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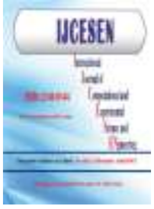

Research Article

Influence of Film Thickness on Structural and Optical Properties of Copper Sulfide Thin Films Prepared by Pulsed Laser Deposition (PLD)

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Abstract:

Copper sulfide (CuS) thin films with varying thicknesses were fabricated via pulsed laser deposition (PLD), and their structural and optical characteristics were comprehensively investigated. X-ray diffraction (XRD) analyses confirmed the presence of a hexagonal covellite phase, exhibiting enhanced crystallinity with increasing thickness. Field-emission scanning electron microscopy (FESEM) revealed a homogeneous surface morphology and improved grain connectivity in thicker films. UV-Vis spectroscopy showed an increase in absorbance and a redshift in the absorption edge, corresponding to a reduction in the bandgap from 2.35 eV to 2.1 eV. These observations are attributed to quantum confinement effects and improved crystallographic ordering. Compared to similar studies, this work offers deeper insight into the thickness-driven optimisation of CuS films, underscoring their potential in photovoltaic and optoelectronic device applications.

1. Introduction

Copper sulfide (CuS) thin films are promising candidates for optoelectronic and photovoltaic applications due to their tunable bandgap, strong light absorption, and cost-effective fabrication. Pulsed laser deposition (PLD) offers significant advantages in achieving precise control over film thickness, composition, and crystallinity, making it an ideal method for producing high-performance CuS films. Despite numerous efforts to enhance CuS film properties through doping, substrate variation, and post-annealing, the specific impact of thickness variation has not been sufficiently explored. This research investigates the correlation between film thickness and the structural and optical behaviors of CuS films synthesised via PLD. However, these studies often focus on complex materials or composite systems. By contrast, our study isolates thickness as a singular parameter, contributing clearer design guidelines for functional device integration based on CuS.

2. Experimental Methodology

2.1 Materials and Target Preparation:

High-purity (99.99%) CuS targets were employed. Prior to deposition, targets were cleaned ultrasonically and pre-ablated for 10 minutes to ensure stable plasma generation.

2.2 Deposition Process:

Films were deposited on cleaned glass substrates using a Nd:YAG laser (1064 nm wavelength, fluence of 2 J/cm², repetition rate of 10 Hz). Substrates were heated to 300°C, and the deposition duration was varied to obtain film thicknesses of 100, 200, 300, and 400 nm. The chamber base pressure was kept at 5×10^{-5} Torr.

3. Characterization Techniques:

- X-ray Diffraction (XRD): Used to determine phase structure, crystallinity, and crystallite size via Scherrer analysis.

- Field Emission Scanning Electron Microscopy (FESEM): Employed to assess surface topography and grain size evolution.

UV-Vis Spectroscopy: Utilized to obtain absorbance spectra and estimate optical bandgap using Tauc relation.

