

Review Article

# Thin Film Analysis by Infrared Spectroscopy

Ho Soonmin<sup>1</sup>, Olanami Oluwatoyin O<sup>2</sup>

<sup>1</sup>Faculty of Health and Life Sciences, INTI International University, Putra Nilai, 71800, Negeri Sembilan, Malaysia.

<sup>2</sup>Faculty of Physical Sciences, Department of Physics, University of Ilorin, Ilorin, Kwara State, Nigeria.

<sup>1</sup>Corresponding Author : soonmin.ho@newinti.edu.my

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**Abstract** - Metal chalcogenide thin films have been synthesized through various deposition techniques. These films have found numerous applications, including in solar cells, opto-electronic devices, laser systems, sensors, electroluminescent devices, and light-emitting diodes. A range of analytical tools has been employed for the characterization of these thin films, including X-ray diffraction, atomic force microscopy, scanning electron microscopy, energy dispersive X-ray analysis, UV-visible spectrophotometry, Raman spectroscopy, photoluminescence spectroscopy, and X-ray photoelectron spectroscopy. In this study, different types of thin films were produced using both physical and chemical deposition methods. The analytical method known as Fourier Transform Infrared Spectroscopy is used to identify organic, polymeric, and occasionally inorganic materials. Infrared light is used in the FTIR analysis method to scan test samples and observe chemical properties from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ . FTIR spectra indicated that the characteristic peaks were influenced by variations in experimental parameters such as temperature, heating processes, pH levels, and the presence of complexing agents, solution concentration, deposition duration, and the number of deposition cycles.

**Keywords** - Thin films, Solar cells, Energy efficiency, Energy consumption, Fourier transform infrared spectroscopy.

## 1. Introduction

Thin films are layers of materials with thickness in the order of nanometer to several micrometres and have remained the basis for the development of numerous semiconductor devices [1]. In solar cell fabrication, thin film technology belongs to the second-generation class, an evolution from the first-generation technology based on crystalline silicon. Thin film solar cells employ multiple thin film layers of photovoltaic elements onto a substrate. It has received much attention recently because of its potential for substantial cost reduction advantage over traditional wafer-based crystalline silicon because of its lower material use and fewer processing steps. Thus far, Cadmium Telluride (CdTe), Copper Indium Gallium Selenide (CIGS), and Copper Zinc Tin Sulfide (CZTS) and Amorphous Silicon (a-Si) based thin film solar cells have been most widely commercialized. The common feature of these semiconductor materials is their direct band gap nature, which allows for the use of very thin material. So far, research on thin film technology based on CIGS, CdTe, and CZTS solar cells has recorded laboratory efficiency of 23.35%, 21.0%, and 10.0%, respectively [2]. Recently, numerous researchers have focused their studies on binary, ternary, and quaternary semiconductors. These materials have found applications in various fields, including solar cells, cathode ray tubes, sensors, laser devices, optoelectronic devices, light-emitting diodes, infrared windows [3], and biological applications. Thin film solar cells are less expensive

to manufacture and set up than other solar cell varieties. Thin film cells weigh less than other solar cell types since they require less semiconductor materials. This solar cell can be designed to be semi-transparent, enabling light to filter through. The perfect band gap (approximately 1.5 eV) for a solar cell aligns with the energy of photons found in the solar spectrum. This enables the cell to effectively capture light and transform it into electricity. A strong absorption coefficient enables effective light absorption even in thin material layers. Thin films can be fabricated using a range of deposition techniques, such as chemical bath deposition, electrodeposition [4], thermal evaporation, spray pyrolysis [5], magnetron sputtering, metal-organic chemical vapor deposition, molecular beam epitaxy, sol-gel spin coating [6], pulsed laser deposition, successive ionic layer adsorption and reaction, and e-beam evaporation [7]. Numerous researchers have reported on the properties of thin films produced through these various methods [8]. X-ray diffraction has been employed to ascertain the structural characteristics of the films. Atomic force microscopy and scanning electron microscopy have been utilized to analyze the morphology of the samples. Energy dispersive X-ray analysis has been applied to examine the elemental composition of the materials. The optical properties of the films, including band gap and absorption behavior, have been investigated using UV-visible spectrophotometry. Raman spectroscopy has been employed to ascertain the chemical composition and structure of the samples [9]. Photoluminescence spectra have been analyzed



to explore the electronic structure and properties of the materials. X-ray photoelectron spectroscopy has been used to evaluate the elemental composition, chemical state, and electronic state of the element present [10]. Fourier transform infrared spectroscopy is a technique that utilizes Fourier transform mathematically to analyze the wavelengths that materials absorb. Infrared radiation passes through a sample in infrared spectroscopy. The sample takes in some of the infrared energy while some is transmitted. The spectrum obtained provides the sample with a molecular fingerprint by showing the absorption and transmission of the molecules. No two distinct molecular arrangements yield the same infrared spectrum, like fingerprints. Consequently, infrared spectroscopy is beneficial for numerous analyses. FTIR spectroscopy is founded on the principle that radiation interference between two beams produces an interferogram.

