps, with the difference that the AACVD process onto the MEMS- and ITO/glass-based sensing platforms included the use of shading masks to restrict the deposition to the active region of the sensor, as shown in Figure II.6.

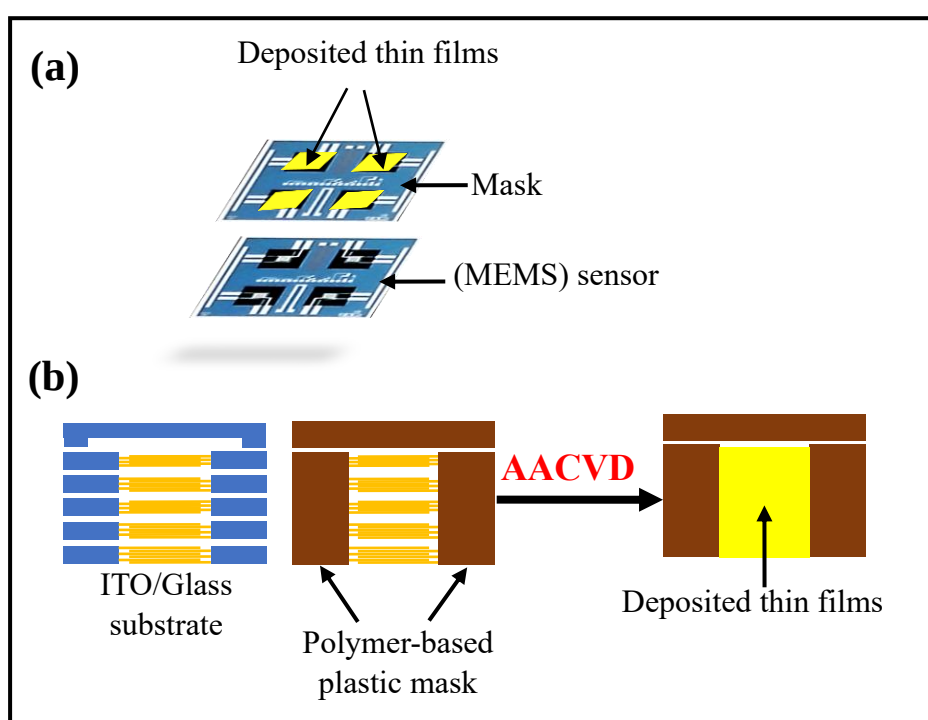


Figure II. 6. Schematic representation of thin film integration via AACVD on (a) MEMS- and (b) ITO/Glass-based sensor platforms.

II.4.2.1. AACVD of copper sulfide

Copper sulfide thin films were deposited onto silicon substrates using $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$ complex as SSP. The complex was dissolved in acetonitrile in a 100 mL round flask. The solution was typically transported into the reactor over a period of approximately one hour, resulting in the formation of uniform and well-adhered thin films. The deposition temperature is a key parameter in the AACVD process, significantly influencing the morphology, crystallinity, and composition of the resulting thin films. To investigate its impact on the growth of copper sulfide films, depositions were carried out over a range

of temperatures from 400 °C to 500 °C. The optimized experimental conditions for each temperature are summarized in Table II.1 and were used as the basis for subsequent characterization and analysis.

Table II. 1. Optimization of copper sulfide deposition conditions.

Deposition temperature (°C)	Solvent, acetonitrile (ml)	Concentration (mM)
400	8	11.9
450	10	11.7
475	10	11.7
500	10	15.6

II.4.2.2. AACVD of zinc sulfide

Zinc sulfide thin films were successfully synthesized via co-deposition onto silicon and glass substrates using AACVD technique. The precursor solution was prepared by dissolving zinc chloride (ZnCl_2 , Sigma-Aldrich, $\geq 98\%$) and tetraethyldiphosphine disulfide ($\text{Et}_4\text{P}_2\text{S}_2$, Sigma-Aldrich), a ligand used as a sulfur source, in 10 ml high-purity acetone (Penta, $\geq 99.5\%$). The solution was aerosolized and transported into the reactor over a period of approximately 30 minutes. The deposition process was carried out at different deposition temperatures summarized in Table II.2.

Table II. 2. Optimization of zinc sulfide deposition conditions.

Deposition temperature (°C)	Solvent, acetone (ml)	Concentration ZnCl ₂ (mM)	Concentration Et ₄ P ₂ S ₂ (mM)
400	10	22	24.3
400	10	22	30.4
450	10	22	24.3
475	10	22	24.3
500	10	22	24.3

II.4.2.3. AACVD of cadmium sulfide

Cadmium complexes [Cd(L1)₂(NO₃)₂] and [Cd(L2)₂(NO₃)₂] were deposited onto silicon and alumina substrates, employing different deposition parameters such as solvent, deposition temperature and precursor concentration. All experimental conditions are summarized in Table II.3.

Table II. 3. Optimization of cadmium sulfide/selenide deposition conditions.

Cadmium complexes	Deposition temperature (°C)	Solvent, tetrahydrofuran (ml)	Concentration (mM)
[Cd(L1) ₂ (NO ₃) ₂]	350	5	6.3
	350	5	15.94
	400	5	6.3
	400	5	15.94
	450	5	15.94

	350	5	5.5
	350	5	13.8
[Cd(L2)₂(NO₃)₂]	400	5	5.5
	400	5	13.8
	450	5	13.8
	500	5	13.8

II.5. Characterization methods of the deposited thin films based on copper and zinc sulfides

To confirm the formation, assess the quality, and evaluate the key properties of the deposited thin films, different physical and chemical characterization techniques were employed. These analyses enable the determination of important parameters such as crystallinity, chemical composition, surface topography, and film thickness; factors that are critical for optimizing the characteristics of the film and evaluating their suitability for targeted applications. In the following sections, we outline the principles underlying these characterization techniques, along with the specific experimental conditions used in these studies, to ensure accurate, reliable, and reproducible results.

II.5.1. Structural characterization and chemical composition

II.5.1.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) is a key technique used for analyzing the crystallographic structure of materials. It relies on the interaction between X-rays and the regularly spaced atomic planes within a crystalline solid. When a sample is exposed to an X-ray beam, constructive interference occurs at specific angles, producing a diffraction pattern that is unique to the material's crystal structure. This phenomenon is governed by Bragg's law, expressed as $2d \sin\theta = n\lambda$, where d represents the interplanar distance, θ is the diffraction angle, λ is the X-ray wavelength, and n is an integer. By measuring the intensity of the diffracted beams across a range of angles, XRD allows for the identification of crystalline

phases, determination of structural properties, and estimation of features such as crystallite size and lattice strain [15].

➤ **Conditions for XRD measurements**

X-ray diffraction (XRD) analyses were performed using a Bruker-AXS D8 Advance diffractometer equipped with a GADDS (General Area Diffraction Detection System) detector. The measurements were conducted using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ angular range of 20° to 55° (Figure II.7). The diffraction patterns were analyzed using Diffract Suite EVA software.

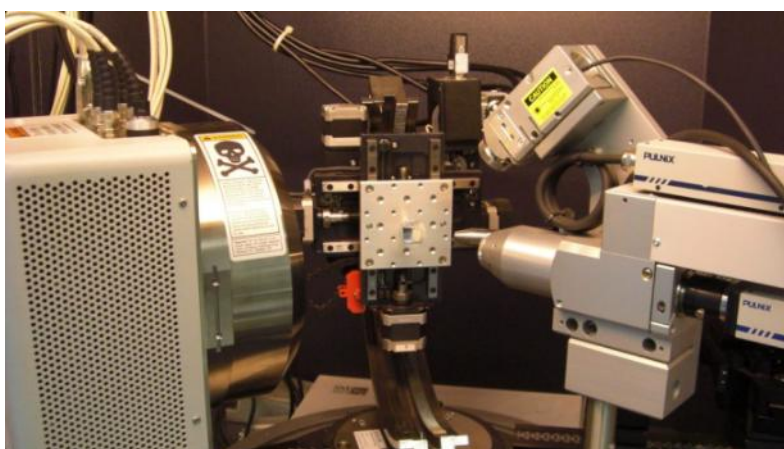


Figure II. 7. Image of Bruker D8 Advance X-ray diffractometer (GADDS) [16].

II.5.1.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique based on the photoelectric effect. In this method, a material is irradiated with high-energy X-rays, which causes the emission of photoelectrons from its surface (only from the top few nm). The kinetic energy of these emitted photoelectrons is characteristic of the elements present on the surface and their chemical bonding or oxidation state. Therefore, it can provide valuable information about the elemental composition of the surface and the nature of chemical bonds and interactions.

XPS is widely used to analyze surface chemistry, quantify elemental concentrations, and assess changes resulting from surface modifications, including material decoration or environmental exposure such as humidity, in the resulting films [17].

➤ Conditions for XPS measurements

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a SPECS spectrometer equipped with a PHOIBOS 150 MCD-9 hemispherical analyzer (Figure II.8). High-resolution spectra for each element were recorded and processed using CasaXPS software. Calibration was performed by setting the binding energy of the C 1s peak to 284.8 eV as a reference. Core-level spectra were fitted with mixed Gaussian-Lorentzian line shapes on a Shirley-type background to accurately determine binding energies and peak areas.



Figure II. 8. Image of the SPECS instrument equipped with a PHOIBOS 150 MCD-9 hemispheric analyzer [18].

II.5.2. Morphological and topographical characterization

II.5.2.1. Scanning electron microscope (SEM)

The scanning electron microscope (SEM) is a powerful imaging technique that utilizes a finely focused beam of electrons to examine the surface morphology of a sample at high resolution. This method is frequently combined with energy dispersive X-ray spectroscopy (EDX or EDS), an analytical technique used to identify and quantify the elemental composition of the sample based on the characteristic X-rays emitted during electron bombardment. The image quality obtained is influenced by the nature of the substrate and the materials being analyzed. Furthermore, cross-sectional imaging enables the visualization and accurate measurement of the thickness of the deposited layers [19].

➤ Operating conditions

SEM observations and compositional analysis of the deposited films were performed using a Zeiss Auriga 40 CrossBeam system equipped with an Oxford EDS detector (Figure II.9). The samples were mounted on stubs using carbon tape, and secondary electron (SE) imaging was performed at an accelerating voltage of 3 kV and a working distance of approximately 5 mm.



Figure II. 9. Image of an AURIGA-ZEISS scanning electron microscope equipped with an EDS spectrometer [20].

II.5.2.2. Transmittance electron microscope (TEM)

The transmission electron microscope (TEM) is an imaging technique that utilizes a high-energy electron beam to penetrate an ultra-thin sample, enabling the visualization of its internal structure in remarkable detail. Unlike the scanning electron microscope (SEM), which primarily examines the surface topography of a sample, the TEM allows to study the morphology, crystallographic structure, and internal defects of materials at the nanoscale [21].

➤ Operating conditions

Sample preparation for TEM analysis involved carefully detaching the structured films from their substrates, suspending the structure in ethanol and re-depositing them by drop-coating onto lacey carbon supported copper grids. Copper is the preferred material for TEM grids due to its minimal interference with the magnetic field of the objective lens, thereby ensuring high-resolution and accurate imaging.

TEM and HRTM images were performed using an FEI Tecnai G2 F20 microscope equipped with a field emission gun, operating at an accelerating voltage of 200 kV (Figure II.10). Image processing and analysis were carried out using ImageJ software.



Figure II. 10. Transmittance FEI Tecnai G2 F20 electron microscope image [22].

II.6. Gas sensing test

Metal sulfide thin films were directly integrated onto the sensing platforms using the AACVD method described in the sections above. The resulting sensors were evaluated under diverse operational conditions, such as exposure to various target gases, different concentration levels, variable temperatures, and distinct activation modes. These tests were carried out at the Institute of Microelectronics of Barcelona (IMB-CNM, CSIC). The corresponding experimental setup used for these evaluations is described in detail below.

II.6.1. Setup for the sensors assembled on the MEMS-based substrates

After deposition of the metal sulfide layer onto the MEMS platforms, the sensor devices were mounted on a TO8 package and bounded, as shown in Figure II.11

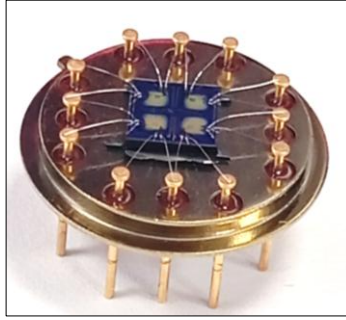


Figure II. 11. Photograph of the encapsulated MEMS-based gas sensor.

➤ **Gas sensing system**

The MEMS-based sensor measurements were carried out in a test chamber where the gas flow was controlled using mass flow controllers. During testing, the sensors were continuously illuminated by a 365 nm ultraviolet light-emitting diode (LED, LC-L1V3, Hamamatsu). This wavelength was chosen based on the energy bandgap of the sensing material, as UV photons at 365 nm possess sufficient energy to excite electrons across the bandgap, enabling photoactivation of the material. Relative humidity and temperature inside the chamber were continuously monitored using an SHT71 sensor (0–100% RH, $\pm 3\%$ RH accuracy, $\pm 0.4\text{ }^{\circ}\text{C}$ accuracy). All tests were conducted with the sensors and chamber maintained at room temperature. Electrical resistance was monitored in real time using a Keithley 2700 multimeter. This setup enables us also, to characterize the sensors in thermoactivated mode by simply switching off the UV lamp.

A schematic diagram of the gas test system is shown in Figure II.12. Further details on the experimental setup for testing chemiresistive sensors under photoactivation measurement of gas detection tests are available in the references cited [23,24].

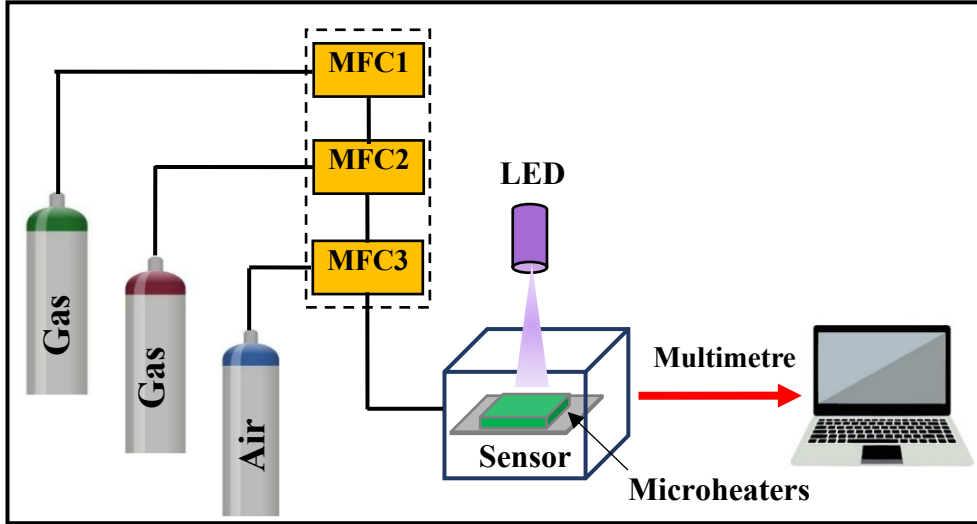


Figure II. 12. Schematic illustration of experimental set-up for photoactivated gas measurements using sensors assembled on MEMS-based substrates.

➤ Test procedure

The sensors were tested at room temperature (24 °C) in a continuous-flow test chamber with a gas flow rate of 200 sccm and exposed to varying concentrations of target gases ethanol (100 ppm), acetone (100 ppm), toluene (200 ppm), hydrogen (100 ppm), and nitrogen dioxide (100 ppm) prepared by diluting certified gas cylinders (Praxair) with synthetic air (3X, Praxair). Humidity was introduced into the system by bubbling the carrier gas through deionized water under controlled conditions at 24 °C. Testing was performed under different UV irradiance levels, not exceeding $1800 \text{ mW} \cdot \text{cm}^{-2}$, as well as under thermoactivation at 150 °C and 250 °C. The sensor was exposed to each analyte gas for a period of 10 minutes, followed by a 30-minute purge with synthetic air to ensure complete recovery of the baseline electrical resistance. This exposure-purge cycle was repeated across various gases and concentrations to assess sensitivity, response dynamics, and reversibility under controlled temperature and humidity conditions.

The electrical sensor response (R) was defined as follows:

- For oxidizing gases (such as NO_2 , O_2 etc.): $R = \frac{R_a}{R_g}$
- For reducing gases (such as H_2 , $\text{C}_2\text{H}_2\text{O}$... etc.): $R = \frac{R_g}{R_a}$

Where R_a and R_g represent the sensor's electrical resistances in air and target gas respectively.

The response time (T_{Res}) is defined as the time required for the electrical resistance to reach 90% of its steady state value following gas exposure. The recovery time (T_{Rec}) is the time required for the sensor's resistance to return to 90% of its initial baseline value in air after gas removed.

II.6.2. Setup for the sensors assembled on the ITO-Glass-based substrates

➤ Gas sensing system

The ITO-Glass based sensors were placed inside a stainless-steel optical chamber designed to allow controlled gas exposure and optical measurements. The sensor response was monitored by exposing the sample to a scan of light across a wavelength range of 200 to 1000 nm, using a spectrometer (AvaSpec-UV/VIS/NIR, Avantes, Apeldoorn). The light source and the spectrometer were coupled to the chamber via optical fibers. Gas delivery was precisely controlled using a mass flow controller (MFC), which regulated the flow of carrier gas and target gases with a total flow rate of 200 sccm. Relative humidity (RH) inside the test chamber was continuously monitored using an SHT71 humidity sensor, calibrated to 40% RH with an accuracy of $\pm 3\%$ RH. Figure II.13 shows an illustration of the experimental set-up used for the gas sensing test.

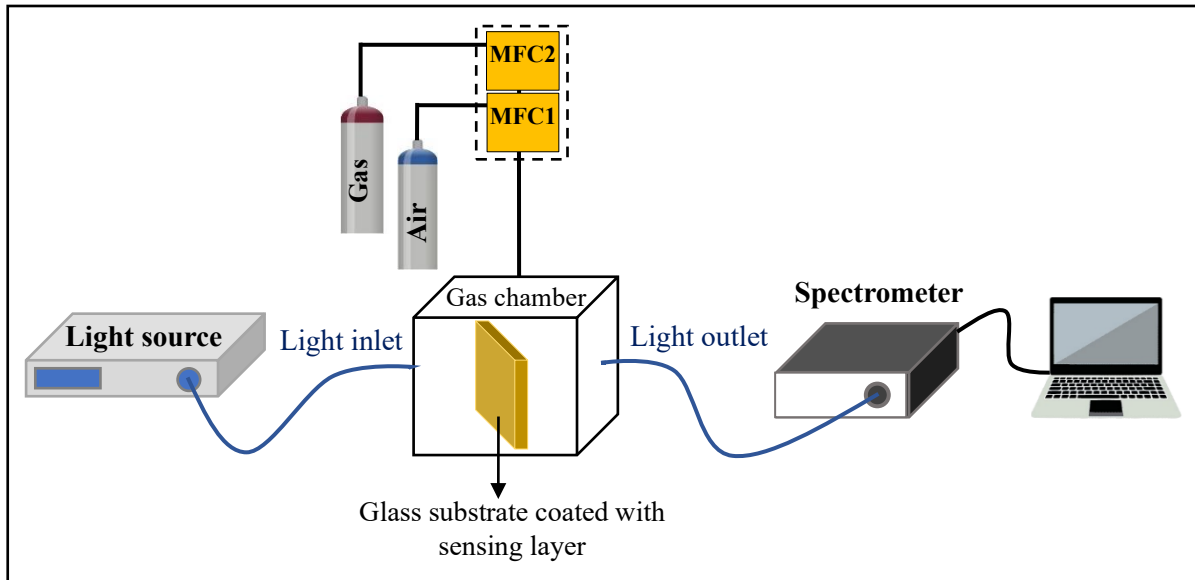


Figure II. 13. Schematic diagram of experimental set-up for gas measurements.

➤ Test procedure

The gas sensing measurements were conducted at room temperature (26 °C), with purified air used as the carrier gas to dilute the target analytes to specific concentrations: ethanol (100 ppm), acetone (100 ppm), toluene (200 ppm), hydrogen (100 ppm), carbon monoxide (100 ppm), and nitrogen dioxide (100 ppm). The optical response of the sensor was evaluated based on the change in the transmitted light intensity at a wavelength of 360 nm.

The optical response (R) of the sensor is defined as follows:

$$Response (R) = \frac{I_a}{I_g}$$

where I_a and I_g represent the transmitted light intensity of the sensor in air and target gas respectively.

II.7. Conclusion

In summary, three metal complexes, $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$, $[\text{Cd}(\text{L1})_2](\text{NO}_3)_2$ and $[\text{Cd}(\text{L2})_2](\text{NO}_3)_2$, were successfully synthesized and characterized by infrared (IR) and nuclear magnetic (NMR) spectroscopies. Thermogravimetric analysis (TGA) of the copper complex provided crucial insights into its thermal decomposition behavior, enabling the identification of an optimal deposition temperature for use in AACVD technique. In particular, the copper based complex $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$ proved adequate for the AACVD of films under the varied conditions detailed in Tables II.1 and II.3. Similarly, the synthesis of a zinc complex with the $\text{Et}_4\text{P}_2\text{S}_2$ ligand was attempted, however, it proved unsuccessful, likely due to the weak Zn–ligand interactions. Therefore, a mixture of zinc chloride and the $\text{Et}_4\text{P}_2\text{S}_2$ ligand was co-deposited using AACVD under the parameters outlined in Table II.2.