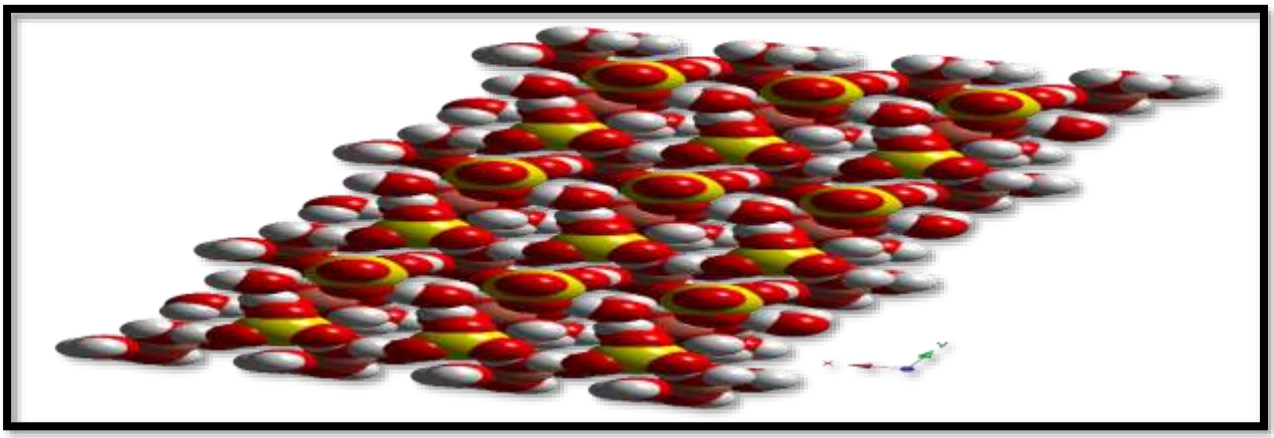

Figure1. *Crystal structure of the copper sulfide [1].*

Figure2. *High-purity (99.99%) CuS targets*

Figure 3. *PLD system.*

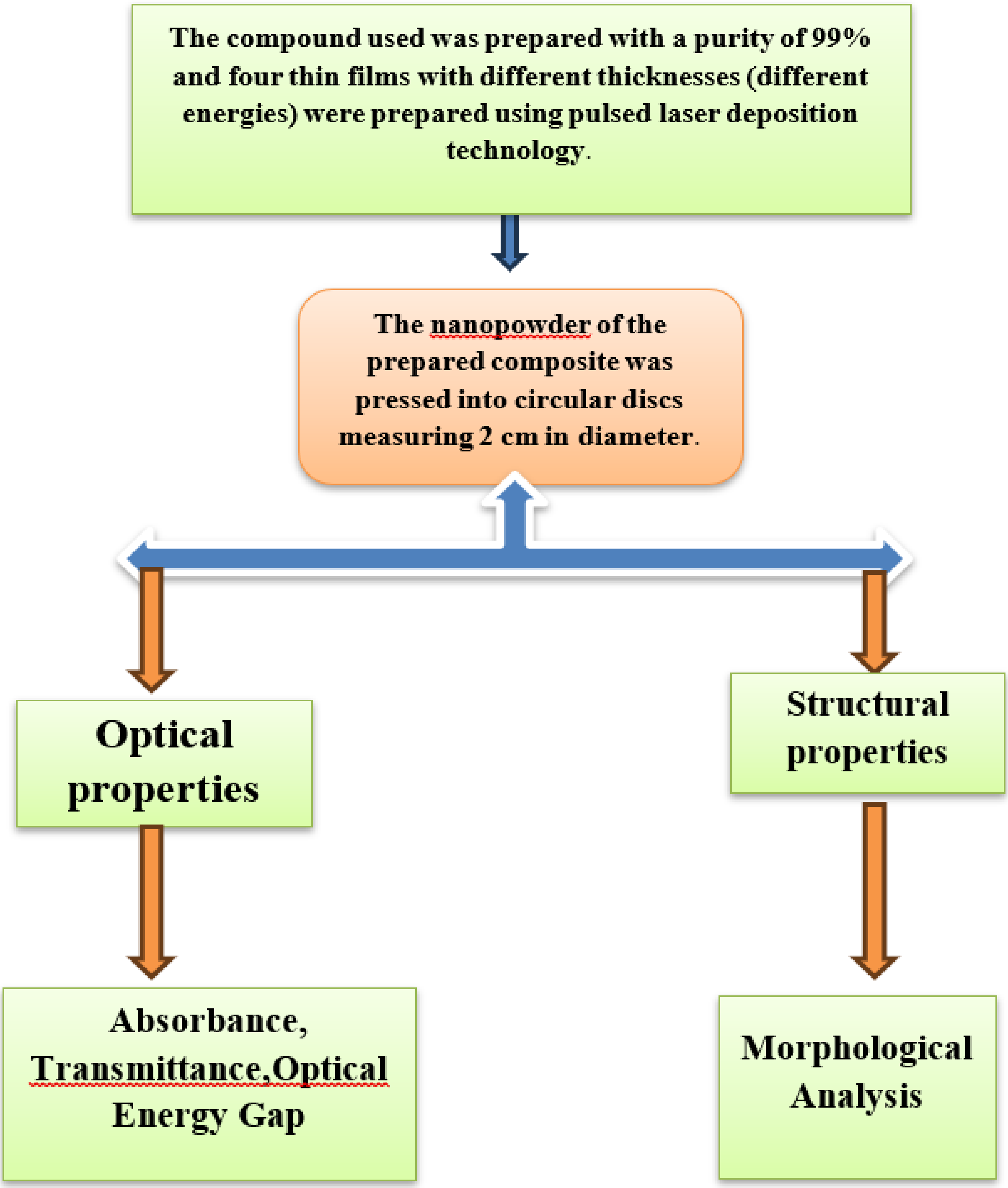

Figure 4. *Detailed workflow diagram*

4. Results &Discussion

4.1 Structural Properties:

XRD patterns revealed a dominant (102) peak, characteristic of the hexagonal covellite CuS phase. The intensity and sharpness of diffraction peaks increased with thickness, indicating improved crystallinity. The calculated crystallite size grew from approximately 12 nm in the 100 nm film to 25 nm in the 400 nm sample. An increase in the frequency of laser pulses during Pulsed Laser Deposition (PLD) results in a greater material deposition, yielding thicker films. This directly influences the XRD peak intensities for various reasons: 1. Enhanced Crystallinity: An increase in pulse frequency results in greater material deposition, hence improving crystallisation. This enhances the intensity of diffraction peaks. 2. Increase in Film Thickness: Thicker films augment the amount of diffracted X-rays, hence enhancing peak intensity. Thin films often exhibit diminished peaks due to limited material interaction with X-rays. 3. Improved Grain Growth: A higher number of pulses can enhance grain growth and minimise flaws, resulting in stronger diffraction signals. 4. Preferred Orientation: As the film thickness increases, some crystal planes may align preferentially, resulting in enhanced intensity of specific peaks. 5. Decreased Amorphous Content: At reduced pulse counts, the film may exhibit a greater degree of disorder or be partially amorphous. Augmenting the pulse count facilitates improved atomic organisation, enhancing peak intensity. For the production of a high-efficiency solar cell, it is preferable to select a thin film that exhibits optimal crystallisation and minimal crystalline flaws, as these factors influence electrical conductivity and electron transmission within the material. The XRD curves in the image reveal the following observations. An augmentation in the quantity of pulses results in an enhancement of peak intensity, signifying superior crystallisation. However, it is essential to consider the dimensions of the crystal grains and their orientation, as certain crystallographic directions may facilitate electron transport more effectively