The latter represents a signal generated because of the change in path length between the two beams reflected off two mirrors. The two areas of distance and frequency can be converted into one another through mathematical techniques. The major components of FTIR are emphasized Table 1. The Michelson interferometer is the key distinction between an FTIR and an IR spectrometer. It is essential for the FTIR spectrometer to divide a single light beam into two, thereby establishing distinct paths for both beams. It then merges the two beams and directs them into the detector, where the variations in the intensity of these beams are assessed based on the difference in their paths. In FTIR spectroscopy, employing an interferometer presents numerous benefits, including significantly enhanced optical throughput thanks to a slit-less optical design, leading to an elevated signal-to-noise ratio. The capability to gather data across various wavelengths simultaneously without requiring scanning through a moving prism.

Enhanced wavenumber resolution by employing a laser source for precise digital signal sampling and increasing the movement distance of the mirror in the interferometer. Drawbacks of FTIR methods include the fact that the molecule needs to be reactive in the infrared spectrum. For absorption to be detected when exposed to IR radiation, at least one vibrational motion must alter the net dipole moment of the molecule. Minimal elemental information is given to many samples. The substance under examination needs to be clear in the relevant spectral range. Choosing materials for interfacial engineering is crucial because the functional groups of the interfacial material can engage with the solar cells. Effective interfacial materials possess various functional groups, yet there are typical effects that the primary functional groups provide. The carboxyl group consists of carbon, oxygen and hydrogen. It is an organic functional group where a carbon atom creates a double bond with one oxygen atom and a single bond with a hydroxyl group. The carboxyl group undergoes ionization by shedding a hydrogen atom from the OH group, which releases a free proton. The carboxyl group

participates in Lewis's acid-base reaction with metal ions. Materials containing carboxyl groups as interfacial modifiers can achieve band alignment and defect motivation, while conductivity can be enhanced due to increased charge mobility. Moreover, the alkyl chain, the hydrophobic part of the molecule, contributes to strong water stability in the solar cells. An amine group refers to a functional group that consists of a nitrogen atom bonded to two hydrogens along with an alkyl or aromatic group. A material with an amine group at the interface can act as a Lewis base and provide a nitrogen lone electron pair to the empty orbital of the under-coordinated lead ions in the perovskite solar cells, thereby creating a coordination bond with the perovskite.

This bond coordination slows down the crystallization rate of perovskite, assisting in creating a uniform and dense perovskite film featuring the desired crystal growth orientation and high crystallinity. Like aromatic compounds, aromatic rings are hydrocarbon substances featuring a conjugated planar ring structure. Among these, the most common are benzene, phenyl, thiophene, imidazole, pyrrole, and pyridine. The free  $\pi$  electrons within the aromatic ring enhanced charge transfer, while the conjugated structure supplies electrons for passivating defects in the solar cells. Additionally, the hydrophobic properties of the aromatic ring hinder the ingress of moisture and oxygen from the devices. In this study, nanostructured thin films were synthesized using various deposition techniques, and Fourier Transform Infrared Spectroscopy (FTIR) was utilized to identify the functional groups within the samples. Also, the benefits and limitations of the FTIR method will be described.

## 2. Methodology

To locate research articles published in English related to Fourier transform infrared analysis of thin films, the authors performed a literature review in pertinent journals from 1997 to 2024. The databases explored included Google Scholar, Taylor & Francis, ACS, Scopus, Wiley Online Library, Science Direct, and MDPI. The terms used included "thin film solar cells", "Fourier transform infrared analysis", "binary films", "ternary films", and "quaternary films".

## 3. Literature Survey

### 3.1. FTIR Studies of Binary Thin Films

Fourier Transform Infrared Spectroscopy (FTIR) is recognized as a non-destructive analytical technique [11] that yields insights into the functional groups present in a sample. The radiation source generates infrared radiation that traverses the sample via the interferometer. Common examples of radiation sources include silicon carbide, tungsten halogen lamps, and mercury discharge lamps. The FTIR spectrometer employs an interferometer to modulate the wavelength emitted from a broadband infrared source [12], allowing for rapid signal measurement [13]. The detector quantifies the intensity of light that is either transmitted or reflected, depending on its wavelength. The resulting infrared spectrum

serves as a distinctive fingerprint for thin films, with absorption peaks corresponding to the vibrational frequencies of atomic bonds [14]. Researchers have noted that no two compounds produce identical infrared spectra, as each material represents a unique arrangement of atoms. This characteristic underpins the utility of infrared spectroscopy in qualitative analysis. The advantages and limitations of FTIR and Atomic Force Microscopy (AFM) technique are summarized in Table 1. FTIR is an affordable and sustainable technology for examining the characteristics of thin films. FTIR technique can quickly adapt to new demands and is a strong research resource.