Overall, AACVD depositions were carried out on a range of substrates including silicon, glass, and alumina selected according to the specific characterization requirements of the resulting thin films. The as-deposited films were deeply characterized using SEM-EDX, XRD, XPS, and TEM to assess their morphology, elemental composition, phase purity, and crystallinity. Finally, the optimized films were directly integrated onto MEMS-based and ITO/glass sensing platforms to evaluate their gas sensing properties.

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Chapter III

Results and discussion

III.1. Introduction

This chapter is divided into two main sections. The first focuses on the characterization of synthesized metal complexes, which serve as single-source precursors in the development of the functional materials. The second section presents a detailed analysis of the resulting AACVD thin films, both derived from the SSPs and the co-deposit of two precursors. Results focus on the films' structural, morphological, and chemical properties studied by XRD, SEM, XPS, and TEM. These provide valuable insights into the properties of the materials integrated into the gas sensing devices.

III.2. Characterization of the synthesized complexes (SSPs)

III.2.1. Copper complex $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$

III.2.1.1. Infrared spectroscopy analysis

Infrared (IR) spectroscopy has shown previously that the spectrum of the free ligand $\text{Et}_2\text{P}(\text{S})\text{-P}(\text{S})\text{Et}_2$ exhibits an intense band at 547 cm^{-1} , corresponding to the antisymmetric $\nu(\text{P}=\text{S})$ stretching vibration [1]. The IR spectra acquired for the copper complex synthesized in this thesis show that after the complexation process, this characteristic band shifts by 31 cm^{-1} to higher wavenumbers due to the interaction of the ligand with copper. This is observed in Figure III.1, which reveals a weak $\nu(\text{P}=\text{S})$ band at 578 cm^{-1} for the copper complex. This shift confirms the coordination of the sulfur atom with the copper ion and the formation of the $\text{P}=\text{S}\text{-M}$ bond, leading to an increase in the frequency of the $\nu(\text{P}=\text{S})$ band of the synthesized complex. The spectral change can be explained by ligand-metal charge transfer ($\text{S} \rightarrow \text{Cu}$), highlighting the complex dynamics of the molecular interaction [2].

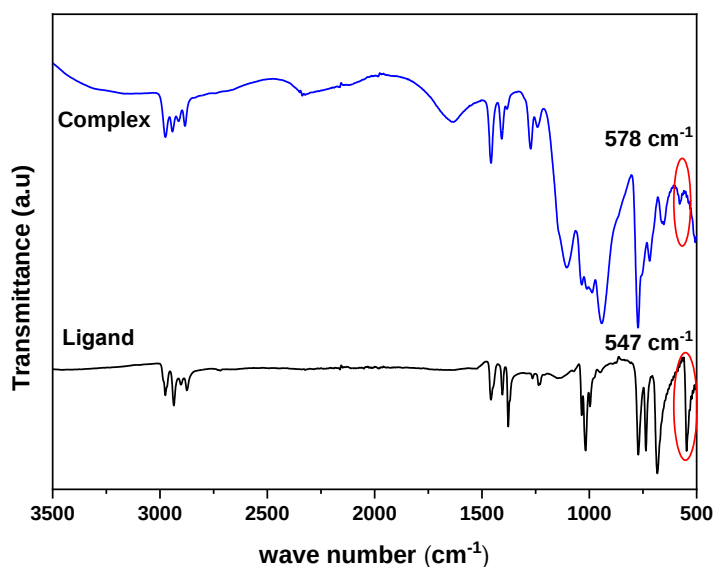


Figure III. 1. IR spectra of the free ligand (black) $\text{Et}_4\text{P}_2\text{S}_2$ and the copper complex (blue) $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$ marking the $\nu(\text{P}=\text{S})$ band for the ligand and the complex.

III.2.1.2. Thermogravimetric analysis (TGA)

The decomposition behavior of the copper complex was studied using thermogravimetric analysis (TGA), as shown in Figure III.2. The results of the TGA analysis revealed two decomposition stages. The first stage shows a significant mass loss of 58.44 % in the temperature range between 134 and 275 °C. The second stage shows a mass loss of 19.12 % between 275 °C and 345 °C. Complete decomposition of the complex occurs at 345 °C, giving a final residue of 22.44 %, corresponding to Cu_2S (calculated percentage: 23.31 %). In the light of these results, AACVD of the complex was carried out at temperatures above 345 °C.

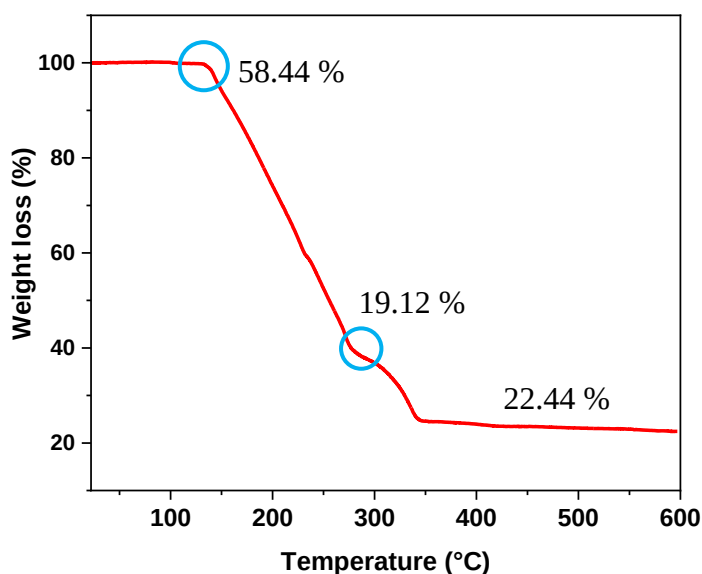


Figure III. 2. Thermogravimetric analysis of the $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$ complex at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen.

III.2.2. Cadmium complexes $\text{CdL}_2(\text{NO}_3)_2$

III.2.2.1. NMR spectroscopy

$^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (proton-decoupled) was used to confirm the formation of the sulfide (L1, $(\text{Me}_2\text{N})_3\text{PS}$) and selenide (L2, $(\text{Me}_2\text{N})_3\text{PSe}$) ligands synthesized in the previous chapter, as well as to confirm the complexation process.

➤ Cadmium complex with L1

The ^{31}P NMR spectrum of the commercial ligand $(\text{Me}_2\text{N})_3\text{P}$ show a signal at 122 ppm [3]. After coordination of a sulfur atom to the phosphorus center, forming $(\text{Me}_2\text{N})_3\text{PS}$, the electron density around the phosphorus decrease, resulting in significant shielding to the low frequency to 81.80 ppm, as shown in Figure III.3(a). This change in chemical shift provides clear spectroscopic evidence for the formation of a P=S bond.

After complexation with cadmium, the ^{31}P NMR spectrum of the ligand $(\text{Me}_2\text{N})_3\text{PS}$ exhibit a significant chemical shift of $\Delta\delta=7.77$ ppm to low frequency values (Figure III.3(b)), indicating a decrease in electron density around the phosphorus atom. The observed change in chemical shift confirm the direct interaction between sulfur and cadmium ($\text{P}=\text{S}\rightarrow\text{Cd}$) and then the formation of the complex.

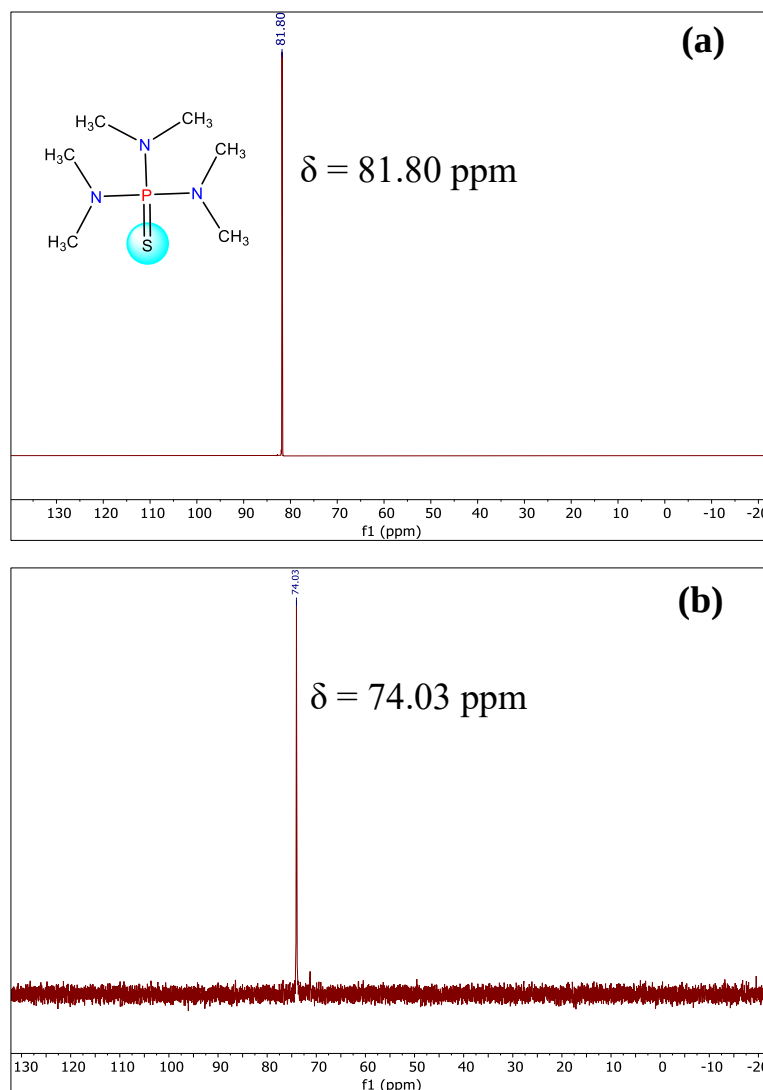


Figure III. 3. (a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the free ligand L.1 and (b) the cadmium complex.

➤ Cadmium complex with L2

The ^{31}P NMR spectrum of the $(\text{Me}_2\text{N})_3\text{PSe}$ ligand was also compared with that of the commercial ligand, revealing a significant shift from 122 ppm to 82.59 ppm (Figure III.4(a)), consistent with the presence of a selenium atom directly bonded to phosphorus $(\text{Me}_2\text{N})_3\text{PSe}$. After the complexation process, the ^{31}P signal further shifted by $\Delta\delta = 9.35$ ppm (Figure III.4(b)). This chemical shift, confirm the coordination of the ligand to the metal center ($\text{P}=\text{Se}\rightarrow\text{Cd}$) and provides strong evidence for the formation of the cadmium complex.

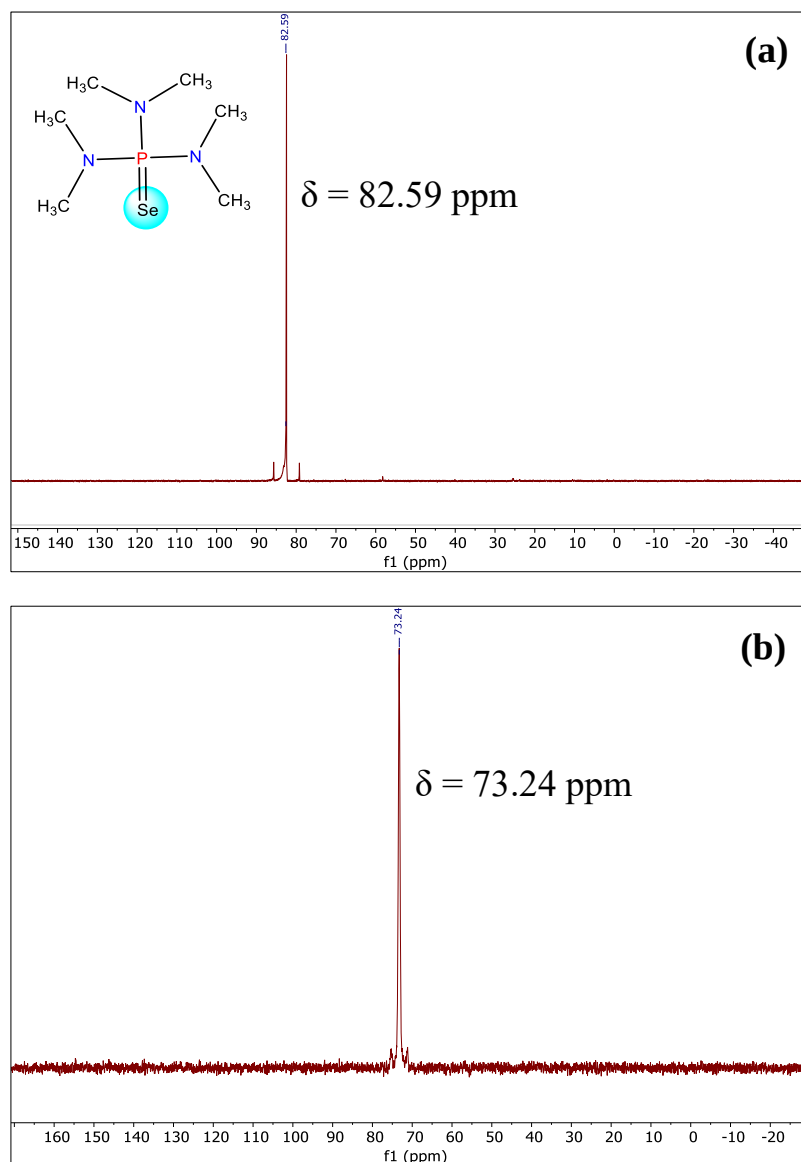


Figure III. 4. (a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the free ligand L.2 and (b) the cadmium complex.

III.2.2.2. Thermogravimetric analysis (TGA)

➤ Cadmium complex with L1

The decomposition behavior of cadmium complex based on L1 was studied using thermogravimetric analysis (TGA), as shown in Figure III.5. The results of the TGA analysis revealed two decomposition stages. The first stage shows a significant mass loss of 38.38 % in the temperature range between 100 °C and 160 °C. The second stage shows a mass loss of 34.29 % between 160 °C and 300 °C. Complete decomposition of the complex occurs at 300 °C, giving a final residue of 27.33 %, corresponding to CdS (calculated percentage: 23.5 %). In the light of these results, AACVD of the complex was carried out at temperatures above 300 °C.

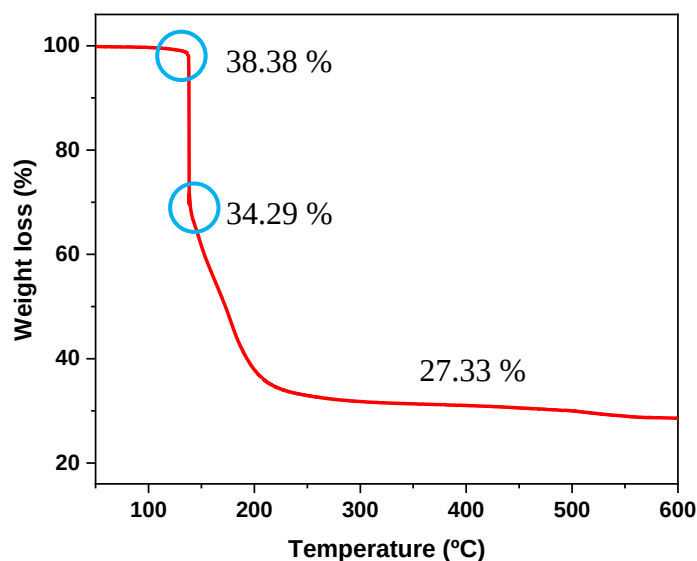


Figure III. 5. Thermogravimetric analysis of the cadmium complex with L1 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen.

➤ Cadmium complex with L2

The decomposition of cadmium complex based on L2 in Figure III.6, revealed three decomposition stages. The first stage shows a significant mass loss of 47.31 % in the temperature range between 159 °C and 170 °C. The second stage shows a mass loss of 28.93 % between 170 °C and 300 °C. Complete decomposition of the complex occurs at 300 °C, giving a final residue of 23.76 %, corresponding to CdSe (calculated percentage: 26.55 %). In the light of these results, AACVD of the complex was carried out at temperatures above 300 °C.

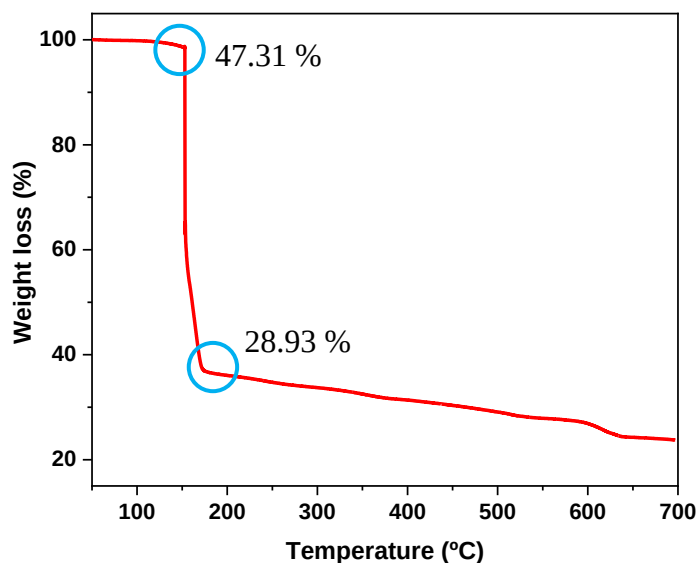


Figure III. 6. Thermogravimetric analysis of the cadmium complex with L2 at a heating rate of 10 °C min⁻¹ under nitrogen.

III.3. Characterization of the AACVD films derived from SSPs

III.3.1. Copper sulfide (Cu₂S) thin films

The Cu₂S thin films deposited on silicon substrates exhibited good adhesion and a uniform surface morphology across all samples. A clear dependence of film color on deposition temperature was observed: films deposited at 400 °C appeared dark black, while those prepared at higher temperatures (450 °C, 475 °C, and 500 °C) displayed a progressively lighter brownish color, as illustrated in Figure III.7. Importantly, no change in color was observed after the annealing process.

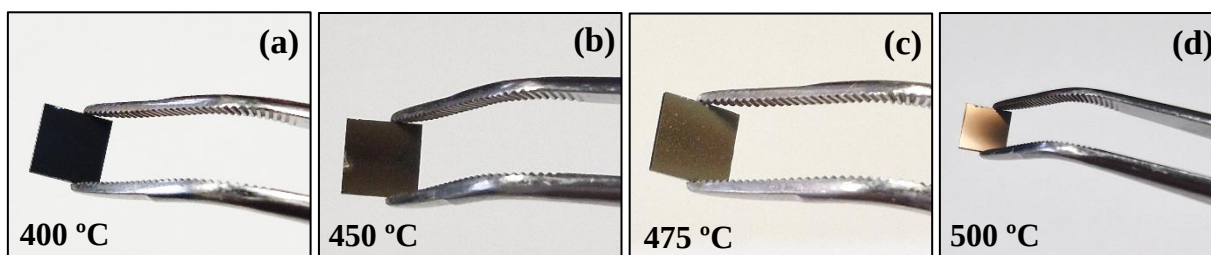


Figure III. 7. Photographs of Cu₂S films deposited on silicon substrates at increasing deposition temperatures: (a) 400 °C, (b) 450 °C, (c) 475 °C, and (d) 500 °C.

III.3.1.1. Effect of deposition temperature

➤ Structural properties

X-ray diffraction patterns of Cu_2S films deposited on silicon substrates at different temperatures (400, 450, 475 and 500 °C) are shown in Figure III.8. The patterns reveal the presence of a tetragonal Cu_2S crystalline phase (space group P43212, ICDD no. 04-024-2237), characterized by a very intense peak located at 32.591° (2θ), corresponding to the (111) plane. Other less intense peaks of the Cu_2S phase, are also observed. In addition, the formation of copper phosphide as secondary phase was observed, assigned to Cu_2P_7 for films deposited at 400 and 450 °C, and Cu_3P for films deposited at 475 °C. A diffraction peak at 33° (2θ) attributed to the silicon substrate was also observed for samples deposited at 450 °C and 475 °C.

For the films deposited at 500 °C, very low diffraction intensities were observed, likely due to the low film density at this elevated temperature.