than others. The presence of an optimal thickness for the thin film is crucial. An excessively thick coating may lead to heightened recombination, diminishing the cell's efficiency. What is the optimal number of pulses? A poorly crystalline layer formed after 100 pulses may be unsuitable due to its high electrical resistance. Utilising 400 pulses may yield high crystallinity; however, if the layer becomes excessively thick, it could increase light absorption without enhancing energy conversion efficiency. The best number of pulses may be between 200 and 300, which helps find a balance between crystallisation, layer thickness, and crystal orientation.

4.2 Morphological Analysis:

FESEM images demonstrated uniform and compact morphology across all samples. Thicker films exhibited increased grain size and enhanced surface continuity, which contribute to reduced electron scattering and better electrical performance. morphology of CuS thin films with varying thicknesses. These high-resolution images allow for the visualization of grain size, surface uniformity, and structural changes induced by thickness variation. Such morphological information is essential to correlate the film's microstructure with its optical properties, helping to explain observed changes in transmittance, absorbance, and band gap energy.

4.3 Optical Properties:

UV-Vis spectroscopy showed a strong absorption across the visible spectrum. As thickness increased, a redshift in the absorption edge was observed, corresponding to a progressive reduction in the optical bandgap from 2.35 eV to 2.1 eV. This trend supports the presence of quantum confinement effects and a more ordered microstructure.

4.4 Literature Comparison:

Compared with reports such as Opt. Express 33 (2025) and IEEE Trans. MTT (2024) presents a focused investigation on thickness dependence. While those studies emphasise material complexity or hybrid systems, our results provide a direct pathway to optimise film performance through a single-variable strategy

4.5 Application Challenges and Limitations:

Despite the promising improvements in crystallinity and absorbance, practical implementation faces several challenges: scalability, environmental degradation, and weak film-substrate adhesion. Overcoming these requires further engineering efforts, including buffer layer design and encapsulation strategies