**Table 1. Advantages and limitations of the FTIR technique**

Advantages	Limitations
FTIR	
Brightness	Cannot detect atoms [18]
Simple mechanical design [15]	Hard to analyse, especially in an aqueous solution
Universal technique	Cannot detect nitrogen and oxygen
Easy technique	complex spectra were produced [16]
Inexpensive technique	artifacts were produced
Internally calibrated	
Better sensitivity [17]	
All the frequencies could be recorded simultaneously.	
AFM	
achieve high-resolution images	scan a single image at a time
provide qualitative and quantitative information	images can contain artifacts

Tin oxide films have gained popularity as transparent conductors due to their excellent optical transparency in visible areas, mechanical stability, chemical corrosion resistance, and the raw materials' cost-effectiveness. These films possess a quadrangular structure and exhibit a band gap energy ranging from 3.7 to 4.2 eV. Ala and colleagues [18] have documented the production of high-purity SnO<sub>2</sub> films with a polycrystalline structure characterized by a tetragonal cassiterite phase. Examining the films through Field Emission Scanning Electron Microscopy (FESEM) images reveals they are free from cracks, exhibit uniformity, and possess a continuous grain distribution.

An FTIR analysis indicates two peaks at 613 cm<sup>-1</sup> (Sn-O-Sn) and 3451 cm<sup>-1</sup> (hydroxyl group), which are accountable for water (environmental humidity). Cadmium Sulfide (CdS) nanocrystalline displays three crystal structures: hexagonal quartzite, cubic zinc blend, and high-pressure rock-salt phase, demonstrating size-dependent properties. Its applications include serving as window material in heterojunction solar cells, being utilized as n-type material alongside p-type

materials, and functioning in light-emitting diodes, photodetectors, field effect transistors, and electrically driven lasers. Hadeel and co-workers [19] have examined the optical and structural characteristics of CdS nanoparticles produced by the sol-gel technique with the surfactant Cetrimonium Bromide (CTAB).

The FTIR results demonstrated that the -OH group is responsible for a sizable absorption peak corresponding to 3450 cm<sup>-1</sup> and represents the stretching vibration of the absorbed water on the CdS surface. The OH bending vibration of water molecules is responsible for the absorption band observed at 1635 cm<sup>-1</sup>. The intense peak of the absorbed CO<sub>2</sub>'s C-O stretching vibration is located at 1033 cm<sup>-1</sup>. The O=C=O asymmetric stretching vibrations are responsible for the absorption peak at 1394 cm<sup>-1</sup>. The nanostructured CdS film [20] has been produced via a microemulsion-mediated sonochemical method.

Fourier Transform Infrared spectra reveal three prominent peaks at 635.54 cm<sup>-1</sup> (indicating the stretching frequency of the CdS bond), 3429 cm<sup>-1</sup> (corresponding to OH stretching), and 1629 cm<sup>-1</sup> (representing the OH bending mode). A chemical deposition of 0.45 μm thick copper oxide films was achieved on glass substrates through 20-second microscope glass slides [21] immersion in solutions containing copper complex and 1 M Sodium Hydroxide (NaOH). While the copper solution was kept at an ambient temperature, the NaOH solution's temperature was raised to 70 °C. The films' as-deposited and 200 °C-annealed spectra exhibit a prominent band with a single transmittance minimum of around 627 and 619 cm<sup>-1</sup>, respectively. The phonon spectrums of Cuprous Oxide (Cu<sub>2</sub>O) and Cupric Oxide (CuO), which have wavenumbers of approximately 619 cm<sup>-1</sup> and 532 cm<sup>-1</sup>, respectively, are present in the films that have been annealed at 300 °C.