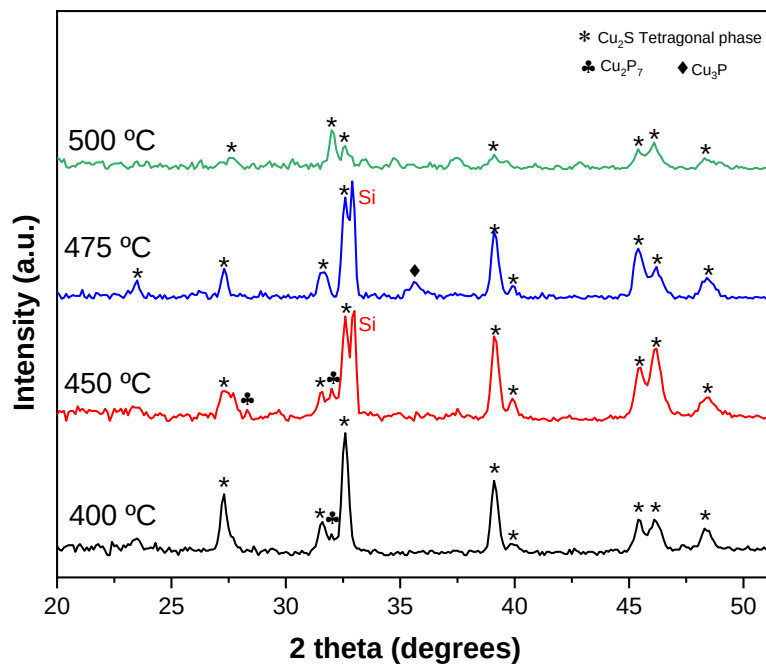


Figure III. 8. X-ray diffractograms of the Cu_2S films deposited at 400, 450, 475 and 500 °C on silicon substrates.

➤ Morphological properties

Cu₂S films show different morphologies as a function of deposition temperature (Figure III.9). Films deposited at 400 °C exhibit a particle-like structure, with sizes ranging from 60 to 100 nm, and agglomerated particles reaching around 400 nm (Figure III.9a). As the deposition temperature was increased to 450 °C and 475 °C, the morphology evolved into flake-like structures, characterized by irregular orientation (Figures III.9b and III.9c). At 500 °C, a notable morphological change occurred, with the formation of nanowires, with a length ranging from 80 to 110 nm (Figure III.9d).

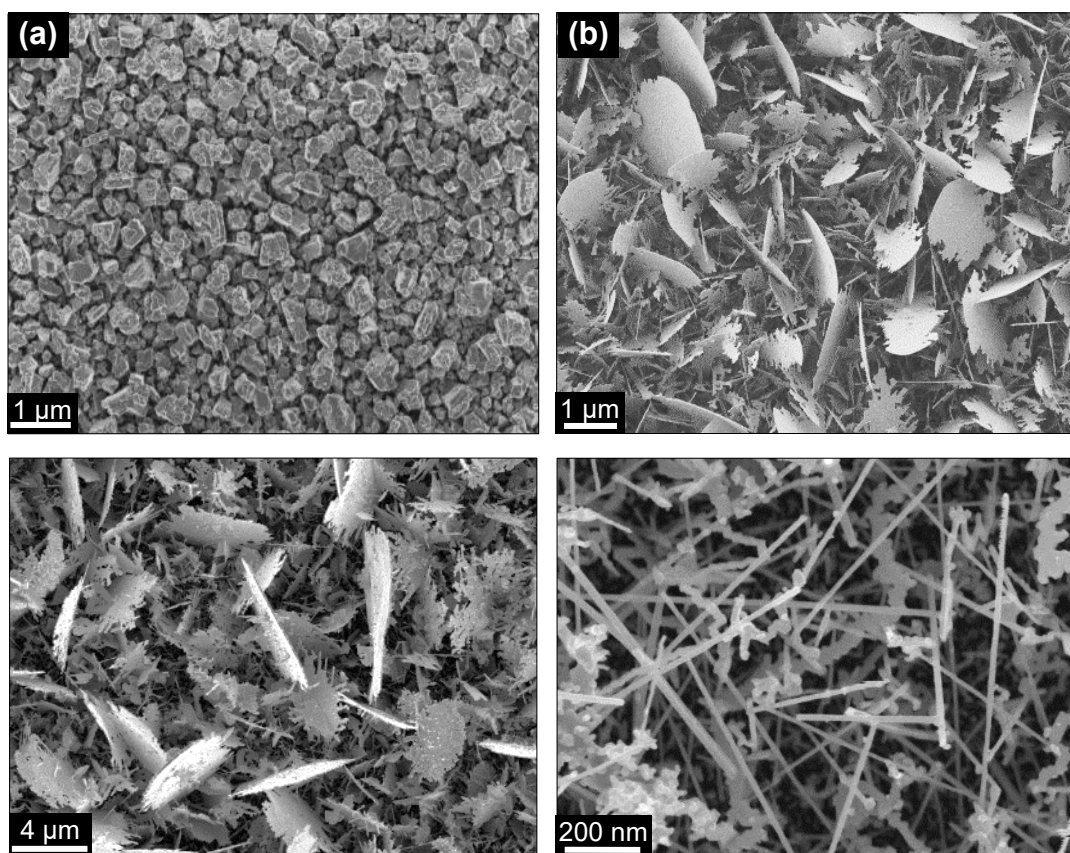


Figure III. 9. SEM images of Cu₂S films deposited from [Cu(Et₄P₂S₂)Cl]₂ by AACVD on silicon substrates: (a) 400 °C, (b) 450 °C, (c) 475 °C and (d) 500 °C.

Films deposited at 475 °C and 500 °C exhibited significant material loss at these elevated deposition temperatures. As a result, only films deposited at 400 °C and 450 °C were selected for in-depth characterization, with a view to their integration into gas sensing platforms and evaluation of their sensing performance.

In order to examine the morphology of the films deposited at 400 °C and 450 °C in greater detail, higher magnification images were obtained, as illustrated in Figure III.10a and b

successively. Cross-sectional observation revealed structures with an approximately length of 1.3 μm for samples deposited at 400 $^{\circ}\text{C}$ (Fig. III.10c) and between 20 μm and 22 μm for those deposited at 450 $^{\circ}\text{C}$ (Fig. III.10d).

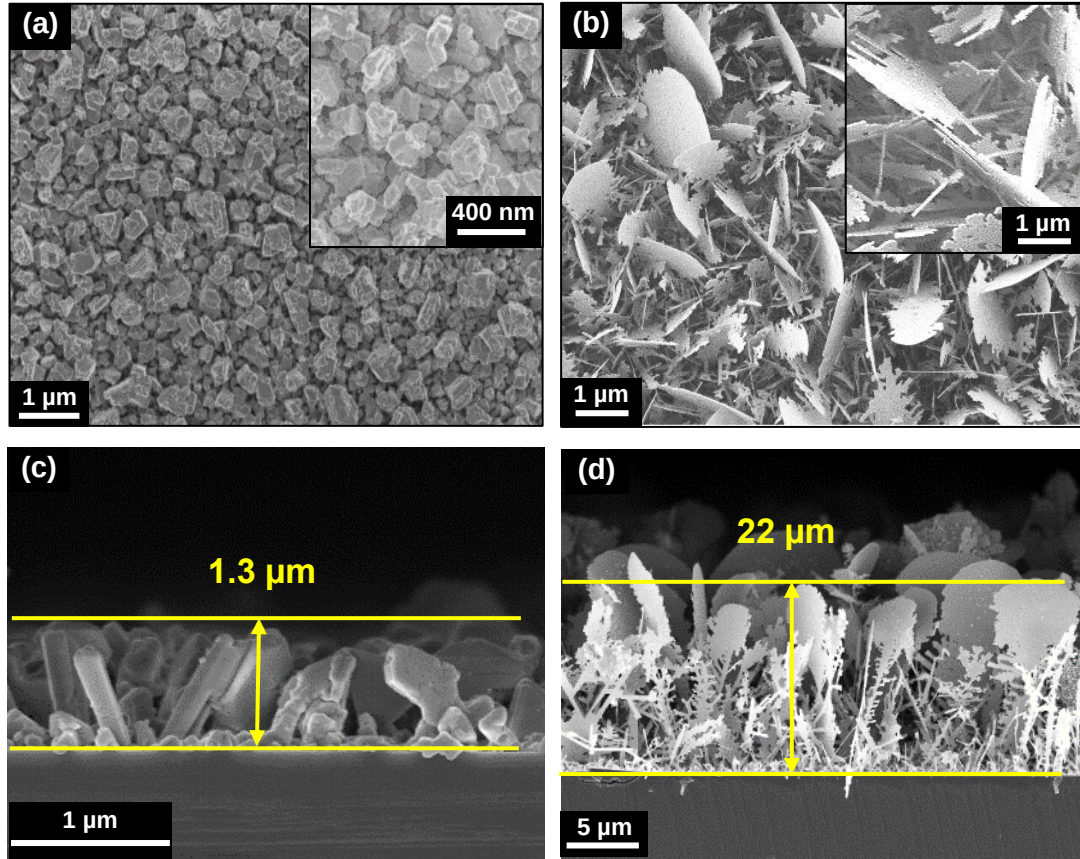


Figure III. 10. Top (a, b) and cross-sectional (c, d) SEM images of Cu_2S on Si substrates at 400 $^{\circ}\text{C}$ (left) and 450 $^{\circ}\text{C}$ (right).

➤ Compositional properties

EDX analysis of the films confirmed a Cu:S atomic ratio of approximately 2 for films deposited at 400 $^{\circ}\text{C}$ (corresponding to particles) and 1.9 for those deposited at 450 $^{\circ}\text{C}$ (associated with flake-like structures). These values are in agreement with the stoichiometry of the Cu_2S phase identified by XRD (theoretical calculation for Cu_2S , Cu:S = 2). Trace phosphorus contamination was also detected, with concentrations of 0.72 at. % in the particles and 0.13 at. % in the flakes. The lower amount of phosphorous in the flake-like structures is most likely related to the evaporation of this element due to the higher deposition temperature needed to process the flakes, as compared to the nanoparticles.

The films deposited at 400 and 450 °C were analyzed by XPS to examine the surface chemical composition and oxidation state of Cu₂S (Figure III.9). The spectra reveal the presence of the main elements constituting the films and substrate, namely Cu, S and Si, as well as contamination by C, P, and Cl coming from the copper complex.

In addition, characteristic Cu Auger electron peaks are also observed between 500 and 800 eV [4], although they are not explicitly annotated on the spectra in Figure III.11. Finally, signals associated with nitrogen can be attributed to residues of the solvent acetonitrile (C₂H₃N), as well as to the nitrogen carrier gas used during AACVD deposition.

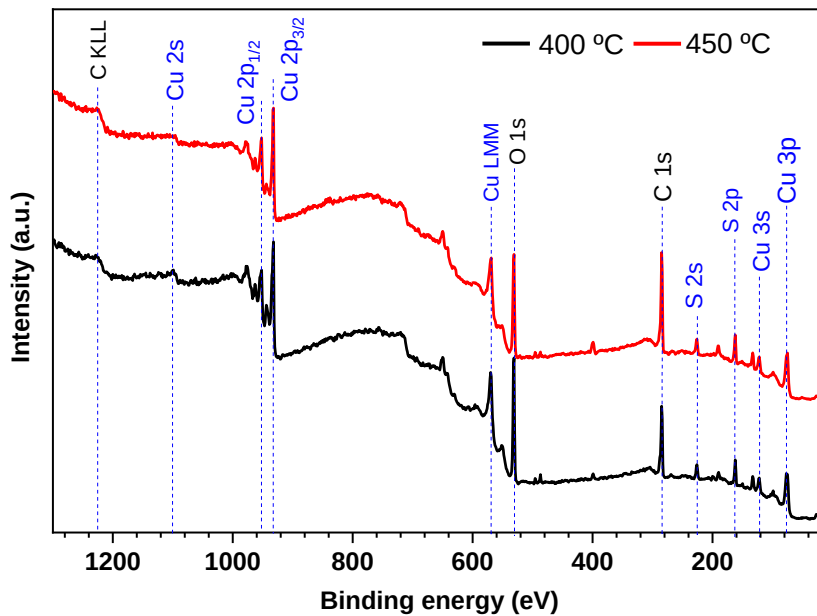


Figure III. 11. XPS overview spectra of Cu₂S films obtained from the films deposited at 400 °C (nanoparticles) and 450 °C (flakes).

The Cu 2p core-level spectra of the particle- and flake-like structures are shown in Figure III.12 a and b, respectively. Both spectra display two main binding energies located at 932.4 eV and 952.3 eV, with a difference of 19.9 eV between them, as previously reported in the literature [5]. These peaks are associated with the Cu 2p_{3/2} and Cu 2p_{1/2} photoelectron states of the Cu⁺ state. The presence of monovalent copper ions is most likely linked to the predominant Cu₂S phase identified in the XRD analysis. This is also in agreement with the S 2p spectra recorded on the samples (Figure III.12c and d), which indicate the presence of components at 161.75 eV (S 2p_{3/2}) and 163.00 eV (S 2p_{1/2}) for the nanoparticles (with a shift of around -0.2 eV for the flake structures), both associated with S²⁻ in Cu₂S [6].

Further analysis of the Cu 2p spectra reveals the presence of other components at binding energies of 934.6 eV and 954.5 eV, corresponding to the Cu 2p_{3/2} and Cu 2p_{1/2} photoelectron states of divalent copper ions (Cu²⁺). Similarly, the S 2p spectra show additional components: one at 162.57 eV for the nanoparticle films, attributed to a disulfide species (S₂²⁻), and another at 163.34 eV, possibly linked to a non-stoichiometric sulfide defect (S_d²⁻). The binding energies of these two components are shifted by ±0.1 eV in the flake structures.

The presence of these components in the spectra confirms the existence of two copper oxidation states: Cu(I), formulated as (Cu⁺)₂(S₂²⁻), corresponding to Cu₂S, and Cu(II), formulated as (Cu²⁺)(S₂²⁻), which could be attributed to non-crystalline CuS₂ existing on the film surface [7,8].

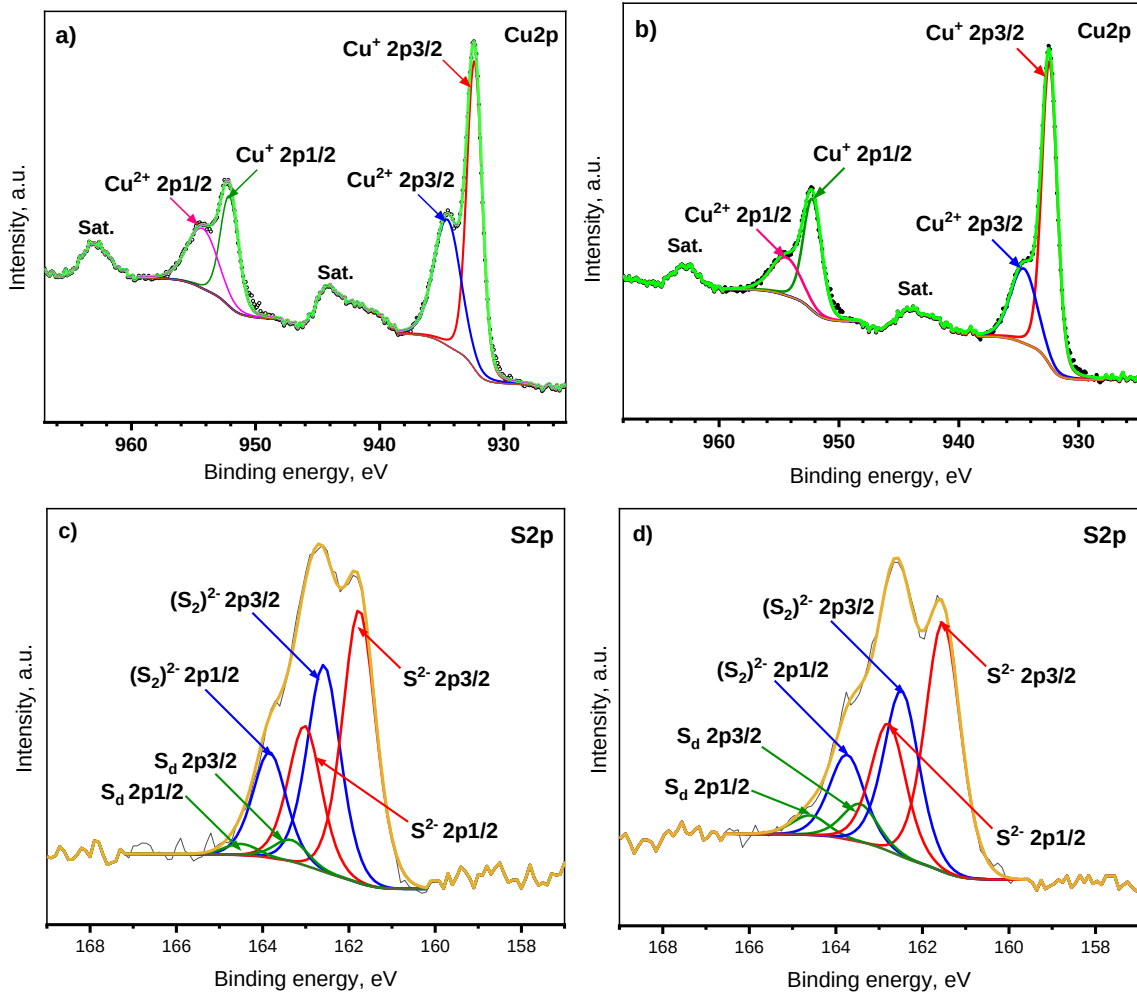


Figure III. 12. XPS spectra of Cu 2p (a, b) and S 2p (c, d) for the films deposited at 400 °C (nanoparticles - left) and 450 °C (flakes - right).

The formation of CuO at the surface cannot be ruled out either (despite the absence of components associated with this oxide in the O 1s spectra, (Figure III.13), particularly in view of the satellite shake-up peaks recorded at 944 eV and 963 eV in the Cu 2p spectra, which are generally associated with CuO copper oxide [9].

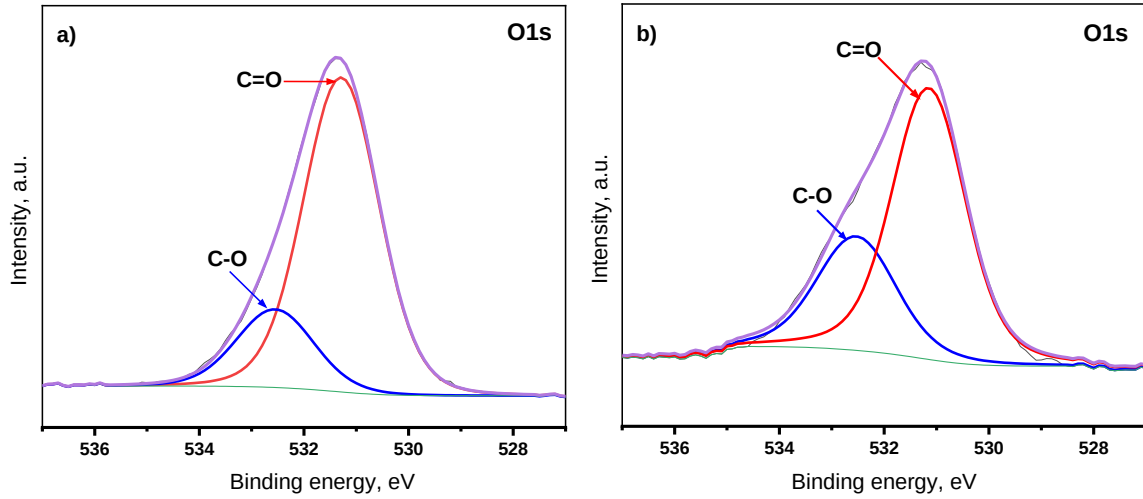


Figure III. 13. XPS spectra of the O 1s for the as deposited films based on (a) nanoparticles and (b) flakes.

Additional information on the binding energy, spin-orbit decoupling, and FWHM (Width at Half-Maximum) extracted from the Cu 2p and S 2p XPS spectra recorded on the nanoparticles and flake-based films is presented in Table III.2.

Table III. 1. Binding energy, spin-orbit splitting and FWHM of Cu and S elements in as-deposited Cu₂S thin films. NPs: Nanoparticles, Fs: Flakes.

		Peaks		BE (eV)	Spin-orbit (eV)	FWHM
Films deposited at 400 °C	NPs	Cu ⁺ 2p	3/2	932.35	19.75	1.44
			1/2	952.10		1.7
		Cu ⁺² 2p	3/2	934.54	19.72	2.53
			1/2	954.26		
		S ⁻² 2p	3/2	161.75	1.26	0.90
			1/2	163.00		0.90
		(S ₂) ⁻² 2p	3/2	162.57	1.26	0.90
			1/2	163.83		0.90
		S _d 2p	3/2	163.34	1.16	0.90
			1/2	164.5		0.90
Films deposited at 450 °C	Fs	Cu ⁺ 2p	3/2	932.43	19.77	1.51
			1/2	952.20		1.79
		Cu ²⁺ 2p	3/2	934.6	19.8	2.54
			1/2	954.4		2.89
		S ⁻² 2p	3/2	161.52	1.26	0.95
			1/2	162.78		0.95
		(S ₂) ⁻² 2p	3/2	162.48	1.26	0.95
			1/2	163.74		0.95
		S _d 2p	3/2	163.44	1.16	0.95
			1/2	164.6		0.95

➤ Wettability properties

The surface wettability of the synthesized Cu_2S nanostructures, evaluated via water contact angle measurement shown in Figure III.14, was recorded as 133° and 137° for the nanoparticles deposited at 400°C and the flakes at 450°C , respectively. This variation is primarily attributed to differences in Cu_2S film morphology, which plays a crucial role in determining wettability properties. In fact, previous studies have reported a wide range of wettability behaviors for Cu_2S , from a hydrophilic nature in Cu_2S granular-like films with a contact angle of 65° [10] to superhydrophobic behavior in Cu_2S flower-like films with a contact angle of 163° [11,12]. This suggest that the wettability of the thin films depends on its surface morphology, which is connected with the roughness and chemical composition.