Broader peaks at around 535 cm<sup>-1</sup> for the films that were annealed at 400 °C are similarly ascribed to the CuO stretching. It is also noted that for annealing temperatures above 300 °C, there is a clear peak at roughly 1120 cm<sup>-1</sup>. After annealing at 300 °C, the FTIR spectroscopy observations verified that Cu<sub>2</sub>O had transformed into CuO due to the disappearance of Cu<sub>2</sub>O-associated peaks. Cadmium Selenide (CdSe) nanocrystals are employed in creating light-emitting diodes, solar cells, lasers, and other nanoscale devices, as well as helping comprehend the phenomenon of the quantum confinement effect. Many application studies have been conducted because of this material's blue shift in the band gap with decreasing grain size. Sodium selenosulphate is used as a Se<sup>2-</sup> source during the chemical growth of CdSe (E<sub>g</sub> = 1.7 eV), a direct band gap semiconductor [22]. Trisodium citrate, the capping agent utilized in this work, is confirmed to be present by the existence of the band at 1387 cm<sup>-1</sup> and 1561 cm<sup>-1</sup>, according to FTIR investigations. It is possible to attribute the latter band to the asymmetric COO<sup>-</sup> and the former band

to the symmetric stretching of  $\text{COO}^-$ . Meanwhile, the band at  $3368\text{ cm}^{-1}$  is attributed to OH stretching of trisodium citrate. Cadmium Selenide thin films were fabricated through a wet chemical synthesis approach [20]. The FTIR analysis identified several peaks at  $624\text{ cm}^{-1}$  (stretching frequency of the CdSe bond),  $3432\text{ cm}^{-1}$  (OH stretching), and  $1628\text{ cm}^{-1}$  (OH bending mode). Because of its excellent optical and solid-state properties, Zinc Selenide ( $\text{ZnSe}$ ), a group II-IV semiconductor compound, has attracted a lot of interest in the manufacture of solar energy devices.

It is a key component used in the creation of solar cells. It is a sort of direct band gap transition.  $\text{ZnSe}$  is a material of choice for visible transmission and low absorptiveness at infrared wavelengths, making it ideal for use in lenses, window layers, and output couplers.

Zinc Selenide thin films built on nanotechnology have a large direct band gap (3.87), good transmittance in the visible range, and are very desirable for use in optoelectronics and photonics applications. Using a chemical deposition approach, dye-sensitized  $\text{ZnSe}$  thin films were formed onto microscopic glass slides [23]. For sixty minutes, the films were placed at an even  $80\text{ }^\circ\text{C}$ . The presence of hydroxyl groups (O-H stretch, H-bonded) is indicated by a strong and broad peak obtained at  $3235\text{ cm}^{-1}$ .

This observation may be related to the dye component phenol's easy ability to form intermolecular hydrogen bonds with water as well as the dye's easy electrophilic aromatic reaction with phenol, xanthophyll, and tannin. The C-H stretch is responsible for another prominent and wide spectrum peak located at  $3390\text{ cm}^{-1}$ . Several contaminants were visible, including hydroxyl (O-H) and alkyne (C-H).

Hydroxyl groups could potentially. The chemical bath deposition of zinc selenide thin films was conducted under acidic conditions at a temperature of  $80\text{ }^\circ\text{C}$ , with varying deposition durations (60-240 minutes). FTIR analysis revealed peaks at  $637$  and  $1148\text{ cm}^{-1}$  (stretching vibration),  $877\text{ cm}^{-1}$  (C-H bending),  $1412\text{ cm}^{-1}$  (bending vibration of  $\text{CH}_2$ ), and  $1587$ ,  $3261$ , and  $3473\text{ cm}^{-1}$  (OH stretching mode) across all prepared samples [24].

Depending on its composition, zinc sulfide can have a large direct band gap (less than 3.5 eV), placing it in the II-VI group materials. Zinc sulfide, or  $\text{ZnS}$ , is a significant semiconducting material promising for optoelectronic devices like photovoltaic cells and electroluminescent devices due to its broad direct band gap and n-type conductivity.

$\text{ZnS}$  thin films are made using the spray pyrolysis method. Basically, spray pyrolysis is a chemical deposition technique where a heated substrate is sprayed with fine droplets of the desired material solution. The optical characteristics and composition of the film structure

are highly dependent on the deposition temperature, as observed by Djelloul and colleagues [25]. Films are amorphous when the deposition temperature is low. The films developed a stoichiometric  $\text{ZnS}$  composition and a polycrystalline (111) preferential orientation as the temperature increased.  $\text{ZnS}$  nanoparticle formation is confirmed by FTIR data. All samples exhibited weak, distinctive vibrations of zinc sulfide, which were found at  $611$  and  $680\text{ cm}^{-1}$ . The formation of  $\text{ZnS}$  nanoparticles is responsible for the other peaks.  $\text{ZnS}$  films (spray pyrolysis method) exhibited a significant wide band gap of over 3.5 eV. FTIR analysis detected several weak vibrational peaks, specifically at  $611.45\text{ cm}^{-1}$  and  $680\text{ cm}^{-1}$  for films prepared at temperatures of  $350\text{ }^\circ\text{C}$  and  $400\text{ }^\circ\text{C}$ , respectively.

Zinc oxide absorbs and blocks harmful UV radiation. Its visible spectrum transparency allows it to penetrate the semiconductor layers underneath. Its chemical stability protects against environmental deterioration and ensures long-term durability. Its compatibility with thin-film deposition methods, such as casting and spraying, makes it a viable option for manufacturing processes as well. This enhances solar panels' overall performance and dependability when exposed to UV radiation.

Although manufacturers can add  $\text{ZnO}$  to adhesive,  $\text{ZnO}$ -based coatings can only be applied externally to solar panels that have already been installed. The right matrix and cost-effective deposition technique are needed for external  $\text{ZnO}$ -based coatings to be effective. When zinc oxide was employed for solar cell applications, some polymers such as polyvinyl butyral (encapsulant) and ethylene vinyl acetate (as layer) played an important role. PVB is well known for shielding surrounding elements by enclosing solar cells and blocking UV rays. To be more precise, PVB's primary duty in terms of protecting EVA is to assist in encasing and shielding the complete solar cell structure.

By keeping dust, moisture, and other external elements away from solar panels, PVB can prevent potential damage. As shown in Figure 1, several peaks could be found at  $665$ - $750\text{ cm}^{-1}$  and  $1450$ - $1500\text{ cm}^{-1}$ , representing the C=C bond and the C-H bond, respectively. 3D transition metal impurities in semiconductor nanoparticles have attracted much attention recently due to their influence on emission band tuning. Analyzing commercially doped  $\text{In}_2\text{S}_3$  will provide an alternative viewpoint for understanding the material's energy-related applications.

In addition to being less expensive, commercial  $\text{In}_2\text{S}_3$  powder produces equally encouraging results compared to laboratory-made powder. Researchers conducted a thorough investigation into the properties of  $\text{In}_{2-x}\text{S}_3\text{Ni}_x$  powders with 0, 2, 4, and 6 atomic proportions of nickel. FTIR data confirmed that all  $\text{In}_{2-x}\text{S}_3\text{Ni}_x$  films were crystalline. All samples displayed semiconductor behavior, according to the impedance

analysis, and resistance dropped as Ni content rose.

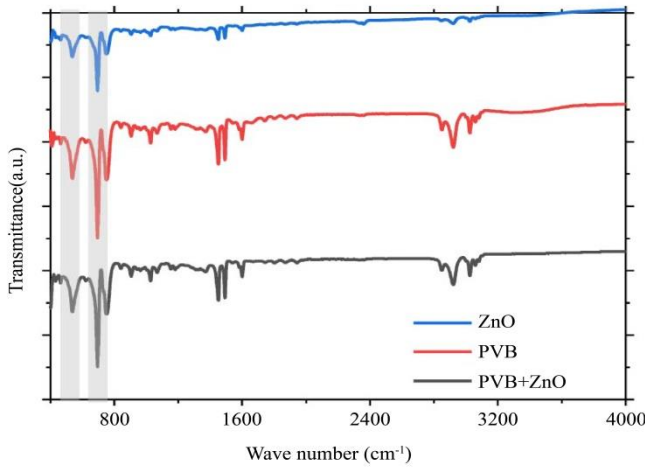


Fig. 1 FTIR of ZnO and PVB-ZnO samples [28]

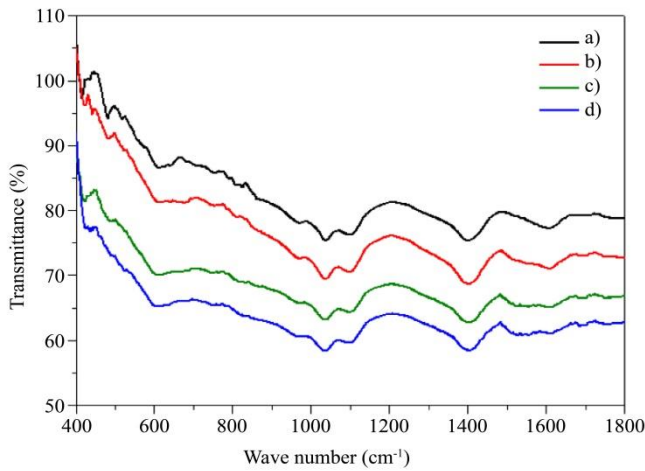


Fig. 2 FTIR spectra of different samples (a-In<sub>2</sub>S<sub>3</sub>, b-2% Ni-In<sub>2</sub>S<sub>3</sub>, c-4% Ni-In<sub>2</sub>S<sub>3</sub>, and d-6% Ni-In<sub>2</sub>S<sub>3</sub>) [29]