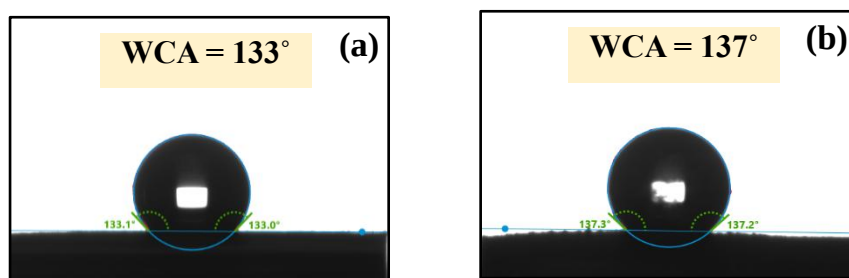


Figure III. 14. Static water contact angle measurement of Cu_2S thin films deposited at (a) 400°C and (b) at 450°C .

III.3.1.2. Effect of annealing on the morphology and structure of Cu_2S thin films

The films are intended for gas sensing applications, possibly involving thermal or photo-activation in an oxygen-containing environment. Therefore, the stability of the Cu_2S films was assessed by subjecting the samples to annealing processes run under different temperatures (150 , 250 and 350°C) in air for two hours.

➤ Structural properties

The XRD results of the annealed samples are summarized in Figures III.15. Interestingly, despite annealing the films at 150°C and 250°C in air, the structure keeps the same Cu_2S tetragonal phase as identified in the as-deposited samples. At 250°C , new diffractions appear, indicating the presence of a cubic Cu_2S phase (ICDD card no. 00-053-0522) in both particle- and flake-based films. The Cu_2P_7 phase remains present in both types of

samples after annealing at 150 and 250 °C, suggesting relative thermal stability of this phase under these conditions.

Above 250 °C, and particularly at 350 °C, a significant change is observed in the diffractograms of both films. Indeed, the tetragonal Cu₂S phase disappears, while a new CuO phase, characterized by intense diffraction peaks at 35.5° 2θ and 38.8° 2θ, and a weaker peak at 49° 2θ, is formed. This evolution reflects the transformation of the initial phases (tetragonal and cubic) into a monoclinic CuO phase (ICDD card no. 00-005-0661).

Complementary EDX analysis of samples annealed at 350°C confirmed a Cu:O atomic ratio close to 1 (Cu: 32.39 at. %, O: 36.45 at. %), indicating the presence of CuO, as well as a small amount of residual sulfur (6.28 at. % for particles and 4.57 at. % for flake structures). Previous studies have also observed the transformation of Cu₂S to copper oxide (Cu₂O) after heat treatment in air above 260 °C, followed by further oxidation to CuO at temperatures above 350 °C [13]. This indicates that sulfur atoms are replaced by oxygen atoms when the temperature exceeds 260 °C in an oxidizing atmosphere, which is consistent with our results.

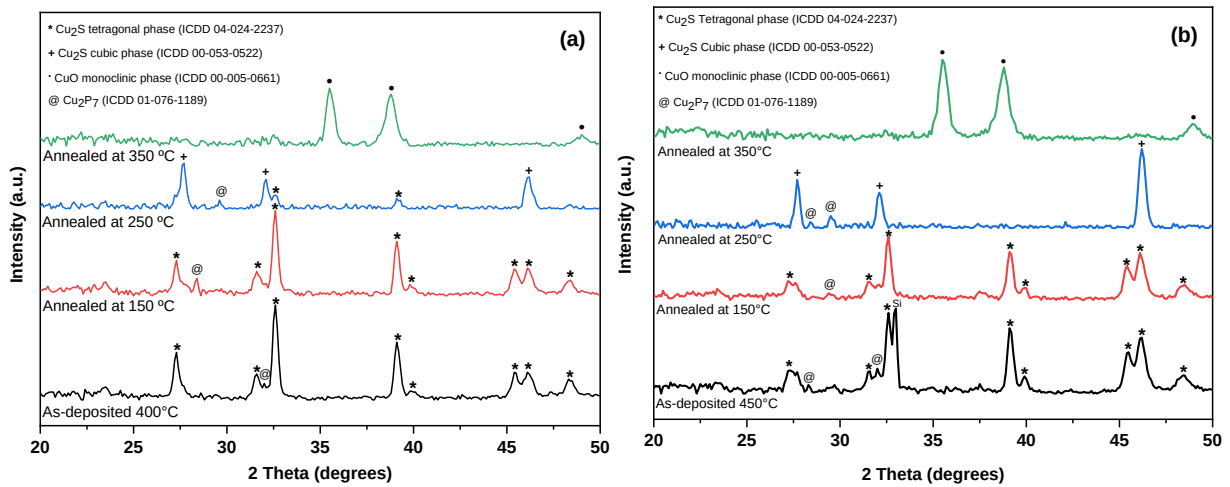


Figure III. 15. XRD patterns of Cu₂S deposited at (a) 400°C and (b) 450°C on silicon substrates after 2 hours of annealing in air at 150 °C, 250 °C, and 350 °C.

➤ Morphological properties

The effect of annealing on the morphology of films deposited at 400 °C and 450 °C was also study. The results showed that annealing the particle- and flake-based films at 150°C and 250°C did not significantly alter their morphology, as illustrated in Figure III.16. However, cross-sectional SEM images reveal an increase in the structure length, from 1.3

μm to $1.8 \mu\text{m}$ for particles and from $22 \mu\text{m}$ to $26 \mu\text{m}$ for flakes, after the annealing process at 250°C . In contrast, annealing at 350°C resulted in noticeable changes in material size and morphology, revealing the appearance of spongy agglomerates in the particle-based films and a less smooth surface for the flake-based films.

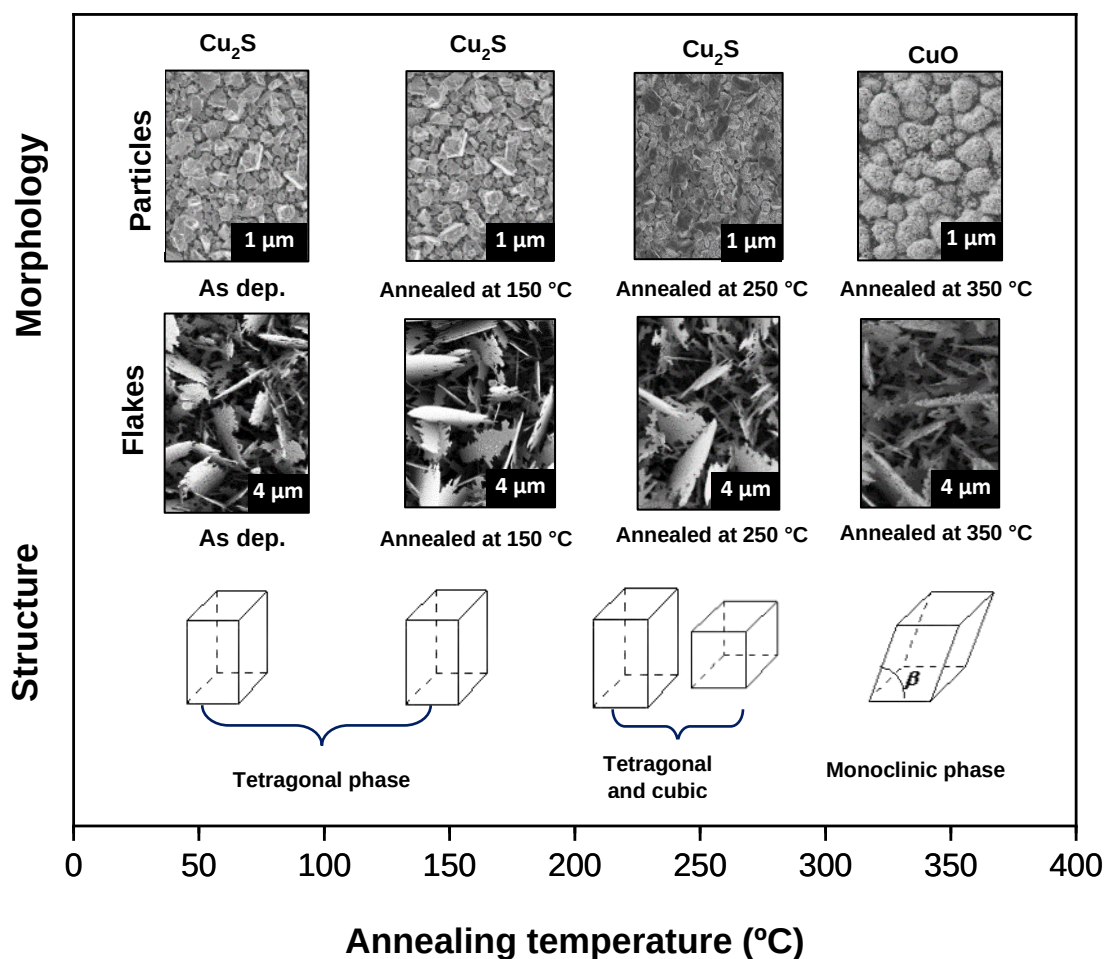


Figure III. 16. Illustration summarizing the annealing effect on film morphology and structure of Cu_2S .

➤ Compositional properties

The XPS spectra of the annealed nanoparticles and flake-like Cu_2S films are shown in Figure III.17. They reveal the presence of elements similar to those detected in the films before annealing. However, a decrease in the intensity of the nitrogen peaks and the disappearance of the chlorine peak in the case of the flakes are observed, indicating that annealing helps to reduce the contamination of certain elements. In addition, an increase in the intensity of the O 1s peak is noted, consistent with annealing under an oxidizing atmosphere.

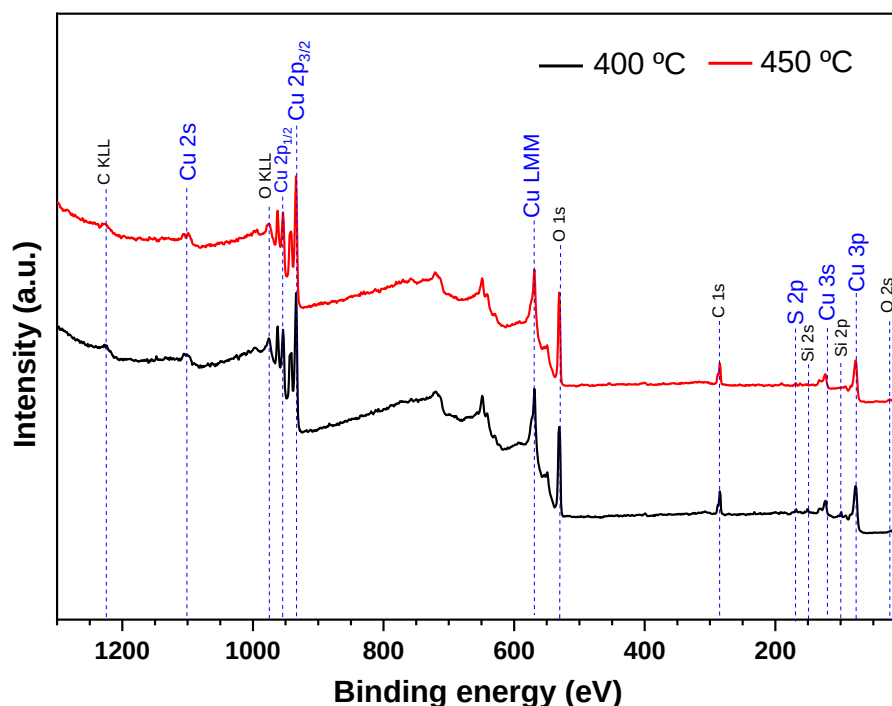


Figure III. 17. XPS spectra of Cu₂S films recorded on nanoparticle- and flake-based films deposited at 400 °C and 450 °C, respectively, after 2 hours of annealing in air at 250 °C.

XPS analysis was also carried out to determine Cu 2p binding energies in Cu₂S films annealed at 250 °C, as shown in Figure. III.18. The Cu 2p spectrum of the particle- and flake-based films shows a more intense divalent copper oxide satellite compared to the initially deposited samples, which is most likely related to CuO formation at the surface [14]. Furthermore, we observed a shift of the S 2p spectrum towards higher binding energies, i.e. 168.51 eV (S 2p_{3/2}) and 169.76 eV (S 2p_{1/2}) for nanoparticles (shifted by - 0.2 eV for flake structures), indicating the formation of metal sulfate (CuSO₄²⁻), probably due to sulfide oxidation in the presence of air [15]. These results suggest that samples annealed at 250 °C contain a surface layer of divalent copper oxide.

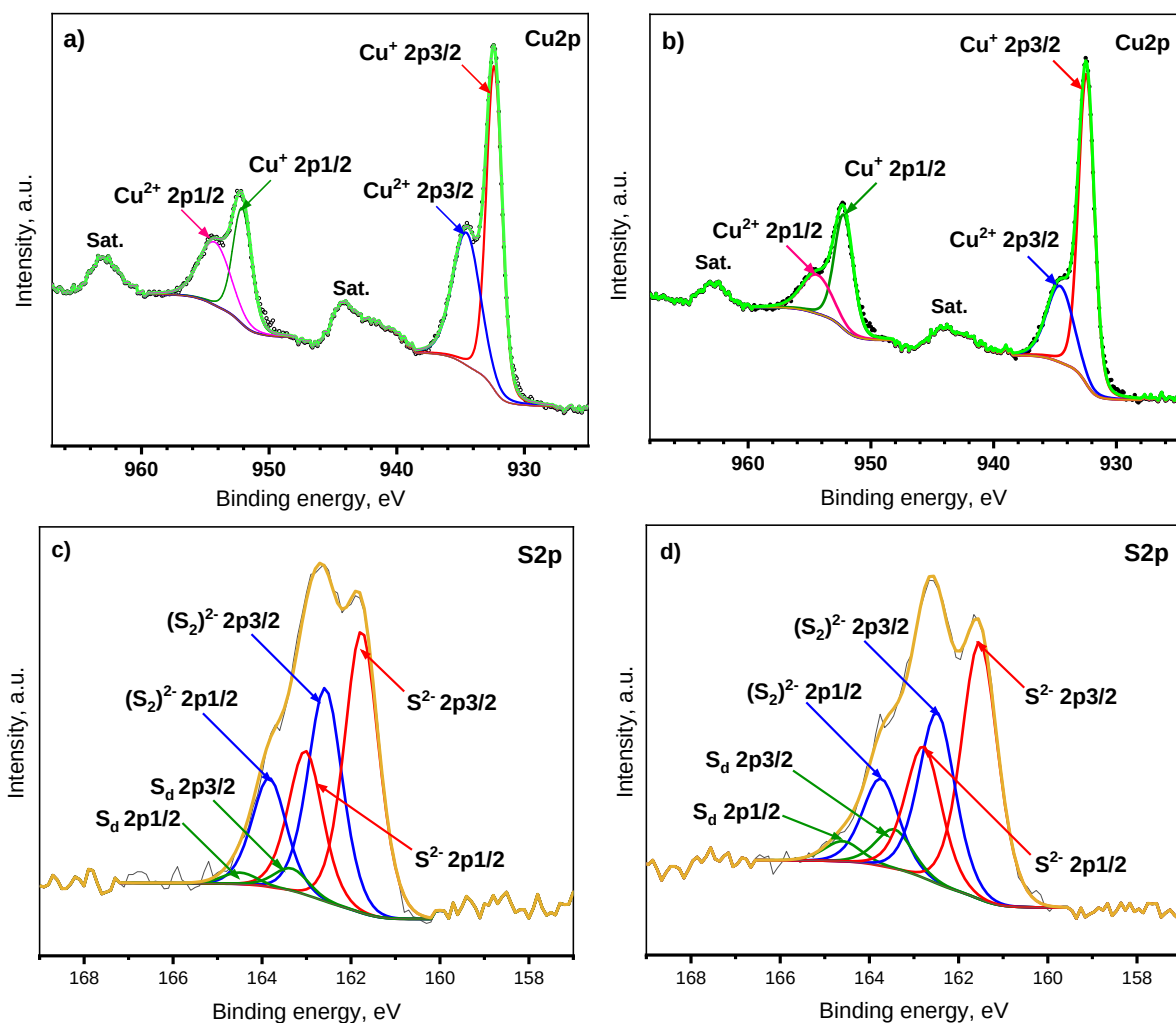


Figure III. 18. XPS spectra of the Cu 2p (a, b) and S 2p (c, d) levels for annealed (250 °C) nanoparticle-based (left) and flake-based (right) films.

This observation is in agreement with the XPS spectrum of O 1s (Figure III.19), which shows a binding energy of 529.6 eV for the particle- and flake-based films, indicating the presence of CuO, while the central crystal structure remains composed of copper sulfide as registered by the XRD analysis above. Additional information on the binding energy of the elements present in the annealed Cu₂S films (Cu 2p and S 2p) is presented in Table III.3.

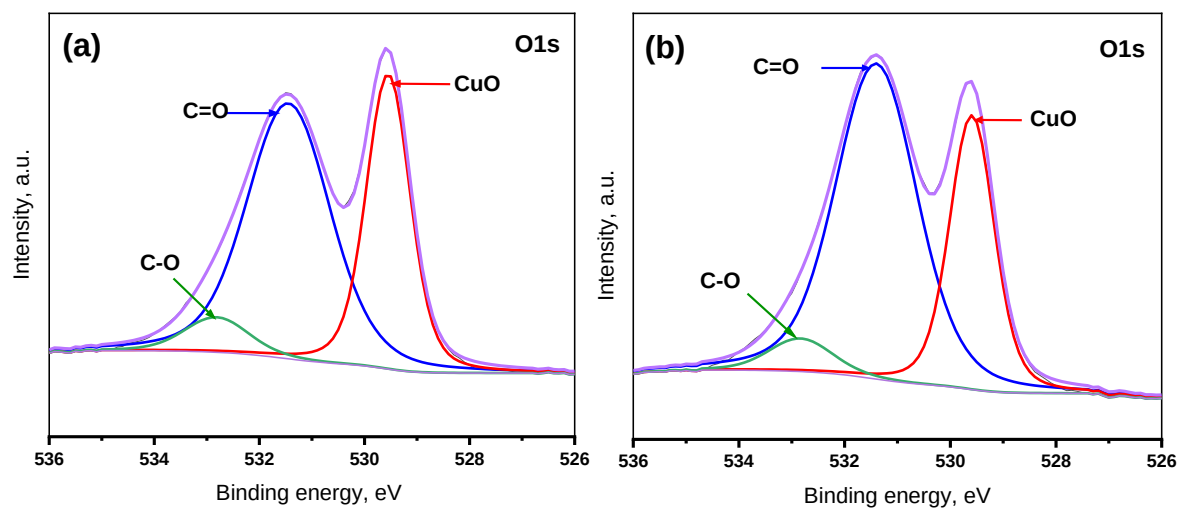


Figure III. 19. XPS spectra of the O 1s for the annealed films based on (a) nanoparticles and (b) flakes.

Table III. 2. Binding energy, spin-orbit splitting, and FWHM of Cu and S elements in annealed Cu₂S thin films. NPs: Nanoparticles, Fs: Flakes.

		Peak		BE (eV)	Spin-orbit (eV)	FWHM
Annealed films at 250 °C	NPs	Cu ⁺ 2p	3/2	933.28	19.84	2.3
			1/2	953.12		2.5
		Cu ²⁺ 2p	3/2	934.78	19.89	2.5
			1/2	954.67		2.5
		S 2p	3/2	168.51	1.26	1.5
			1/2	169.76		1.5
	Fs	Cu ⁺ 2p	3/2	933.45	19.79	2.6
			1/2	953.24		2.6
		Cu ²⁺ 2p	3/2	934.90	19.92	2.7
			1/2	954.82		2.7
		S 2p	3/2	168.32	1.2	1.34
			1/2	169.52		1.34

III.3.2. Cadmium sulfide (CdS)/selenide (CdSe) thin films

AACVD of cadmium complexes with L1 and L2 onto Si substrates yielded uniform black films with good adhesion, as illustrated in Figure III.20. SEM revealed distinct morphologies: CdS formed a dense, bulky film (Figure III.20a), whereas CdSe exhibited a nanoparticle structure with particle sizes ranging from 200 to 500 nm across all deposition conditions outlined in Chapter II.

Surprisingly, EDX analysis failed to detect the expected elemental of Cd, S, or Se in each film. Instead, carbon was the dominant element observed, accounting for 36.26 % in the CdS sample and 43.7 % in the CdSe sample. Furthermore, XRD analysis of the samples

(all tested conditions) showed no diffraction peaks, discarding the formation of a crystalline material. These observations imply that precursor decomposition may have occurred primarily in the gas phase (homogeneous pathway), without sufficient surface-mediated reaction to yield the target metal chalcogenides. Consequently, the deposited material appears to consist largely of carbonaceous residues derived from precursor breakdown.