Information regarding the chemical composition of each sample was revealed by the FTIR spectral fingerprints in the 100–600  $\text{cm}^{-1}$  wavenumber range [27]. Figure 2 shows three absorption bands, indicative of the stretching of C=O bonds and the O-H and C-H bond extensions at 1000–1500  $\text{cm}^{-1}$ . With the rapid development of the photovoltaic industry, the aesthetic performance of solar modules is becoming more and more significant. One example of this is the development of integrated photovoltaic systems. Multicrystalline silicon solar cells manufactured in industrial mass production usually have a layer of SiN<sub>x</sub>:H on the front surface, which is deposited using plasma-enhanced chemical vapor deposition. This layer acts as a passivation and antireflection layer. When the SiN<sub>x</sub>:H ratio is optimized for thickness and refractive index, the colors of solar cells appear light blue. Minghua [30], along with others, has focused on depositing a SiO<sub>2</sub> layer over the standard SiN<sub>x</sub>:H after the conventional mc-Si cell fabrication process using the electron

beam (e-beam) evaporation technique and replacing the single SiN<sub>x</sub>:H layer with SiO<sub>2</sub>/SiN<sub>x</sub>:H DARC. The band in the range of 1040–1150  $\text{cm}^{-1}$  is identified as stretching vibration Si-O. A distinct Si-O intensity peak (1074  $\text{cm}^{-1}$ ) is observed for the oxygen supplement during the SiO<sub>2</sub> deposition.

### 3.2. FTIR Studies of Ternary Thin Films

CuInSe<sub>2</sub> has emerged as a top material for large-scale applications. It features excellent thermal stability, stability against photodegradation, a direct band gap, and a high absorption coefficient ( $>10^3 \text{ cm}^{-1}$ ). Its high absorption capacity allows it to absorb over 90% of the photon energy. One of the most inexpensive and promising materials for thin-film solar cells is CuInSe<sub>2</sub>. As a result, these solar cells are among the best available for producing solar light, a renewable energy source. Using the electrodeposition method, CuInSe<sub>2</sub> thin films were created at pH 2.1, with deposition potentials of -500 or -600 mV in relation to a saturated calomel electrode and at different temperatures [29]. Several peaks were attributed to CuInSe<sub>2</sub> at 2345  $\text{cm}^{-1}$  and CuInSe<sub>2</sub> at 3650 and 3844  $\text{cm}^{-1}$  for the films prepared at 25 °C and -500 mV. Also, distinct absorption peaks at 2857  $\text{cm}^{-1}$  and 3295  $\text{cm}^{-1}$  (attributed to CuInSe<sub>2</sub>) were observed (40 °C, -600 mV). Using the electrodeposition technique, ternary compounds, more precisely Cu-S-Se films, were created on fluorine-doped tin oxide glass substrates. All samples showed the presence of two distinct peaks at 1110  $\text{cm}^{-1}$  (stretching vibration of CuSe) and 615  $\text{cm}^{-1}$ , linked to the stretching vibration of CuS.

Peak intensity has been changed in response to the changes in selenium and sulfur ion composition, as shown by the FTIR spectra [30]. High-quality crystalline Cu<sub>2</sub>SnSe<sub>3</sub> thin films have been shown to form on fluorine-doped tin oxide glass substrates. Strong peaks between 3300 and 2800  $\text{cm}^{-1}$ , corresponding to C-H and N-H stretching vibrations, were seen in the as-deposited thin films. However, after being heated to 370 °C, the strength of these peaks decreased [31]. CuInS<sub>2</sub> has gained significant attention recently as a potentially useful material for the absorber layer in photovoltaic devices due to its high absorption coefficient ( $10^5 \text{ cm}^{-1}$ ), good stability for solar radiation, and direct band gap of approximately 1.5 eV, which falls within the ideal spectrum range for solar energy conversion. Additionally, n- and p-type solar cells can be produced by adjusting the CuInS<sub>2</sub> stoichiometric deviation, which is advantageous for both homojunction and heterojunction solar cells. Films rich in indium can form n-type CuInS<sub>2</sub>, whereas films rich in copper can form p-type CuInS<sub>2</sub>. Furthermore, because CuInS<sub>2</sub> does not contain any toxic elements like tellurium and selenium, it can be synthesized in an environmentally friendly environment. As a result, the environmental threat posed by chemical toxicity can be reduced. The electrodeposition method was used to synthesise copper indium disulfide thin films on fluorine-doped tin oxide glass at pH 12.5, with a sulfurization step that followed.