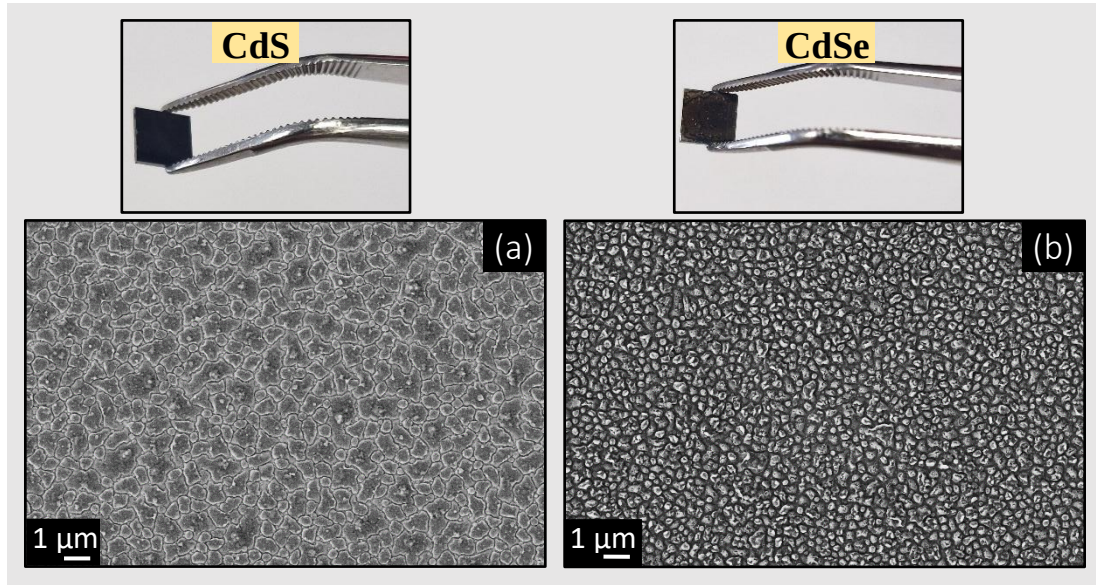


Figure III. 20. SEM images of the deposited films at 400 °C on Si substrates derived from the SSPs (a) $\text{Cd}(\text{L1})_2(\text{NO}_3)_2$ and (b) $\text{Cd}(\text{L2})_2(\text{NO}_3)_2$.

III.4. Characterization of the AACVD thin films derived from the co-deposition of precursors

III.4.1. Zinc sulfide (ZnS)

The AACVD co-deposition of ZnS thin films on silicon substrates showed good adhesion and uniform surface morphology throughout all samples, displaying a greyish to transparent appearance.

III.4.1.1. Effect of deposition temperature

ZnS films were deposited employing various temperatures: 400 °C, 450 °C, and 500 °C. Films deposited at temperatures below 450 °C show no continuous or adherent films, whereas films deposited at 450 °C and 500 °C exhibited similar structural and morphological characteristics. Hence, films deposited at 450 °C were

selected for detailed analysis of its structural, morphological, and compositional properties.

➤ Structural properties

The XRD diffraction patterns of the as-deposited ZnS thin films on Si substrates are shown in Figure III.21. The pattern of these films indicates the presence of a hexagonal ZnS phase (P63mc (186) space group, $a = 3.820 \text{ \AA}$, $b = 3.820 \text{ \AA}$, $c = 37.560 \text{ \AA}$; ICDD card No. 04-012-6799), with a prominent peak at $28.615^\circ 2\theta$ ($d = 3.12 \text{ \AA}$), corresponding to the (104) plane. Similar hexagonal (ZnS) phase has been reported previously in the literature using metal-organic chemical vapor deposition (MO-CVD) at a relatively low deposition temperature of 360°C [16]. In addition to MO-CVD, the hexagonal ZnS phase has also been achieved via various other deposition techniques, including chemical bath deposition [17] and solvothermal process [18].

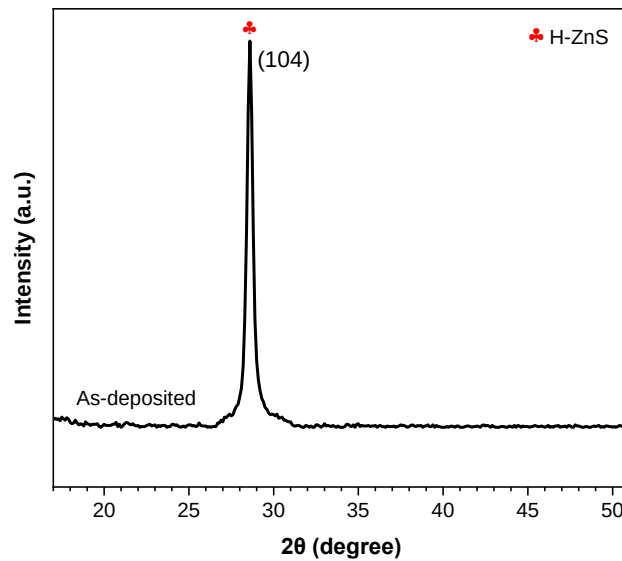


Figure III. 21. XRD patterns of the as-deposited ZnS thin films H: Hexagonal-phase.

➤ Compositional properties

XPS analysis was also performed to investigate the surface chemical composition and the oxidation state of the elements present in the as-synthesized ZnS films. The survey spectrum, shown in Figure III.22, reveals the main elements present in the sample and substrate, including Zn 2p, S 2p, and Si 2p. Additionally, the spectrum indicates contamination from P 2s, which is attributed to the ligand ($\text{Et}_4\text{P}_2\text{S}_2$) used during the deposition process.

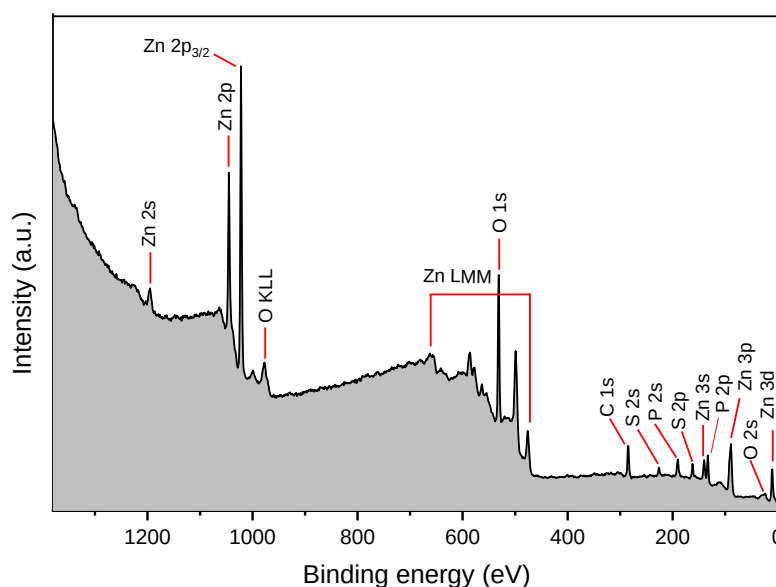


Figure III. 22. XPS spectrum of ZnS thin films deposited on silicon substrates at 450 °C.

Zn 2p, S 2p high-resolution spectra are shown in Figure III.23a and b. The Zn 2p core level spectrum displays prominent peaks at 1022.3 eV and 1045.4 eV, corresponding to the Zn 2p_{3/2} and Zn 2p_{1/2} states of Zn^{2+} , respectively. Additionally, two smaller peaks, at 1020.7 eV and 1043.8 eV, associated with the Zn 2p_{3/2} and Zn 2p_{1/2} states of Zn^+ are also present, as observed earlier for ZnS films [19]. The doublets of Zn^{2+} and Zn^+ are separated by 23.1 eV, which is consistent with values previously reported in the literature [19,20]. The deconvolution of the S 2p spectrum displayed in Figure III.23b reveals two main components at 161.6 eV and 162.8 eV, corresponding to the S 2p_{3/2} and S 2p_{1/2} states of S^{2-} , which confirms the formation of ZnS [21]. Additional sulfur-related components are observed at 162.4 eV (S 2p_{3/2}) and 163.5 eV (S 2p_{1/2}), which may be attributed to S_2^- in ZnS_2 (represented as Zn^+S_2^-) [22]. A further peak at 163.34 eV is likely associated with a non-stoichiometric sulfide defect (S_d^{2-}). The sample also reveals O 1s core-level XPS spectra, as shown in Figure III.23c, which can be fitted with two

components, at 531.5 eV and 532.3 eV, attributed to C=O and C–O–C functional groups, respectively. No component associated to metal–oxygen bond is identified in this spectrum. Additionally, the C 1s spectrum, displayed in Figure III.23d, also exhibits components associated to C=O and C–O–C bonds, apart to that related to adventitious carbon (C–C). These results indicate the absence of a metal oxide at the surface and the presence of carbon-based contaminants most likely originated from the ligand and solvent residual species.

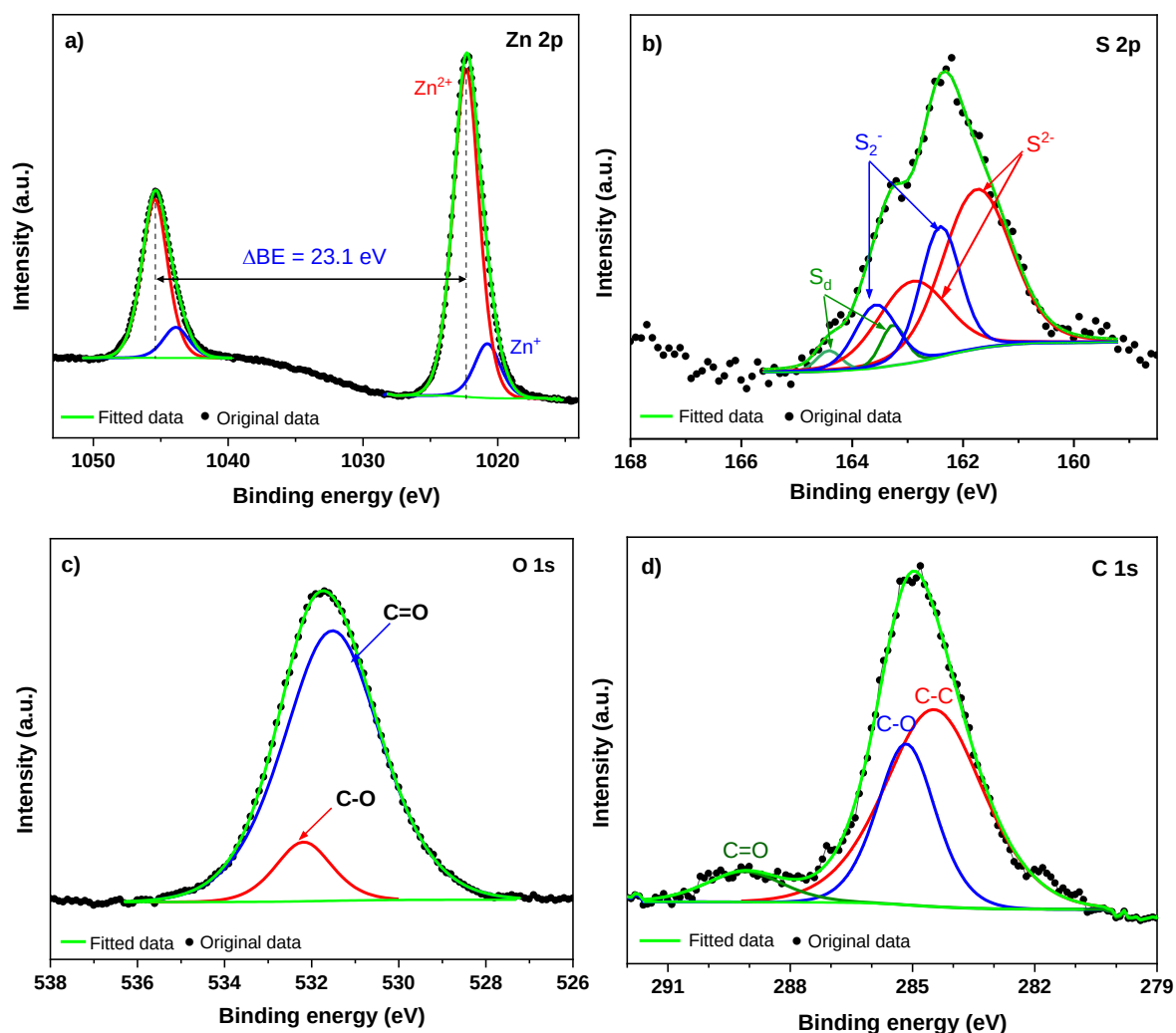


Figure III. 23. Core level XPS spectra of (a) Zn 2p, (b) S 2p, (c) O 1s and (d) C 1s of the as-synthesized ZnS films.

➤ Morphological and surface wettability properties

Figure III.24 presents SEM images of the AACVD ZnS film deposited on silicon substrate. Low-magnification image, in Figure III.24a, and high-magnification image, in Figure III.24b, demonstrate the formation of leaf-like ZnS nanostructures, with small

particles (from 20 to 50 nm in size) distributed across the leaf surface. The approximate length of these leaves ranges between 600 and 700 nm, as noticed in the cross-sectional SEM images, Figure III.24c, while their thickness is about 30 nm, estimated from the top and cross-sectional images.

The surface wettability of the synthesized ZnS nanostructures, evaluated via WCA measurement, was recorded as 109° , see Figure III.24d. Previous studies have reported a wide range of wettability behaviors for ZnS, from a hydrophilic nature in ZnS nanoparticles with a contact angle of 38.5° [23] to superhydrophobic behavior in ZnS nanowires with a contact angle of 153.8° [24]. This variation is primarily attributed to differences in ZnS film morphology, which plays a crucial role in determining wettability properties.

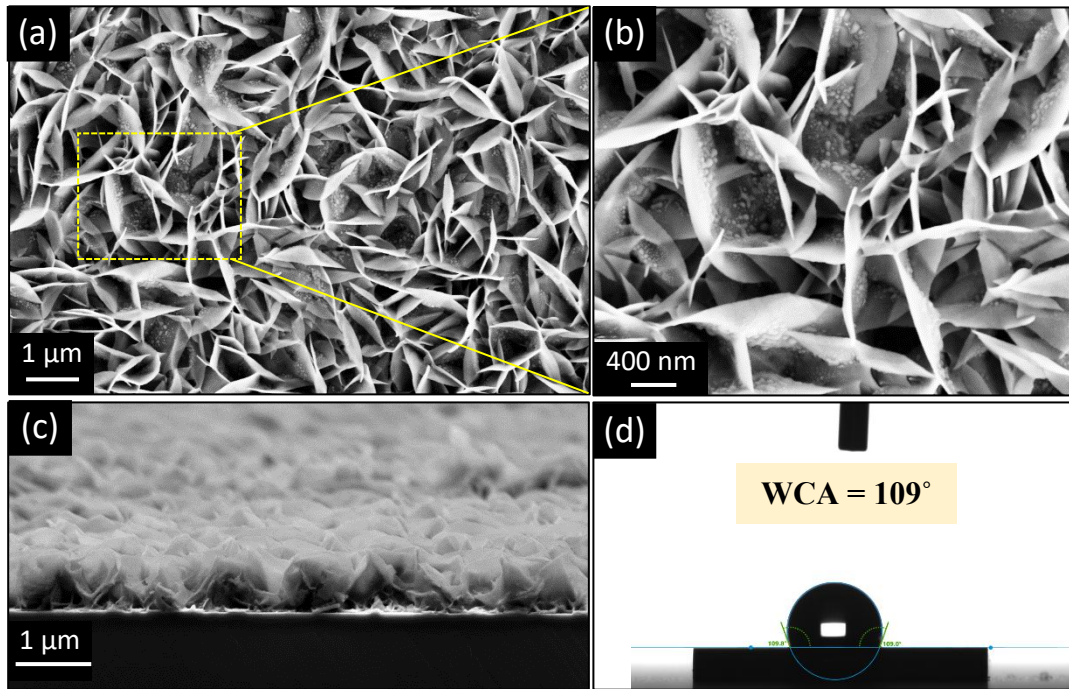


Figure III. 24. SEM images of AACVD ZnS leaf-like structures. (a) low and (b) high magnification top view, (c) cross-sectional view and (d) static water measurements.

Similarly, TEM images of the ZnS films displayed leaf-like structures, Figure III.25a, corroborating the SEM observations. HRTEM images of these structures, Figure III.25b, show an interlayer lattice spacing of approximately 0.311 nm, in agreement with the (104) plane of the hexagonal ZnS identified by XRD. This is consistent with the Fast Fourier Transform (FFT) pattern of the sample, Figure III.25c, which reveals a single-crystalline system with distance between the diffraction spots and the center of approximately 0.311 nm.

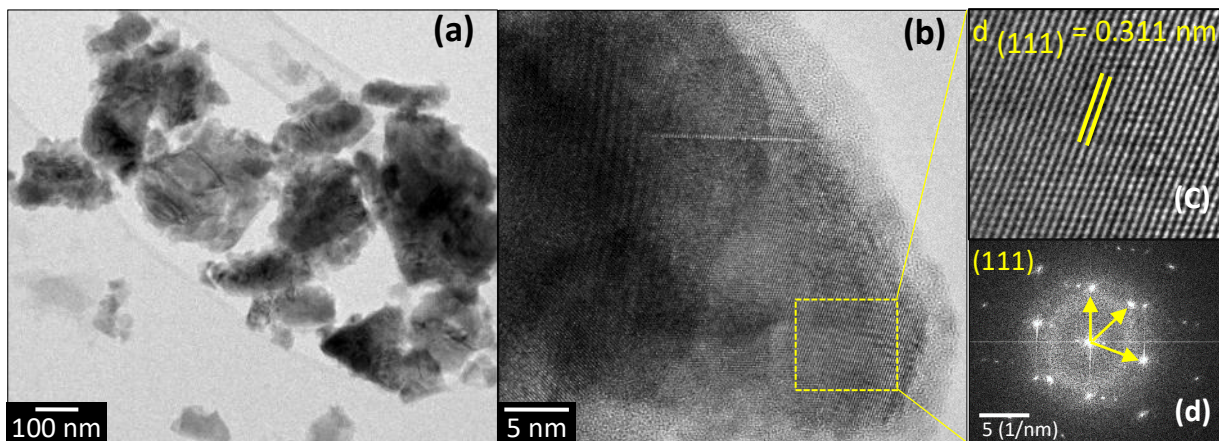


Figure III. 25. (a) Low and (b) high resolution TEM images, (c) high-magnification image of the yellow rectangle area in (b) and (d) FFT pattern of the ZnS leaf-like structures.

➤ Optical properties

Figure III.26 shows the transmittance and absorption spectra of the films, measured across the wavelength range of 200 nm to 1100 nm. Results demonstrate strong absorbance in the UV region of ≈ 95 % and a transmittance of ≈ 60 % in the visible region (between 500 and 600 nm). Notably, the measured transmittance exceeds previously reported values by 10 %, which are typically around 50 % in the same visible wavelength range [25,26]. These results highlight the enhanced optical transparency of the AACVD films.

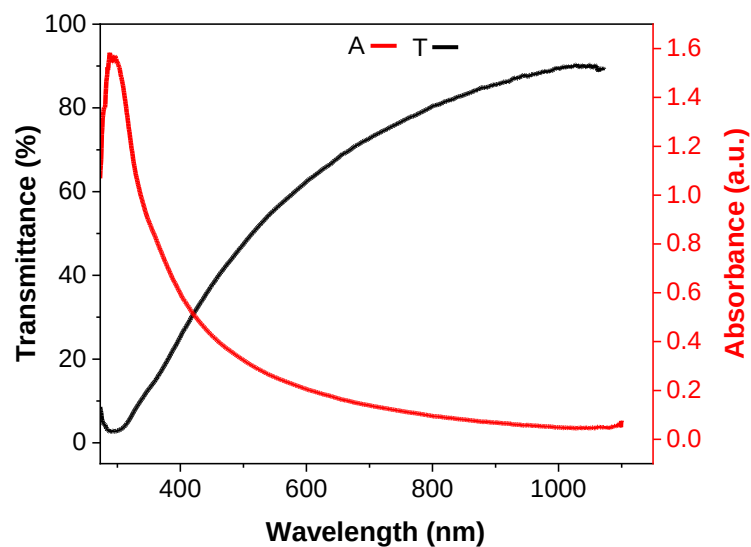


Figure III. 26. UV-visible spectroscopic study of the absorption and transmittance of zinc sulfide (ZnS) thin films deposited on glass substrates.

The band gap energy of ZnS thin films was determined using the Tauc plot formula [27], represented by: $(\alpha h\nu)^2 = A(h\nu - E_g)^n$, where α is the absorption coefficient, h is the Planck constant, ν is the frequency of the photon and A is a constant depending on the type of electronic transition. The exponent n defines the nature of the optical transition ($n = 1/2$ or $n = 2$, which correspond to direct or indirect allowed transition successively). The band gap energy E_g is determined by extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $(h\nu)$ plots to the x-axis. The results, as shown in Figure III.27, indicate that AACVD ZnS films exhibit a bandgap energy of 3.58 eV, corresponding to an absorption wavelength of 346 nm. This value is consistent with those reported in the literature [28,29].

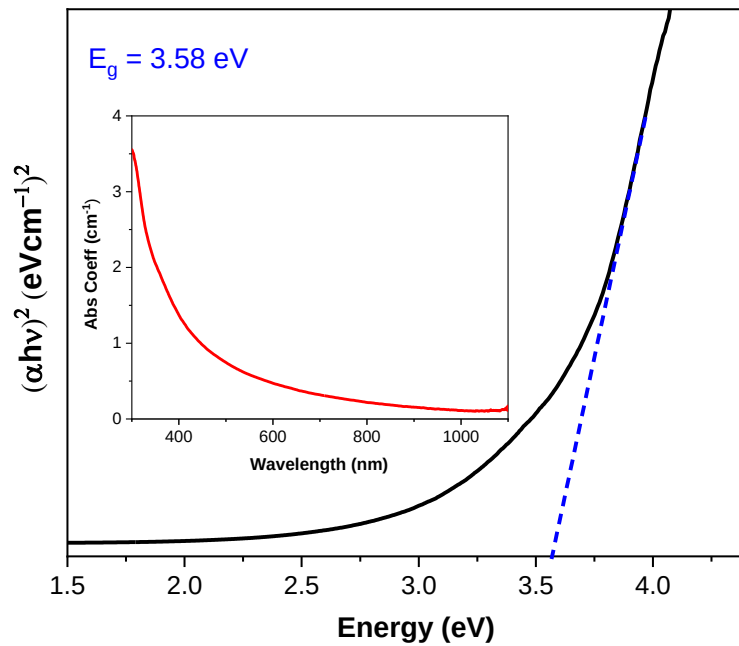


Figure III. 27. Tauc plot $(\alpha h\nu)^2$ versus $(h\nu)$ of the deposited ZnS thin film derived from the inset absorption coefficient spectrum.

III.4.1.2. Effect of annealing on the morphology, and structure of ZnS thin films

A similar pattern is observed in the annealed films (300 °C and 400 °C in air for 1 h), as shown in Figure III.28a. Though new diffraction peaks at 33° and 45.4° 2θ become visible and the intensity of the (104) plane of ZnS decreases. These slight changes in the diffraction pattern after annealing are also connected with a subtle morphological change of the ZnS structures, from well-defined highly oriented leaf-like structures to less structured and poorly oriented ones, consistent with previous observations for this material [30,31].

Indeed, SEM images reveal that the nanoleaves morphology remains largely unchanged after annealing at 300 °C. However, annealing at 400 °C leads to a significant transformation: from well-defined, highly oriented nanostructures into less structured and poorly oriented morphologies.

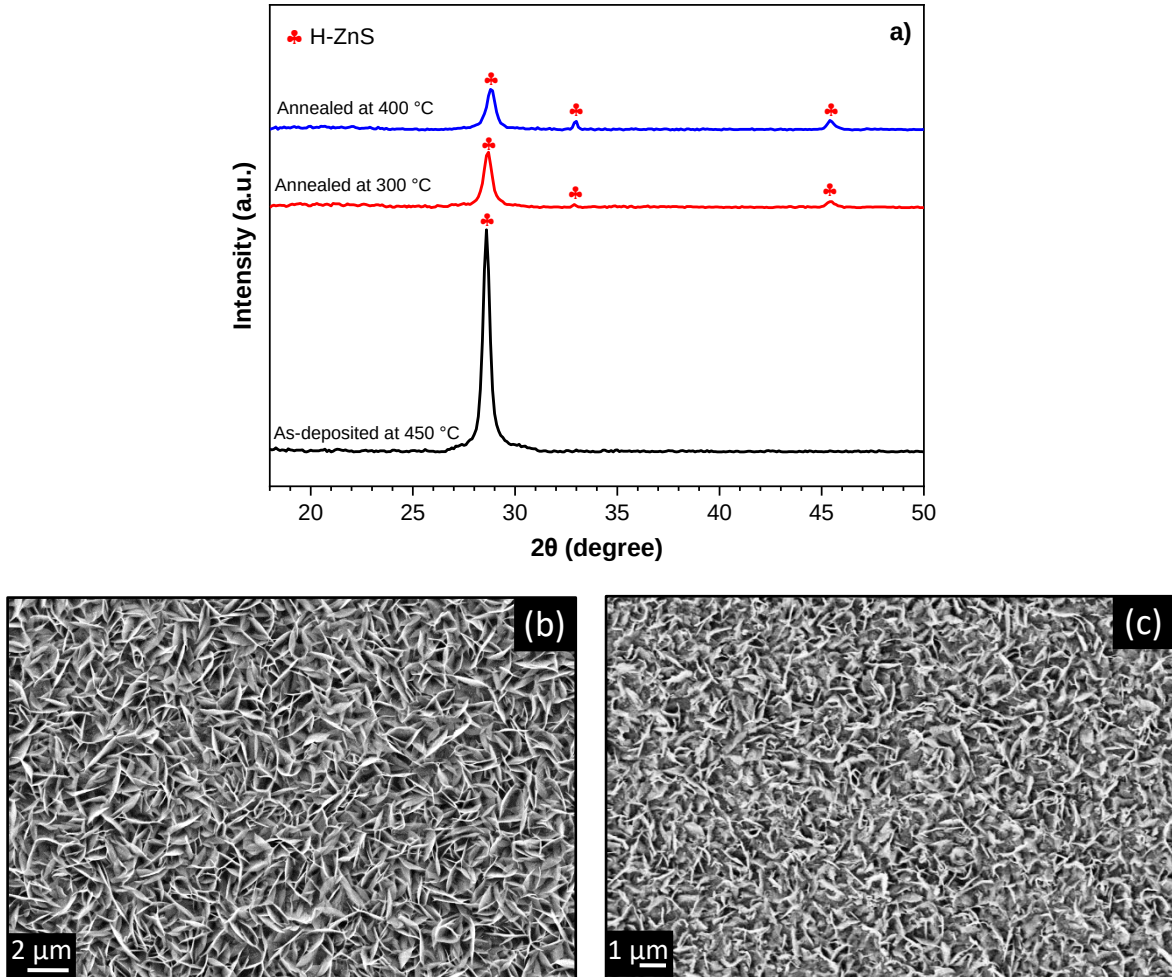


Figure III. 28. (a) XRD patterns of ZnS thin films on Si substrates, both as-deposited and annealed. SEM images of ZnS nanoleaves after annealing at (b) 300 °C and (c) 400 °C.

III.4.1.3. Effect of annealing on the optical properties of ZnS thin films

Figure III.29a and c presents the transmittance and absorption spectra of ZnS thin films annealed at 300 °C and 400 °C, respectively, measured over the same wavelength range as the as-deposited films. Compared to the as-deposited samples, the annealed films exhibit similar UV absorption ($\approx 95\%$) but show a noticeable reduction in visible-range transmittance, decreasing from approximately 60 % to 30 % between 500 and 600 nm. Furthermore, the optical band gap energy (E_g) of both annealed samples is reduced by

0.43 eV relative to the as-deposited film (Figure III.29b and d), which has a band gap of 3.58 eV.

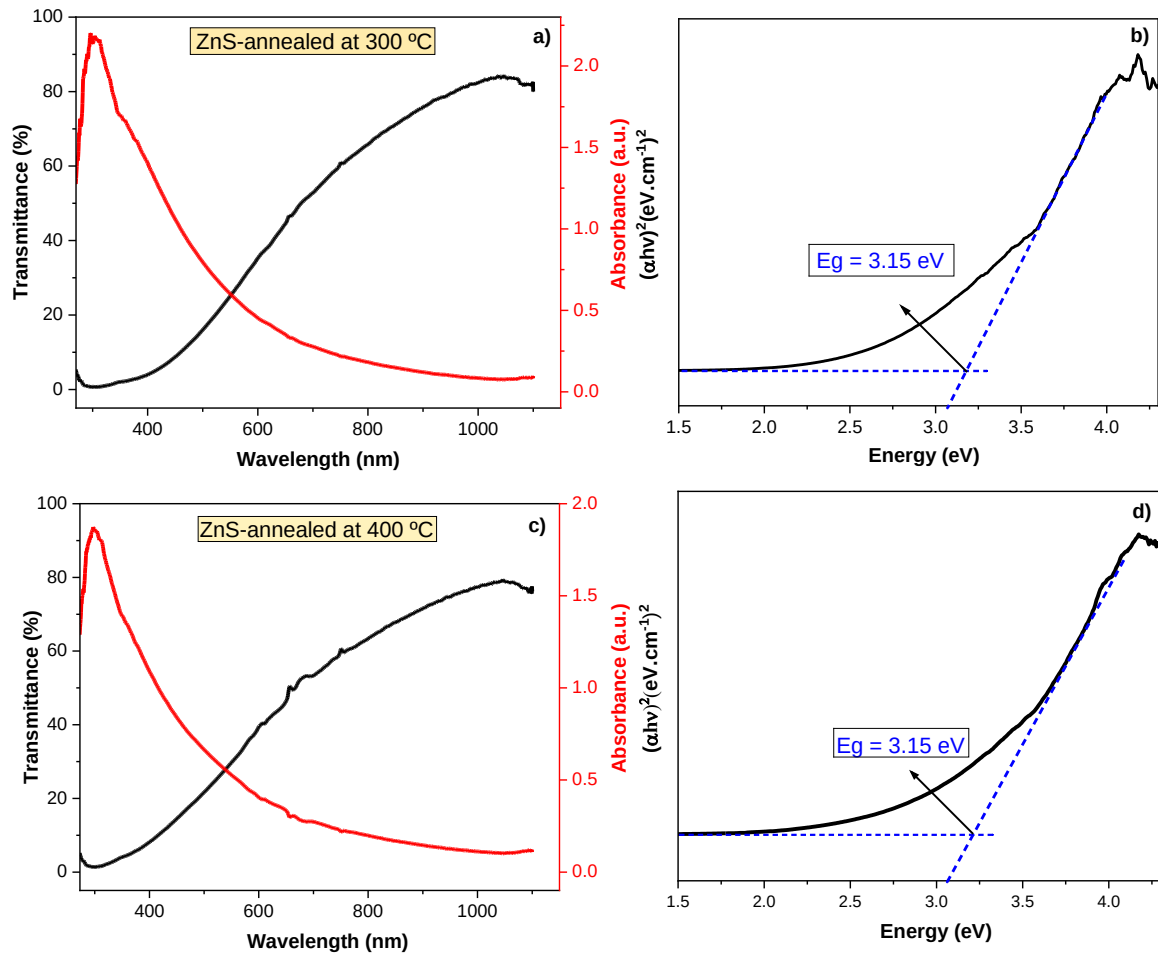


Figure III. 29. UV visible absorption and transmittance spectra and Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$ for ZnS annealed at 300 °C (a, b) and 400 °C (c, d).

III.6. Conclusion

Results confirmed the successful synthesis of the metal complexes, namely $[\text{Cu}(\text{Et}_4\text{P}_2\text{S}_2)\text{Cl}]_2$, $[\text{Cd}((\text{Me}_2\text{N})_3\text{PS})_2(\text{NO}_3)_2]$, and $[\text{Cd}((\text{Me}_2\text{N})_3\text{PSe})_2(\text{NO}_3)_2]$, demonstrating their structural stability and their high purity. Notably, the copper complex featuring the $\text{Et}_4\text{P}_2\text{S}_2$ ligand was shown to function as a single-source precursor (SSP) for the AACVD deposition of Cu_2S thin films. In contrast, the cadmium analogue did not exhibit the same reactivity and stability under a variety of AACVD conditions applied.

Furthermore, it was demonstrated that employing a mixture of precursors (i.e., ZnCl_2 and $\text{Et}_4\text{P}_2\text{S}_2$ ligand), co-deposited in one-step, enables the successful synthesis of structured ZnS thin films. These findings highlight the versatility of the precursor approach, illustrating that target materials can be efficiently obtained either from single-source precursors or by co-depositing two precursors in the same solution.

The structural, morphological, and compositional characterization of Cu_2S and ZnS thin films processed via AACVD revealed their favorable physicochemical properties, including high crystallinity and well-defined surface morphology. Thermal annealing studies demonstrated the thermal stability of Cu_2S films up to $250\text{ }^\circ\text{C}$, while ZnS films remained stable up to $400\text{ }^\circ\text{C}$ before undergoing oxidation to their respective metal oxides. Furthermore, the properties of Cu_2S and ZnS indicated their strong potential for integration into gas sensing platforms. Their performance in detecting a range of target gases is presented and discussed in the following chapter.

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Chapter IV

Application: Gas sensing

IV.1. Introduction

Rapid industrialization and urbanization have led to a significant increase in emissions of air pollutants such as nitrogen dioxide (NO_2), nitrogen oxide (NO), ammonia (NH_3), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and volatile organic compounds (VOCs). When their concentrations exceed recommended thresholds, these substances can have harmful effects on both human health and the environment. Therefore, the development and implementation of advanced gas sensing technologies are essential for effective monitoring and real-time management of air quality [1]. Such technologies are also used in a wide range of applications, including medical diagnostics [2], environmental monitoring [3], and industrial processes control [4,5], as illustrated in Figure IV.1.

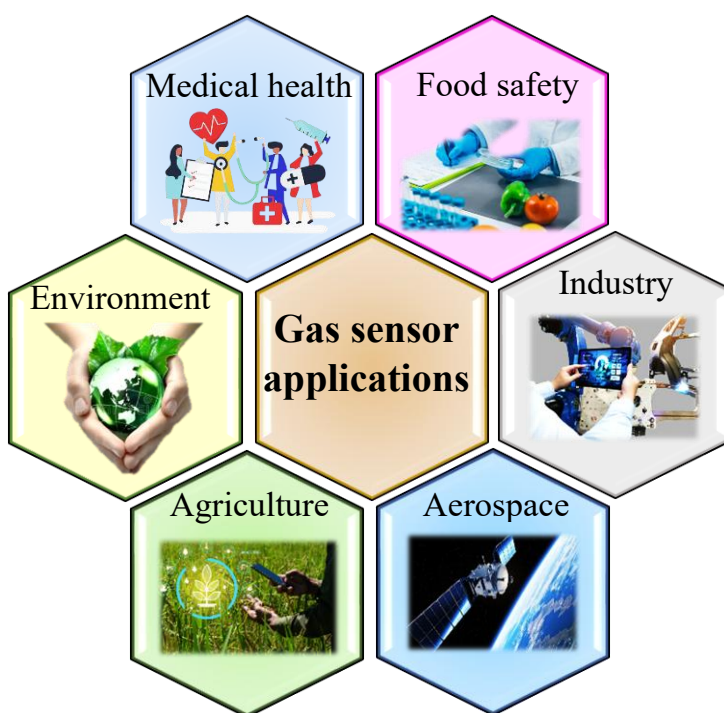


Figure IV. 1. Multidisciplinary applications of gas sensing technologies.

A wide variety of gas sensors have been developed to detect toxic and hazardous gases, leveraging diverse sensing materials such as metal oxides, metal sulfides, polymers, and graphene. Among these, metal sulfides have emerged as particularly promising candidates for use as sensitive layers in gas sensor platforms. Recent studies show that their integration can significantly enhance sensor performance offering high sensitivity,

stable operation at ambient temperatures, and consequently, reduced energy consumption [6].

This chapter primarily presents the performance of gas sensors based on copper sulfide (Cu_2S) and zinc sulfide (ZnS). For the Cu_2S -based sensor, the resistive responses of as-deposited thin films based on nanoparticles and flakes films are compared. Additionally, the influence of the annealing process and the humidity on sensor response are investigated. In the case of the ZnS -based sensor, the study focuses on its optical response to gases and the evaluation of how humidity affects sensor response.

IV.2. Copper sulfide (Cu_2S)-based gas sensors

Cu_2S films deposited at 400 °C and 450 °C, before and after annealing at 250 °C, were directly integrated into silicon-based MEMS platforms using the AACVD technique, as shown in Figure IV.2. Their sensing performance was carried out in the presence of various gases in dry and humid environments, including ethanol, hydrogen, acetone and toluene. Gas sensing tests were conducted under thermal and photo activation. Overall, thermal activation at 200 °C showed no response to the analytes tested. In contrast, a detailed study of the response under photoactivation ($\lambda = 365 \text{ nm}$) at room temperature (RT) revealed a sensitivity to different NO_2 concentrations (1 ppm, 3 ppm, and 5 ppm).

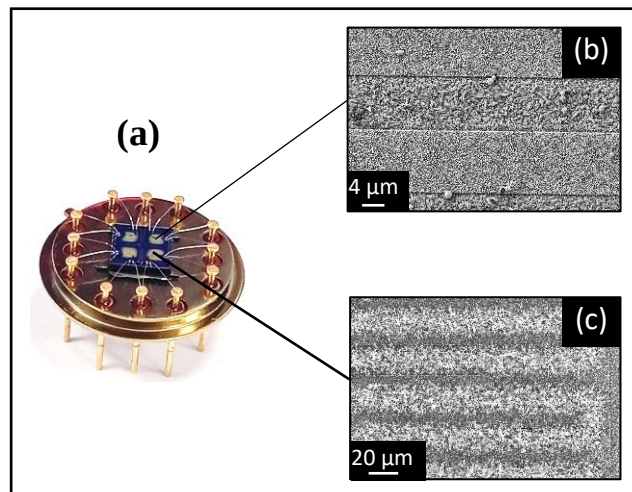


Figure IV. 2. Photograph of the set of 4 microsensors mounted on a standard TO8 packaging (a), SEM images showing one of the coverages of the electrodes with Cu_2S particles deposited at 400 °C (b) and Cu_2S flakes deposited at 450 °C (c).

The following section investigates how morphology, thermal annealing, and exposure to humid environments influence the sensors' response.

IV.2.1. Effect of the morphology on the sensor's response in dry air

The gas sensing responses of the as-deposited Cu₂S-based particle and flake films to different concentrations of NO₂ in a dry environment under photoactivation are presented in Figure IV.3. Results register a response to NO₂ after each injection of the gas in different concentrations into the test chamber. These responses are reversible and more intense for the flake-based sensor at all gas concentrations, which can be explained by the change in material morphology and the higher surface-to-volume ratio of flake-based films compared with particle-based ones [7,8]. Also, the response times of the sensors are significantly influenced by the morphology of the structures demonstrating faster response times for the flakes (e.g., 120 s for 5 ppm of NO₂) than for the particles (e.g., 160 s for 5 ppm of NO₂).

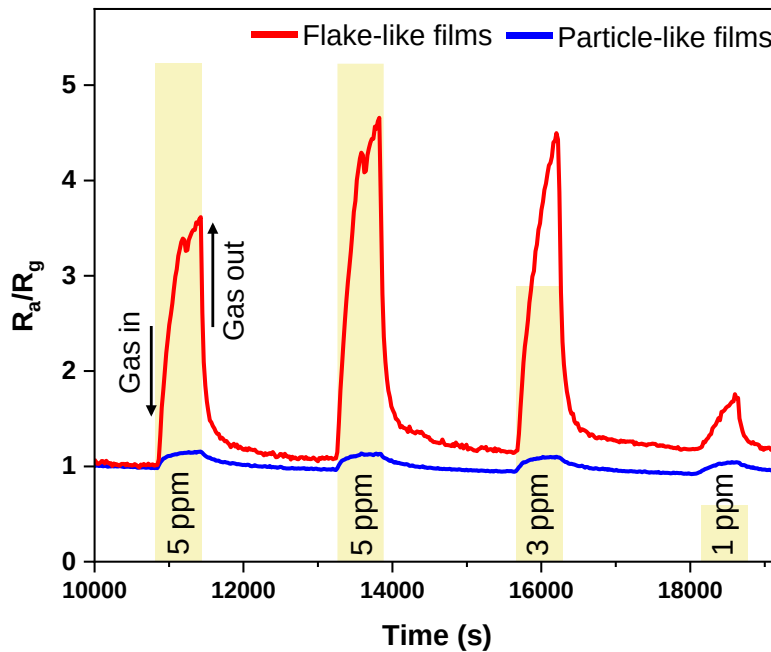


Figure IV. 3. Gas sensor response upon NO₂ in dry environment by the as-deposited Cu₂S particle- and flake-like films. The yellow bars represent the timing of analyte injection.

IV.2.2. Effect of annealing process on the sensor's responses to NO₂

Results of the annealed sensors at 250 °C, presented in Figure IV.4, demonstrate significant improvement compared to the as-deposited films. The responses of the annealed films are more stable, reversible and intense than the as-deposited films. This

improvement in stability is particularly noticeable for sensors based on annealed flakes, which show better response and repeatability to 5 ppm of NO₂ ($R = 5.2$). On the other hand, sensors based on annealed particles exhibit a more pronounced response intensity across all tested NO₂ concentrations ($R = 2.5$). Additionally, annealing significantly reduces the response time by approximately half compared to the as-deposited sensor, for the annealed flakes (e.g., 60 s for 5 ppm for NO₂) and for the particles (e.g., 80 s for 5 ppm for NO₂). Estimation of the sensitivity of both sensors using a power-law fit ($R = a.C^b$, where the prefactor “a” represents the sensitivity “S” of the sensor) highlights a higher sensitivity for flake-based sensors ($S = 3.92 \text{ ppm}^{-1}$) than for particle-based sensors ($S = 2.30 \text{ ppm}^{-1}$).