The deposition potential used was -0.75 V concerning Ag/AgCl. Several distinctive peaks were visible in the films made using Cu (Salen) complexes, including those at 1125 and 1192  $\text{cm}^{-1}$  (phenolic CO bond), 736  $\text{cm}^{-1}$  (phenyl group bonding mode = C-H), and 1630  $\text{cm}^{-1}$  (C=N vibration). The films [32] synthesized with the presence of  $\text{Cu}(\text{acac})_2$  complexes showed clear, sharp peaks at 1415  $\text{cm}^{-1}$  (C=C stretching mode), 782  $\text{cm}^{-1}$  (phenyl group bonding mode = C-H), and a range from 454 to 616  $\text{cm}^{-1}$  (CuO bond). Highly crystalline  $\text{Cu}_2\text{SnS}_3$  films have been created using the chemical bath deposition technique on conductive stainless steel over the course of two hours at a pH of 4 [33]. Multiple peaks in the FTIR spectra indicated the presence of SnS at 1397  $\text{cm}^{-1}$ , CuS and  $\text{Cu}_2\text{S}$  at 619  $\text{cm}^{-1}$ , and  $\text{SnS}_2$  in the sample.

Ethylenediamine tetraacetic acid disodium salt was used as a complexing agent to produce  $\text{Cu}_2\text{SnS}_3$  films (substrate=fluorine-doped tin oxide glass substrates, 2 hours, 80 °C). Films prepared with different deposition times (60-90 minutes) were subjected to an FTIR analysis. Four distinct peaks were visible in the FTIR spectra at 619, 1122, 1397, and 1619  $\text{cm}^{-1}$ . These peaks corresponded to the bending of OH in water, the vibration of the SnS bond, the asymmetric stretching of the carbonyl group, and the vibration of the Cu-S bond.

Furthermore, Sn-Sb-S films [34] were created on fluorine-doped tin oxide glass substrates using the spin coating technique. The pH values were created in the range of 1.56-1.80. The symmetrical stretching vibration mode of the O-C-O bond was found at 1607  $\text{cm}^{-1}$ , the CO symmetric stretching vibration mode was found at 1400 to 1430  $\text{cm}^{-1}$ , the SbS bond was found at 538  $\text{cm}^{-1}$ , and the symmetric Sn-O-Sn was found at 455  $\text{cm}^{-1}$ .

### 3.3. FTIR Studies of Quaternary Thin Films

Research has determined whether the kesterite compound  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) qualifies as a non-toxic, less expensive, and earthy substitute for the binary and quaternary compounds. Because of their large absorption coefficient, over 104  $\text{cm}^{-1}$ , which results in lower material usage, and their direct optical bandgap in the range of 1.4-1.56 eV to exploit a greater magnitude of input solar irradiance from the spectrum, CZTS absorber layers are very promising materials. CZTS thin film is deposited using a new chemical SILAR technique.

Its foundation involves immersing the substrate one time at a time into distinct cation and anion precursor solutions, followed by rinsing with double distilled water to prevent precipitation in between. Ion-by-ion deposition causes the growth of thin films. In addition, surface coagulation of colloidal ions resulted in thin, adherent films. FTIR studies [35] show that a strong band at 3300  $\text{cm}^{-1}$  appears connected to both symmetric and antisymmetric -N-H vibration modes. The NH<sub>2</sub> bending, C=S stretching vibration, and NH<sub>2</sub> rocking

vibration deformation are attributed to the absorption peaks observed at 1645  $\text{cm}^{-1}$ , 1400  $\text{cm}^{-1}$ , and 1100  $\text{cm}^{-1}$ , respectively. Ahmad and colleagues [36] describe the synthesis and characterization of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) thin films made by the sol-gel method at various annealing temperatures and then immersed and deposited on glass substrates. In XRD analysis, tetrahedral kesterite could be observed when the anneal temperature was 450 °C.

FTIR analysis reveals that the sulfur-rich composition of the as-prepared CZTS films is responsible for their extended peak, which spans 3700 to 2500  $\text{cm}^{-1}$ . It was noted that the stretching and bending of oxygen are responsible for a sequence of peaks stretching from 900 to 1600  $\text{cm}^{-1}$ . The Zn-S and S-H bond stretching is visible in the peaks at 575 and 460  $\text{cm}^{-1}$ , respectively. The peak located at 1613  $\text{cm}^{-1}$  may represent the symmetric stretching of the C-S bond. At 1062  $\text{cm}^{-1}$  is the peak linked to the sulfur-rich Kesterite composition. The distinctive absorptions in 2070 and 2330  $\text{cm}^{-1}$  are thiol group fingerprints.