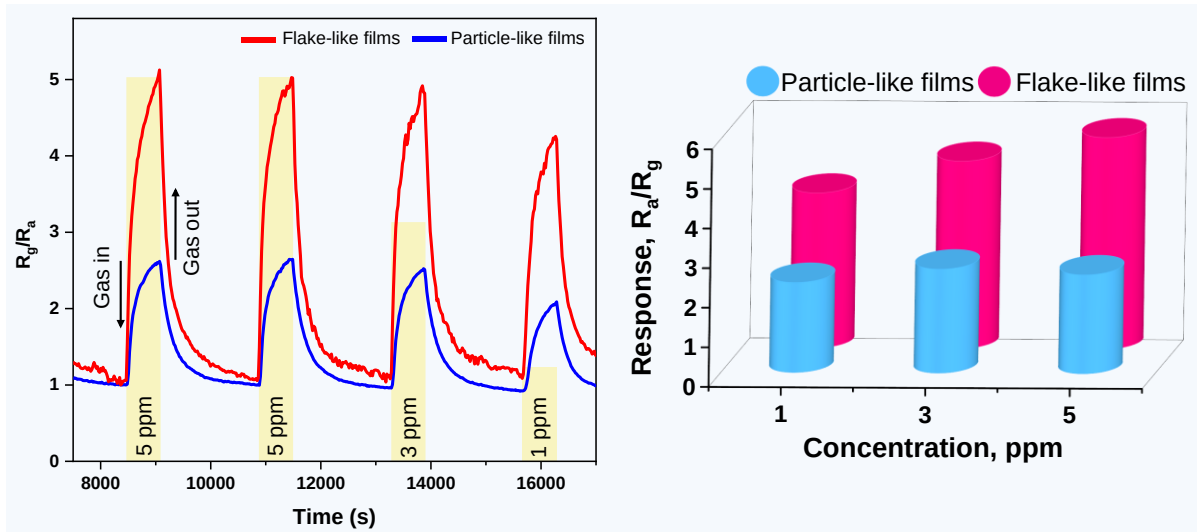


Figure IV. 4. Gas sensor response to NO₂ as a function of concentration (1, 3, and 5 ppm) in dry (0 % RH) environment of the annealed Cu₂S-based particle and Cu₂S-based flake sensors.

IV.2.3. Effect of humidity on the sensor's responses

The responses of the annealed sensors were recorded in humid environments (40 % RH) and were compared to the annealed sensor in dry environments (0 % RH), as shown in Figure IV.5. Results show that the flake-based sensors maintain a similar response to NO₂ in humid conditions, irrespective of concentration, compared with results obtained in dry conditions. In contrast, sensors based on annealed particles show a slight increase of around 10 % in response (compared with dry air) when a humidity level of 40 % RH is introduced into the system. Furthermore, the particle-based sensors also indicated a decrease in response time from 80 s to 60 s at a concentration of 5 ppm of NO₂, whereas

the flake-based sensors maintained a consistent response time of 60 s, as observed in dry air.

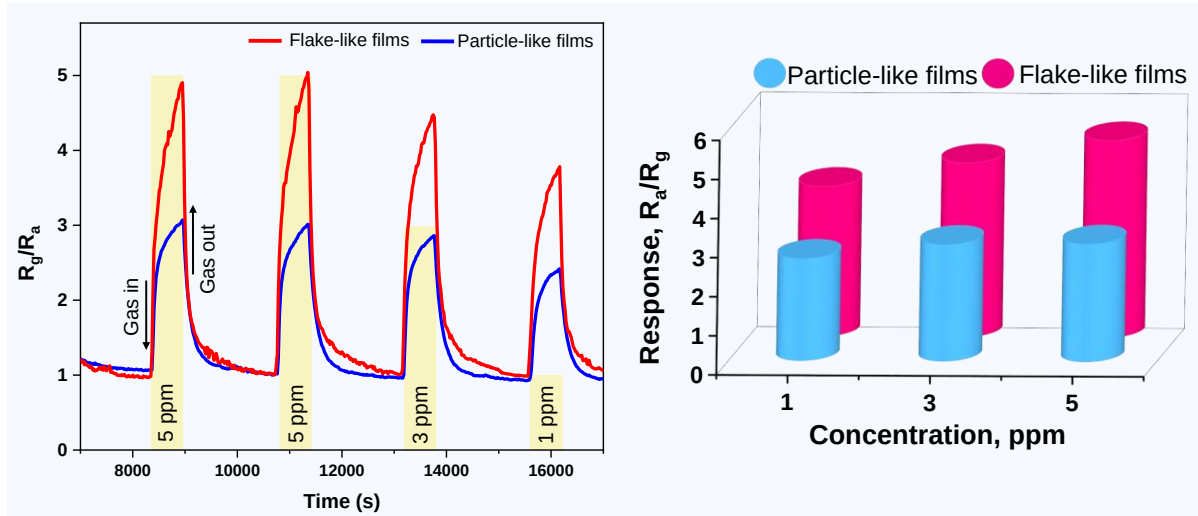


Figure IV. 5. NO_2 gas sensor response of the annealed Cu_2S particle and flake films, in humid environment (40 % RH).

IV.2.4. Gas sensing mechanism of Cu_2S

The sensing mechanism of the sensor is as follows: At room temperature in ambient air, molecular oxygen adsorbs onto the surface of Cu_2S and onto the sulfur vacancy sites, where it captures free electrons to form chemisorbed oxygen ions ($\text{O}_2^-(\text{ads})$). Upon exposure to UV light ($\lambda = 365 \text{ nm}$), electron-hole pairs are photogenerated in the semiconductor, and the resulting holes promote the adsorption and ionization of additional oxygen molecules, forming photoinduced oxygen species ($\text{O}_2^-(h\nu)$).

Upon exposure to NO_2 gas, a reaction occurs between photogenerated oxygen ions ($\text{O}_2^-(h\nu)$) and the gas molecules, resulting in the adsorption of NO_2 onto the surface of Cu_2S and at sulfur vacancy sites as illustrated in Eq. 1.



After the removal of NO_2 gas, the adsorbed molecules desorb from the surface and release the captured electrons, leading to the recovery of the material's baseline resistance.

IV.3. ZnS sulfide (ZnS)-based gas sensors

ZnS nanoleaves were directly deposited on ITO/glass substrate by AACVD at 450 °C, and their response was evaluated toward various reducing gases (ethanol, toluene, hydrogen, carbon monoxide) as well as an oxidizing gas (nitrogen dioxide). Gas sensing tests were conducted at room temperature, in dry (0% RH) and humid (40% RH) conditions. Electrical measurements showed no detectable response to any of the tested analytes, in contrast, a detailed analysis of the optical responses revealed clear sensitivity to the target gases.

IV.3.1. Optical gas sensing response of ZnS in dry air

Generally, the optical gas sensing tests of the films at RT showed variations in the transmitted light intensity at $\lambda = 360$ nm after each target gas injection, suggesting an interaction of the gas molecules with the ZnS surface. Results, under dry ambient conditions in Figure IV.6 showed the most intense responses to toluene followed by carbon monoxide, ethanol, and hydrogen, among reducing gases. Response to nitrogen dioxide (an oxidizing gas) was also registered.

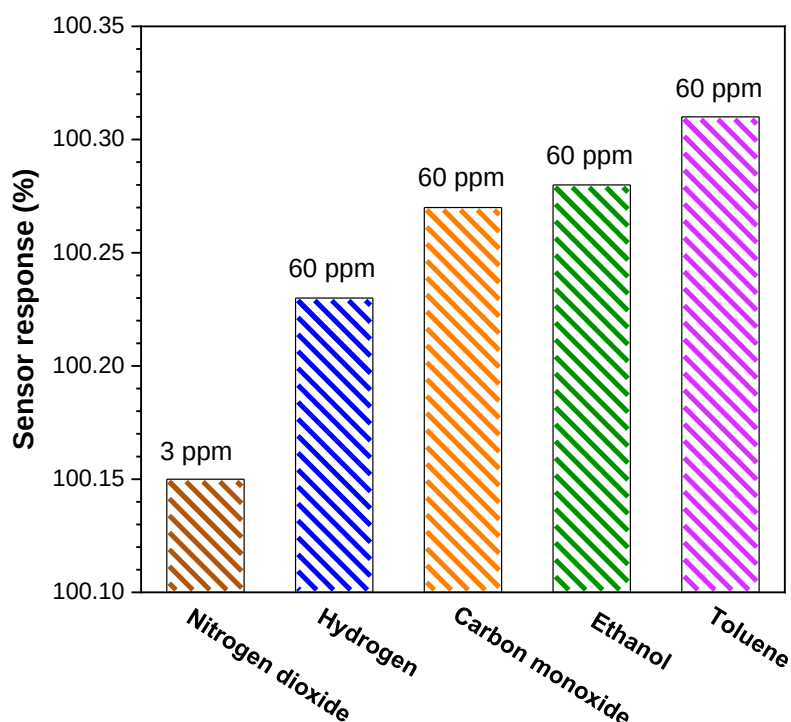


Figure IV. 6. Summary of the ZnS optical responses to 3 ppm of nitrogen dioxide and 60 ppm of hydrogen, ethanol, carbon monoxide, and toluene under dry ambient conditions (0 % RH).

Since the response for the reducing gases was higher towards toluene, results below mainly focuses on this analyte. In Figure IV.7a, one can see the changes in the intensity of transmitted light of the sensor in response to varying concentrations of toluene in dry ambient. The sensor exhibits a reversible response, with decrease in the intensity upon exposure to toluene and recovering upon gas removal. Such a reversibility is also observed in Figure IV.7b, in which the response to 60 ppm of toluene, over multiple cycles, shows a good repeatability with similar changes in light intensity. Overall, tests demonstrated an initial drift of the baseline that stabilizes by the third cycle (approximately 80 minutes), as noticed in both figures IV.7a and 7b. The concentration (C) Vs response (R) curves of the sensor, Figure IV.7c, indicate a linear tendency and a sensitivity of $4 \times 10^{-3} \text{ ppm}^{-1}$, obtained by a fitting the data with the linear equation ($R = aC + b$), where the prefactor a represents the sensitivity.

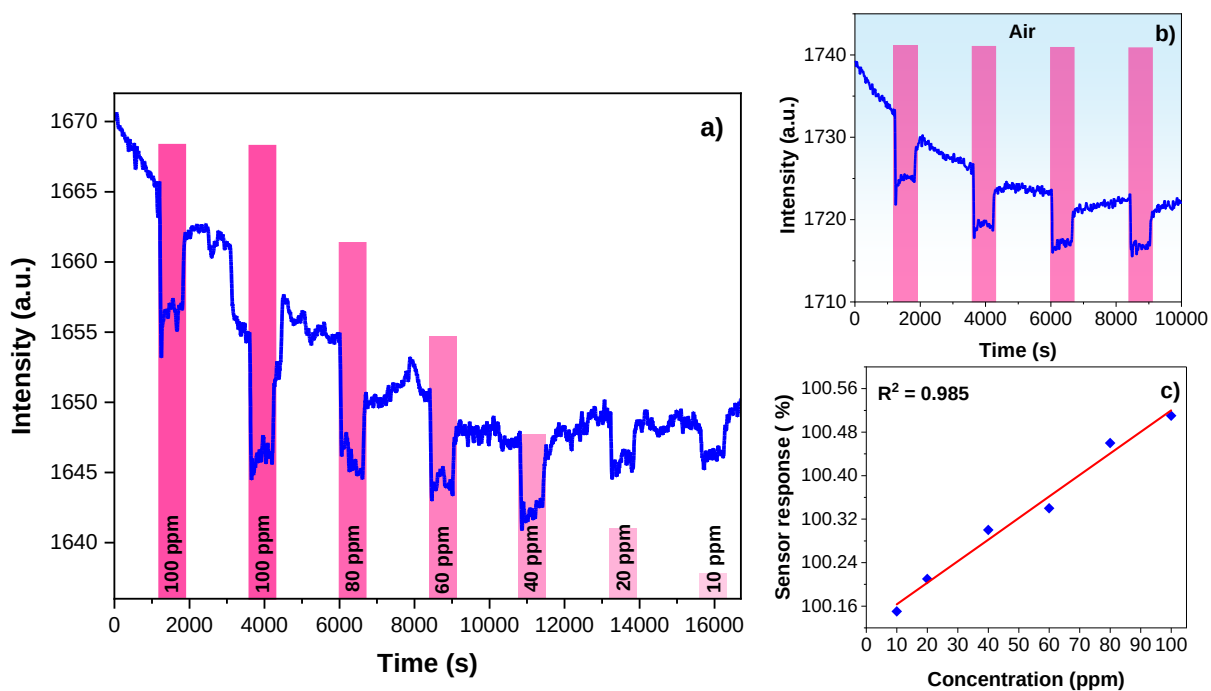


Figure IV. 7. (a) Transmitted light intensity variations as a function of toluene concentration (10–100 ppm), (b) transmitted light intensity signals during repeated exposures to 60 ppm toluene and (c) sensor response as function of toluene concentration. The pink bars represent the timing of analyte injection. Tests were performed in dry (0 % RH) ambient.

The ZnS films also exhibited sensitivity to oxidizing gases, such as nitrogen dioxide (NO_2), in dry air at RT under the same wavelength conditions ($\lambda = 360 \text{ nm}$). As for the reducing gases, the sensor displayed a decrease in the transmitted light intensity. It also demonstrated good reversibility and repeatability with a slight baseline drift over the testing period as depicted in Figure IV.8a. The optical response increased clearly and proportionally with rising NO_2 concentration, as summarized in Figure IV.8b. An approximate sensitivity of 1 ppm^{-1} was obtained by fitting the data to a power-law relationship ($R = a \cdot C^b$), where the prefactor a represents the sensitivity.

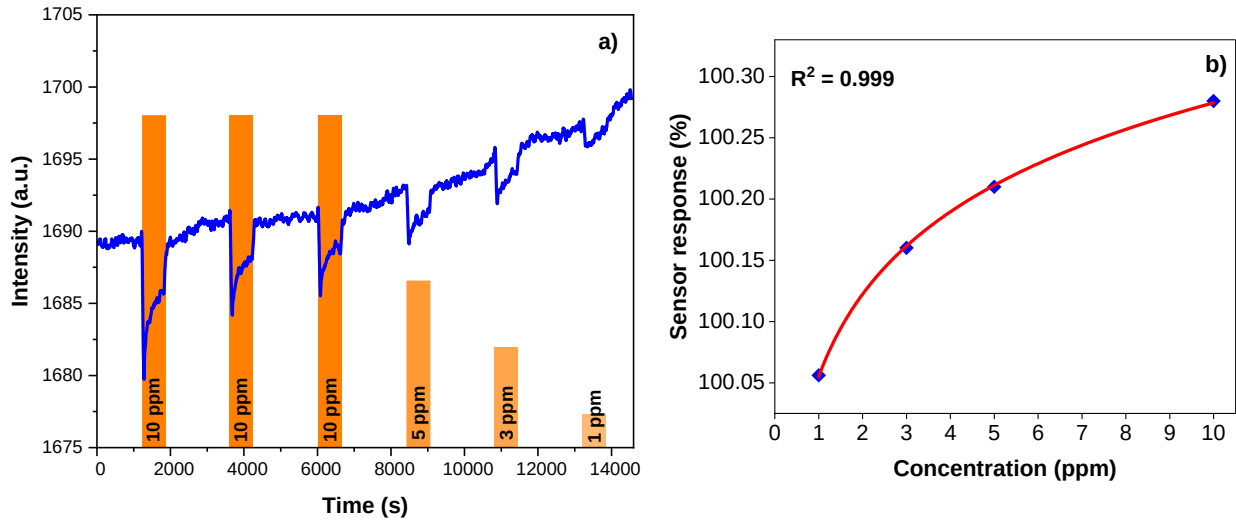


Figure IV. 8. (a) Transmitted light intensity and (b) sensor response as a function of NO₂ concentration (1, 3, 5, and 10 ppm) in dry air (0% RH). The orange bars denote the timing at which NO₂ gas was introduced at the respective concentrations.

IV.3.2. Gas sensing mechanism of ZnS in dry air

The change in the light intensity of the sensor indicate an interaction between the gas molecules with the ZnS surface at RT. Such interactions may be attributed in part to the sulfur vacancies (Sv), identified via the S 2p core-level XPS spectra, which introduce new electronic defect states near the Fermi level. These states have a dual function: acting as electron donors and/or serving as active adsorption sites for gas molecules. Therefore, under illumination in an oxygen containing environment, oxygen molecules (O₂) adsorb onto the vacancies sites and capture electrons, primarily from the sulfur vacancy level to form chemisorbed oxygen species, most likely O₂⁻ (ads) due to the RT operation [9,10]. This process leaves behind holes and may be represented by Eq.2.

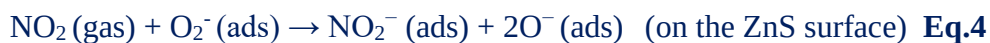


Simultaneously, additional electrons from the conduction band (CB) may also be captured, resulting in additional adsorbed oxygen species O₂⁻ (ads) at the ZnS surface as represented in Eq.3.



When gas molecules such as NO₂ approach the sensor surface, they capture electrons from the conduction band, becoming negatively charged (e.g., NO₂⁻) and subsequently adsorbing onto the surface (see Eq. 4). Moreover, when sulfur vacancy states remain

unoccupied, incoming gas molecules can extract electrons from these localized defect states, forming negatively charged complexes ($S_v + NO_2^-$) [11] (see Eq. 5). This electron transfer depletes the free charge carrier density in the film, thereby changing its optical properties as noticed in our experiments when the transmitted light intensity decreased for ZnS films. This is in agreement with similar observation reported earlier in the literature [12] (see Figure IV.8).



The interaction of the surface with toluene is expected to lead to a similar process, with the difference that this reducing molecule releases electrons into the conduction band and/or fill localized sulfur vacancy states. As a result, there is an increment of the free charge carrier density in the ZnS film that alters its optical properties and contributes to a detectable change in the transmitted light intensity.

IV.3.3. Influence of humidity on the optical response of ZnS

To further evaluate the sensor's performance, additional tests were conducted under humid conditions (40% RH). Figure IV.9 illustrates the effect of humidity on the sensor response toward toluene and nitrogen dioxide. A loss of response to toluene was observed across the concentration range tested (10–100 ppm), see Figure IV.9a. Similarly, the responses to other reducing gases, including ethanol, hydrogen, and carbon monoxide were loss. These results highlight the pronounced influence of humidity on the sensor's optical response to these analytes.

In the same line, the test to NO_2 in 40 % RH exhibited weaker responses, compared to that recorded in dry ambient, with a loss of response for concentrations below 3 ppm, as shown in Figure IV.9b. Notably, the sensor's response to NO_2 under humid conditions also differed significantly from that observed in dry air, displaying an inverse behavior characterized by an increase in the intensity of the transmitted light.

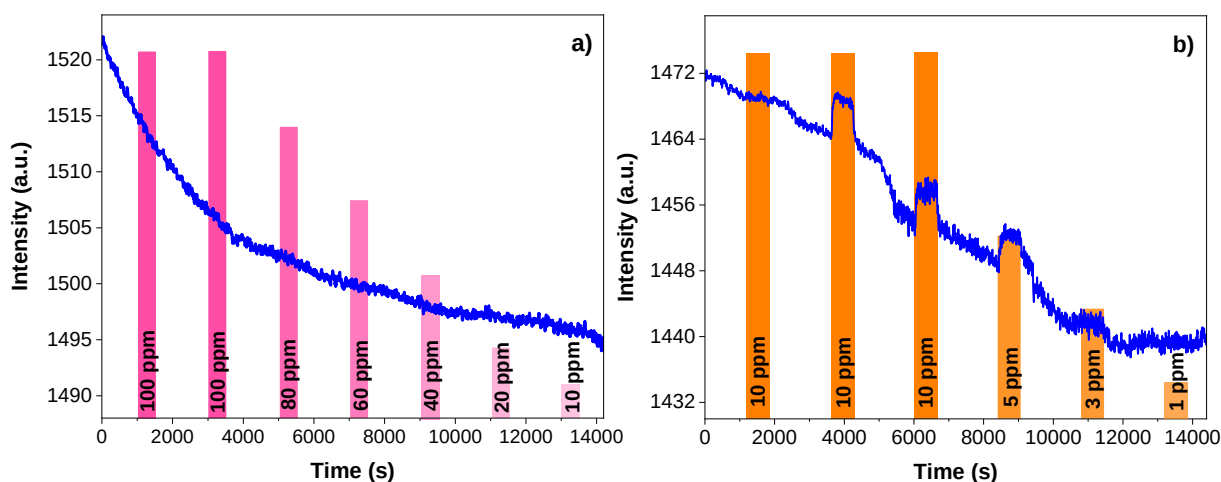


Figure IV. 9. Transmitted light intensity changes of the sensor to (a) toluene and (b) nitrogen dioxide toward different concentrations in humid environment (40 % RH) at $\lambda = 360$ nm.

To understand the effect of humidity on the films and its optical response to gases, new pristine ZnS films, exposed for 4 hours to 40 % RH at RT, were analyzed by XRD and XPS.

XRD analysis, Figure IV.10a, indicate the hexagonal ZnS phase persists after humidity exposure, although the intensity of the (104) diffraction peak is noticeably reduced. No diffraction peaks corresponding to other second phases are observed. In contrast, the XPS spectra obtained after humidity exposure, Figure IV.10b, reveal significant modifications compared to the pristine samples in both the binding energies and the peak shapes associated with the core-level elements of the film (Zn 2p and S 2p) and particularly with the O 1s, Figure IV.10c. Specifically, the Zn 2p spectra exhibits a shift to lower binding energies, e.g., 1.5 eV for Zn^{2+} and 2.6 eV for Zn^+ in the Zn 2p_{3/2} spin orbit peak, while the characteristic sulfur XPS signal, typically observed between 160 and 166 eV, is absent. Furthermore, the O 1s spectrum displays a new component centered at 529.8 eV, suggesting the presence of Zn–O bonds. These results indicate surface oxidation and the formation of a ZnO overlayer on the ZnS surface due to humidity exposure.

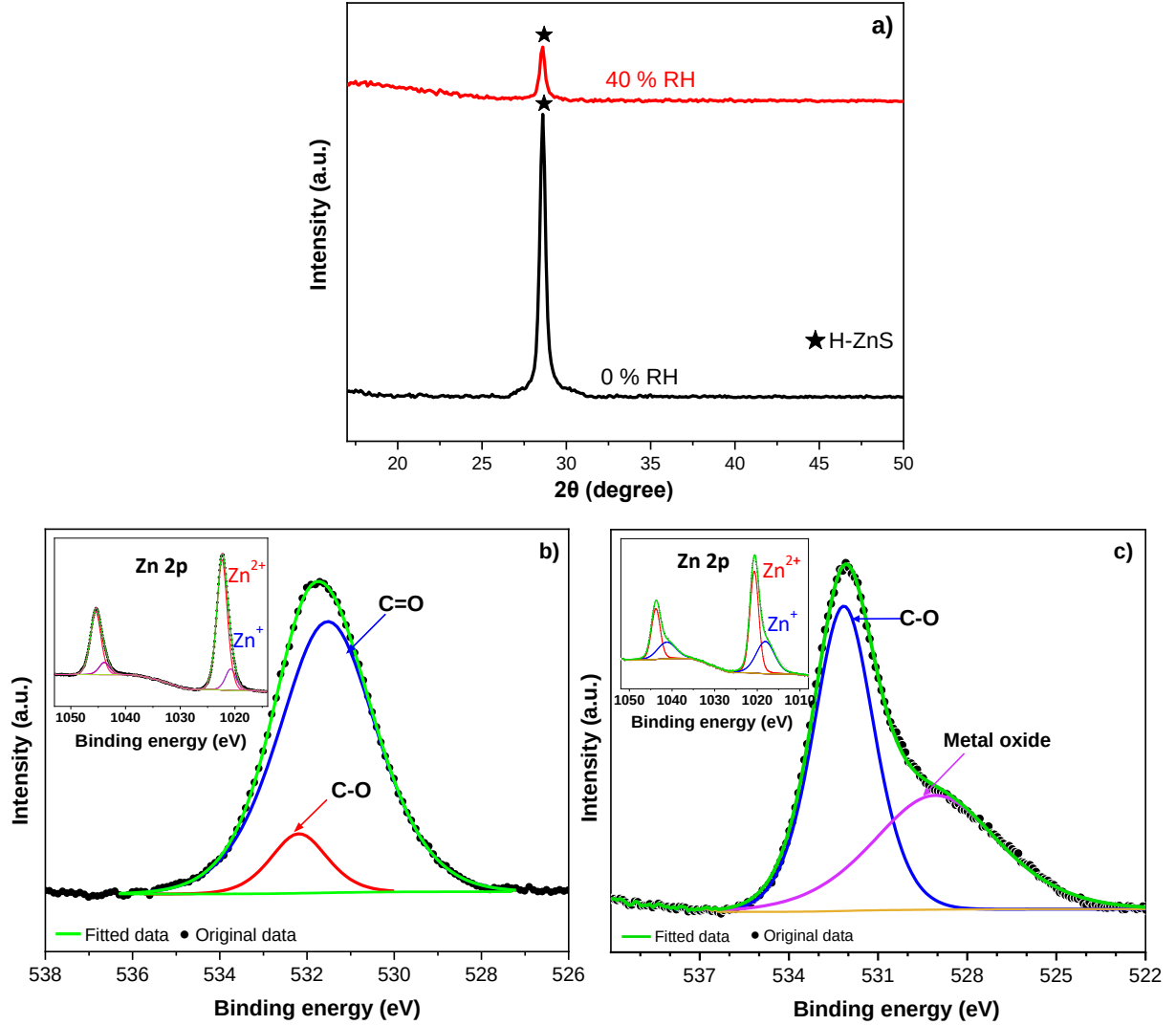


Figure IV. 10. O1s core level XPS spectra of ZnS nanoleaves (a) before and (b) after exposure to 40 % of humidity. The insets in (a) and (b) display the Zn 2p core level peaks. (c) XRD patterns before and after humidity exposure.

Generally, the presence of humidity modulates the sensor's response to target gases either amplifying or suppressing it depending on whether the humidity and gas induced responses act in the same or opposite directions [13]. For ZnS, the optical response to humidity is characterized by a proportional decrease in the transmitted light intensity as the percentage of the relative humidity increases. However, in our study, exposure to toluene resulted in a loss of response instead of an amplified effect, and an inversion of NO₂ response, as shown in Figure IV.9. This suggests the loss and inversion of response in the case of NO₂ under humidity is not primarily driven by surface-adsorbed water molecules on ZnS, but by the ZnS/ZnO heterojunction formed at the surface. This junction causes localized core-shell double depletion layer structure and a larger fall in carrier concentration of the ZnS nucleus, with respect to the pristine ZnS structure [14].

This may be connected with the drop of the base light intensity transmitted for the humid ambient system (Figure IV.9) compared to the dry ambient system (Figure IV.7 and 8) and the loss and eventually inversion of the response to the oxidizing NO₂ gas, most likely due to a dominance of holes in the ZnS nucleus. Such response inversions to oxidizing gases due to the inversion of surface conduction were also noticed in gas sensitive films working under resistive principles [15].

IV.4. Comparative study of the behavior of different metal sulfides towards NO₂ under photoactivation

Previous reports in the literature on photoactivated gas sensors to NO₂ highlight the use of materials such as metal oxides. Other classes of materials, notably metal sulfides, have been less frequently investigated [16]. Among the metal sulfides reporting for gas detection typically involve metals such as Sn [17], Cd [18] and Mo [19]. In this context, the photoactivated response of Cu₂S to low NO₂ concentrations and its improvement by the structuration of this material thanks to the AACVD flexibility is novel for the state of the art.

Table IV.1 shows a comparison of the photoactivated NO₂ sensing performance of the Cu₂S-based sensors tested in this work and the metal sulfide-based sensors in the literature. It is essential to emphasize that gas detection results are highly dependent on experimental conditions, including the type of light used (LED or Xe lamp), wavelength (UV, red, green, or white), light intensity, as well as the method of sensor manufacture and integration (direct in this study). Nevertheless, this comparison remains relevant for assessing the quality of the sensors developed here in relation to existing references.

It can be seen that our Cu₂S-based sensors have a response (R_a/R_g) superior to most sensors reported in the literature, with the exception of SnS₂ nanoplatelet sensors, which achieved a two-times more response than the flake-based sensors of this paper. Additionally, the Cu₂S sensors developed in this work demonstrate an acceptable response and recovery time compared to those reported in the table.

The ZnS-based sensor exhibits a lower optical response (I_a/I_g) than all resistive-type sensors reported in the literature. However, it is important to emphasize that this sensor

operates without any external photo or thermal activation, which makes it significantly more cost-effective and energy-efficient due to its very low power consumption.

In contrast to previously reported ZnS-based sensors, which exhibit no detectable sensitivity toward NO₂ unless incorporated into heterostructures with other metal sulfides (e.g., ZnS/SnS₂ [20]) or metal oxides (e.g., ZnO/ZnS [21]), the ZnS optical sensor developed in this work demonstrates a clear and measurable response to NO₂ without the need for any additional heterostructuring.

Table IV. 1. Comparison of NO₂ responses of photoactivated metal sulfide-based sensors in the literature and Cu₂S sensors developed in this study.

Mat.	Met.	Mor.	C (ppm)	Light	T (°C)	R	t _r /t _{rec} (s)	Ref.
Cu ₂ S	AACVD	P	5	UV-LED	T _{amb}	2,5	80/564	This work
		F				5,2	60/685	
ZnS	AACVD	NL	3	deuterium/halogen illumination	T _{amb}	1.0015 [▪]	-	This work
SnS ₂	HT	NS	8	G-LED	T _{amb}	10.8	164/236	[22]
MoS ₂	CVD	2D	100	UV-LED	T _{amb}	1.35 [▪]	29 /350	[23]
CdS	CVD	NF	5	UV-LED	T _{amb}	1.36 [▪]	36/185	[24]
				V-LED		1.89 [▪]	44/113	
MoS ₂ -Au	-	-	2.5	UV-LED	T _{amb}	1.3 [▪]	4/840	[25]
SnS	EX	NF	3.75	B-LED	60	1.68 [▪]	40/-	[26]

Mat: Materials, Met: Deposition method, Mor: Morphologies, P: Particles, F: Flakes, NS: Nanosheet, NF: Nanofllocons, NL: Nanoleaves, 2D: Two-dimensional layer, HT: Hydrothermal, EX: Exfoliated, C: Concentration, T: Temperature, T_{amb}: Ambient temperature, UV: Ultraviolet, G: Green, B: White, LED: Light Emitting Diode, t_r: Response time, t_{rec}: Recovery time.

[▪] The response, as it appears in this table, is calculated using the data reported in the reference, where the authors define it as $(R_a - R_g)/R_a \times 100 \%$, with R_g and R_a representing the sensor resistances in gas and air, respectively.

* The response, as it appears in this table is calculated using $I_a/I_g \times 100 \%$, with I_g and I_a representing the sensor transmitted light intensity in gas and air, respectively.

IV.4. Conclusion

The copper sulfide (Cu_2S) thin-film-based sensors demonstrated effective detection of nitrogen dioxide (NO_2) under photoactivation ($\lambda = 365 \text{ nm}$) at RT. A comparative study of as-deposited and annealed Cu_2S films revealed that annealing significantly enhances gas sensing performance, yielding improved repeatability and a stronger response. Notably, Cu_2S sensors based on flake-like morphology exhibited superior characteristics: a response of $R = 5.2$, a sensitivity of $S = 3.92 \text{ ppm}^{-1}$, and a response time of 60 s, outperforming their particle-like morphology, which showed $R = 2.5$, $S = 2.30 \text{ ppm}^{-1}$, and a response time of 80 s. Moreover, the sensor maintained stable performance under humid conditions, with responses comparable to those recorded in dry air.

Gas sensing tests of the ZnS -based optical sensor at room temperature (RT) revealed measurable optical responses upon illumination at $\lambda = 360 \text{ nm}$ when exposed to various gases, including toluene, hydrogen, ethanol, carbon monoxide, and nitrogen dioxide, in a dry environment. The best performance was determined for toluene and nitrogen dioxide, which registered a response of $R = 1.0031$ and $R = 1.0015$, respectively, with corresponding sensitivities of $4 \times 10^{-3} \text{ ppm}^{-1}$ and $S = 1 \text{ ppm}^{-1}$. Tests under humid conditions showed a noticeable loss or change in sensitivity, which was attributed to the formation of a ZnO overlayer on the ZnS surface.

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Conclusion and future work

The main objective of this thesis was to synthesize metal complexes based on organochalcogenophosphorus ligands, which were employed as single-source precursors (SSPs). These precursors were subsequently utilized in aerosol-assisted chemical vapor deposition (AACVD) to fabricate metal sulfide (MS) thin films. The resulting MS films were then evaluated as sensitive layers for gas sensing applications, specifically for the detection of nitrogen dioxide (NO_2) and volatile organic compounds (VOCs) such as ethanol, toluene, and carbon monoxide at room temperature.

Based on the results summarized in Table 1, several key conclusions can be drawn regarding the synthetic conditions used to prepare cadmium (Cd), copper (Cu), and zinc (Zn) complexes with organochalcogenophosphorus ligands, as well as their AACVD conditions to synthesize the gas sensitive materials.

- ✚ Among the series of complexes targeted in this work, only the synthesis of copper with $\text{Et}_4\text{P}_2\text{S}_2$ and cadmium with $(\text{Me}_2\text{N})_3\text{P}(\text{S})$ and $(\text{Me}_2\text{N})_3\text{P}(\text{Se})$ successfully yield o stable complexes that allow for fully characterized using IR, NMR, and TGA analyses. The TGA results indicate that complete decomposition of these complexes occurs between 300 and 345 °C. Therefore, the AACVD processes using these complexes as SSPs were carried out at temperatures above this threshold. The corresponding zinc complex was also attempted, but no color change or formation of an oily or precipitate product was observed, suggesting that the complex did not form. Therefore, its precursor reagents (ZnCl_2 and $\text{Et}_4\text{P}_2\text{S}_2$) were directly co-deposited in the AACVD experiments.
- ✚ The AACVD of the copper precursor resulted in the successful growth of Cu_2S thin films, exhibiting distinct morphologies depending on the deposition temperature, particle-like structures were observed at 400 °C, while flake-like morphologies formed at 450 °C. Both morphologies corresponded to the same tetragonal phase. In contrast, the AACVD of the cadmium precursors derived from ligands $(\text{Me}_2\text{N})_3\text{P}(\text{S})$ and $(\text{Me}_2\text{N})_3\text{P}(\text{Se})$ was unsuccessful under all tested conditions (including variations in precursor concentration, deposition temperature, and solvent). The resulting films showed only the presence of

carbonaceous residues on the substrate, indicating these precursors are not suitable for AACVD. Through the co-deposition of ZnCl_2 and $\text{Et}_4\text{P}_2\text{S}_2$ at $450\text{ }^\circ\text{C}$ via AACVD, ZnS nanoleaves were successfully grown, displaying a well-defined hexagonal phase and demonstrating an alternative route for synthesizing metal sulfides.

- ✚ The thermal stability of the deposited materials was further assessed through annealing studies, demonstrating that Cu_2S transforms into copper oxide films at temperatures $\geq 350\text{ }^\circ\text{C}$, whereas ZnS nanostructures remain stable upon annealing at $400\text{ }^\circ\text{C}$.

Table 1. Summary of the synthesis conditions and characteristic of the SSPs and the AACVD metal sulfide thin films processed in this thesis.

Metal precursor (Salts)	OP ligand	Molar ratio (M/L)	Product (SSPs)	Color	Yield (%)	Thermal decomposition (°C)
CuCl ₂	Et ₄ P ₂ S ₂	1/1	[Cu(Et ₄ P ₂ S ₂)Cl] ₂	White powder	80	345
Cd(NO ₃) ₂ .xH ₂ O	L1: (Me ₂ N) ₃ PS	1/2	[Cd(L1) ₂](NO ₃) ₂	White powder	75	300
Cd(NO ₃) ₂ .xH ₂ O	L2: (Me ₂ N) ₃ PSe	1/2	[Cd(L2) ₂](NO ₃) ₂	White powder	60	300
ZnCl ₂	Et ₄ P ₂ S ₂	1/1	×	×	×	
Precursor (SSPs)	Thin film	T _{dep} (°C)	Technique	Morphology	Phase	Length/Thickness
[Cu(Et ₄ P ₂ S ₂)Cl] ₂	Cu ₂ S	400	AACVD	Particles	Tetragonal	L = 1.3 μm
		450		Flakes		L = 20-22 μm
[Cd(L1) ₂](NO ₃) ₂	×	400	AACVD	Bulky	×	×
[Cd(L2) ₂](NO ₃) ₂	×	400	AACVD	Particles	×	×
Co-deposition (ZnCl ₂ + Et ₄ P ₂ S ₂)	ZnS	450	AACVD	Nanoleaves	Hexagonal	L = 600-700 nm T = 30 nm

OP: organochalcogenophosphorus ligand, M/L: metal/ligand, T_{dep}: deposition temperature, L: length and T: thickness of the individual structures composing the film, the red cross indicates that no complex/films was formed.

Table 2 summarizes the gas-sensing performance of the synthesized materials, the ones highlighted in pink in Table 1 (i.e., Cu₂S and ZnS). From these results, several key conclusions can be drawn:

- ✚ The results demonstrate that Cu₂S thin films exhibited sensitivity only to nitrogen dioxide (NO₂) at RT when photoactivated at a wavelength of 365 nm. The responses of both particle- and flake-based sensors improved after annealing at 250 °C. This enhancement is particularly significant for the annealed particle-based sensor, which showed a response twice as high as that of the as-deposited sample ($R = 2.5$). Moreover, the response times of both sensors were reduced by half, with $t_R = 80$ s for the particle-based sensor and $t_R = 60$ s for the flake-based sensor.
- ✚ The higher surface-to-volume ratio of the annealed Cu₂S flake-based sensor resulted in an enhanced response ($R = 5.2$) compared to the particle-based sensor ($R = 2.5$). The sensitivity was also greater for the flakes ($S = 3.92 \text{ ppm}^{-1}$) than for the particles ($S = 2.30 \text{ ppm}^{-1}$). Additional tests in a humid environment (40 % RH) indicated that the sensors maintain a stable response, demonstrating good humidity tolerance.
- ✚ The optical sensor developed using ZnS nanoleaves demonstrated sensitivity toward all the tested gases, including hydrogen, carbon monoxide, nitrogen dioxide, toluene, and ethanol, at RT. The sensor exhibited a stable and reversible optical response specifically to toluene and nitrogen dioxide. However, under humid conditions (40 % RH), the sensor showed no response to any of the tested analytes, along with an inversion in the response toward NO₂. This behavior was attributed to the formation of a ZnO/ZnS heterojunction, as confirmed by XPS analysis.
- ✚ Based on the results discussed in Chapter IV and summarized in Table 2, Cu₂S demonstrated its best performance toward NO₂, whereas ZnS exhibited the best responses for both NO₂ and toluene. The best sensor performances were chosen not only for their higher response magnitudes, but also for the improved repeatability, and stability observed in the sensor signal.

Table 2. Comparison of the sensing performance and the working conditions of the sensors fabricated in this thesis.

Activation mode	Material	Type of the sensor	Best sensor responses	Concentration (ppm)	Response	Operating temperature (°C)	Cross response (tested gases)
Photoactivation ($\lambda = 365$ nm)	As-deposited Cu ₂ S particles	Chemiresistive	NO ₂	5	1.2	RT	No cross response to H ₂ , ethanol and toluene.
	As-deposited Cu ₂ S flakes				4.5	RT	
	Annealed Cu ₂ S particles	Chemiresistive	NO ₂	5	2.5	RT	
	Annealed Cu ₂ S flakes				5.2	RT	
Illumination ($\lambda = 360$ nm)	As-deposited ZnS nanoleaves	Optical	Toluene	60	1.0031	RT	Cross response to ethanol, CO, H ₂ .
		Optical	NO ₂	5	1.0015	RT	

In summary, both Cu₂S and ZnS exhibited promising performance as gas sensing materials operating at RT, however, their advantages differ significantly depending on the target gas and activation conditions. Cu₂S shows high sensitivity and stability toward oxidizing gases such as NO₂ when photoactivated, making it particularly suitable for selective NO₂ detection. In contrast, ZnS offers a broader gas sensitivity, responding effectively to ethanol, toluene, carbon monoxide, hydrogen, and NO₂ under illumination, which makes it preferable for multi gas sensing platforms. From my perspective, Cu₂S is overall a more advantageous choice, as it demonstrates remarkable stability even in humid environments (40% RH). Given that NO₂ is one of the most commonly emitted pollutants from industrial processes, a sensor capable of maintaining both high sensitivity and stable performance under practical conditions is particularly valuable. This combination of reliability and robustness makes Cu₂S a highly suitable candidate for real-world NO₂ monitoring applications. In contrast, ZnS tends to exhibit lower stability under humid conditions, which limits its practical applicability and confines its use primarily to academic or laboratory research rather than real-life sensor implementations.

As a continuation of this work, key perspectives that may be explored include:

- ✚ Functionalization of Cu₂S- and ZnS-based sensors with noble metals such as gold (Au) and platinum (Pt) to investigate their influence on the sensor performance in terms of sensitivity, selectivity, and response time.
- ✚ Synthesis of selenium-based semiconductors using novel SSPs derived from the Ph₃PSe ligand, such as copper selenide (Cu₂Se) and zinc selenide (ZnSe). These materials will then be integrated into both resistive and optical sensor platforms, and their gas-sensing performance will be compared with that of their sulfide counterparts (Cu₂S and ZnS) to evaluate the influence of the chalcogen element (sulfur vs. selenium) under identical testing conditions.
- ✚ In agreement with literature reports, heterojunctions (n–n, n–p, or p–p type) between metal sulfides and metal oxides enhance gas adsorption and consequently improve gas sensing performance. For instance, ZnS/ZnO and MoS₂/ZnO heterostructures have demonstrated notable sensitivity improvements. It would therefore be interesting in future work to investigate similar heterojunction systems and evaluate their sensing behavior toward hazardous gases and VOCs.