$\text{Cu}_2\text{ZnSnS}_4$  (CZTS) films were synthesized using the hydrothermal method, as reported by Indubala and co-workers [37]. The films showed several distinct peaks after three hours of treatment at 650 °C. These peaks included 3433  $\text{cm}^{-1}$ , which indicates the presence of hydroxyl groups; 1638  $\text{cm}^{-1}$ , which is linked to the symmetrical stretching vibrations of the C-O bond; 1366  $\text{cm}^{-1}$ , which is related to the antisymmetric stretching vibrations of CO; 1123  $\text{cm}^{-1}$ , which is the C-O symmetric stretching frequency; and 616  $\text{cm}^{-1}$ , which is related to the ZnS band.

Copper zinc tin sulfide thin films with a direct band gap, multilayer structure, and high absorption coefficient make them appropriate for use in solar cell technology [38]. Equal amounts of zinc, tin, and copper were used to create the films, along with an excess of sulfur in a 1:3 ratio. The process was conducted for 180 minutes at different temperatures (350 to 650 °C). Indubala and co-workers have revealed five major peaks could be observed in these temperatures.

The metal ratios that were used had a big impact on the final CZTS film quality. The films were created under various reaction times and Cu: Sn ratios of 1.7 and 1.8 using acetonitrile as a solvent. FTIR analysis, however, revealed that there were no organic residues. At 320 °C, quaternary thin films, like  $\text{Cu}_2\text{ZnSnS}_4$ , were deposited on the specific substrate (soda lime glass) without the need for further sulfurization [39].

Distinct peaks were visible in the FTIR spectra at 630  $\text{cm}^{-1}$  for ZnS, 1129 and 1651  $\text{cm}^{-1}$  for metal thiourea complexes, 2369 and 2938  $\text{cm}^{-1}$  for SH thiol, and 3460  $\text{cm}^{-1}$  for thiourea. Olelamine (solvent and an electron donor) is selected in the hot injection method to prepare CZTS films [40]. FTIR studies highlighted the capping effect of oleylamine in



forming thin films. FTIR is an affordable and sustainable technology for examining the characteristics of thin films.

**Table 2. Summary of disadvantages and advantages of FTIR, NMR and GPC**

Technique	Disadvantages	Advantages
GPC	The GPC drench has a volume limit, and the effectiveness of chromatography depends on the volume of the macromolecular compound within a stated range.	Study the physico-chemical properties.
NMR	C-13: expensive analysis, a significant quantity of samples needed. H-1: no signals can be detected regarding internal carbon.	The peak positions of the NMR can indicate detailed information regarding the structure, chemical environment and functional groups of the samples
FTIR	Preparing samples is a tedious process. The accuracy resolution remains low.	Capability to show the category and substance of functional groups in the samples. A minimal sample size is needed.

The benefits and drawbacks of Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC) techniques (Table 2) have been emphasized. FTIR technique can quickly adapt to new demands and is a strong research resource. Nuclear Magnetic Resonance (NMR) is a physical occurrence where nuclei within a strong uniform magnetic field are affected by a weak oscillating magnetic field and react by emitting an electromagnetic signal with a frequency specific to the magnetic field at the nucleus. This process occurs close to resonance, where the oscillation frequency aligns with the intrinsic frequency of the nuclei, influenced by the strength of the static magnetic field, the chemical surroundings, and the magnetic characteristics of the involved isotopes.

Gel Permeation Chromatography (GPC), referred to as Size Exclusion Chromatography (SEC), is a method employed to access the average molecular weight distribution of a polymer specimen. By utilizing the correct detectors and analytical methods, one can also acquire qualitative data on long-chain branching or ascertain the composition distribution of copolymers.

As suggested by its name, GPC or SEC classifies the polymer based on size or hydrodynamic radius. This is achieved by introducing a minimal quantity of polymer solution into a series of columns filled with porous beads.

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Smaller molecules can pass through the pores and are thus more than the larger molecules, which move down the columns and elute more quickly.

## 4. Conclusion

The thin film of metal chalcogenides has been produced using multiple deposition methods. These films have discovered various uses, such as solar panels, sensors, optoelectronic devices, laser technologies, sensors, electroluminescent gadgets and light-emitting diodes. A variety of analytical techniques have been used for the characterization of these films. In this research, Fourier Transform Infrared Spectroscopy (FTIR) was employed to recognize the presence of different types of functional groups in the obtained samples. FTIR analysis technique utilizes infrared light to examine samples from 400 to 4000 cm<sup>-1</sup>. FTIR spectra showed that the distinctive peaks were affected by changes in experimental parameters.

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