4.6 Optimization Potential:

Future work may explore extending the detection range of CuS films to applications such as infrared sensing, through nanostructuring or alloying. Moreover, introducing surface passivation or multi-layer architectures could enhance device efficiency and long-term performance, This study presents significant optimization potential by identifying the ideal thickness of CuS thin films that results in the most favorable balance between structural integrity and desirable optical properties. By systematically analyzing how varying thickness affects crystallinity, grain morphology, absorbance, and band gap energy, the research offers valuable insight into tailoring film characteristics for specific applications such as solar cells, photodetectors, or optical coatings. The findings can serve as a guide for optimizing deposition parameters in PLD to achieve high-performance CuS-based devices.An increase in the frequency of laser pulses during Pulsed Laser Deposition (PLD) results in a greater material deposition, yielding thicker films. This directly influences the XRD peak intensities for various reasons: 1. Enhanced Crystallinity: An increase in pulse frequency results in greater material deposition, hence improving crystallisation. This enhances the intensity of diffraction peaks. 2. Increase in Film Thickness: Thicker films augment the amount of diffracted X-rays, hence enhancing peak intensity. Thin films often exhibit diminished peaks due to limited material interaction with X-rays. 3. Improved Grain Growth: A higher number of pulses can enhance grain growth and minimise flaws, resulting in stronger diffraction signals. 4. Preferred Orientation: As the film thickness increases, some crystal planes may align preferentially, resulting in enhanced intensity of specific peaks. 5. Decreased Amorphous Content: At reduced pulse counts, the film may exhibit a greater degree of disorder or be partially amorphous. Augmenting the pulse count facilitates improved atomic organisation, enhancing peak intensity. For the production of a high-efficiency solar cell, it is preferable to select a thin film that exhibits optimal crystallization and minimal crystalline flaws, as these factors influence electrical conductivity and electron transmission within the material. The XRD curves in the image reveal the following observations. An augmentation in the quantity of pulses results in an enhancement of peak intensity, signifying superior crystallisation. However, it is essential to consider the dimensions of the crystal grains and their orientation, as certain crystallographic directions may facilitate electron transport more effectively than others. The presence of an optimal thickness for the thin film is crucial. An excessively thick coating may lead to heightened recombination, diminishing the cell's efficiency. What is the optimal number of pulses? A poorly crystalline layer formed after 100 pulses may be unsuitable due to its high electrical resistance. Utilizing 400 pulses may yield high crystallinity; however, if the layer becomes excessively thick, it could increase light absorption without enhancing energy conversion efficiency. The best number of pulses may be between 200 and 300, which helps find a balance between crystallisation, layer thickness, and crystal orientation.

4.7 Absorbance:

The “absorption spectrum” was measured as a function of wavelength. By analysing the “Absorbance spectrum”, one can determine several optical constants. Measurements were performed over the (λ) range of 100 to 900 nm for all CuS thin films. The UV-VIS measurement results are presented in Fig. 4, which shows the fluctuation of the absorbance spectrum as a function of wavelength. The data demonstrated that absorbance increases with the number of pulses, resulting in increased thickness. The photons can energise the electron, enabling its passage from the Valence Band to the Conduction Band, as the energy of the incident photon surpasses the semiconductor's energy gap. Consequently, absorbance rises with increasing wavelength, consistent with prior studies [1,2,3]. Fig.4 shows the “Absorption Spectrum” of thin films of (CuS) in the (λ) range of 300-1000 nanometers. The curve shows the change in absorbance according to the variation in the number of pulses and energy during the preparation of the films using the (PLD) technique: The green curve (1200mj-100p): shows the lowest absorbance among all the curves, indicating that the layer prepared under these conditions is less dense or thinner. The black curve (200p) demonstrates a distinct rise in absorbance, indicating that an increase in the number of pulses results in an enhanced density and thickness of the film, thereby augmenting absorption. The blue curve (A 3-300p) and the red curve (A 4-400p): They show an additional increase in absorbance with the increase in the no. of pulses, where the absorbance reaches its highest value at the red curve (400p), indicating the formation of a thicker film or improved nanostructures. We observe that the absorption edge shifts gradually with changes in the number of pulses and energy, indicating variations in the crystal size or the electronic structure of the film. The edge shift towards longer wavelengths (Redshift) may be due to an increase in crystal size or the formation of different phases of CuS. On the other hand, if a shift towards shorter wavelengths (Blueshift) occurs, it may indicate a reduction in the size of nanoparticles and quantum effects[4,5].

4.8 Transmittance:

The transmission measurement was conducted across 200 to 900 nm wavelength for all CuS thin films. UV-VIS studies demonstrated that the transmission spectrum displays markedly distinct behavior compared to the "Absorbance Spectrum", as illustrated in Fig. (5). The transmission of the thin film diminished with increasing (λ); furthermore, these results indicated that the thin films exhibit high transmission in the visible and IR spectra, especially between (500 – 760) nm. This range of wavelengths is referred to as the fundamental absorption edge, depicted as a curve, indicating that the film's structure is Polycrystalline. The Absorption and transmission are influenced by various factors, including material composition, thickness, light wavelength, surface characteristics,

Figure 3. *SEM system*

Figure 4. *UV-Vis spectroscopy system*

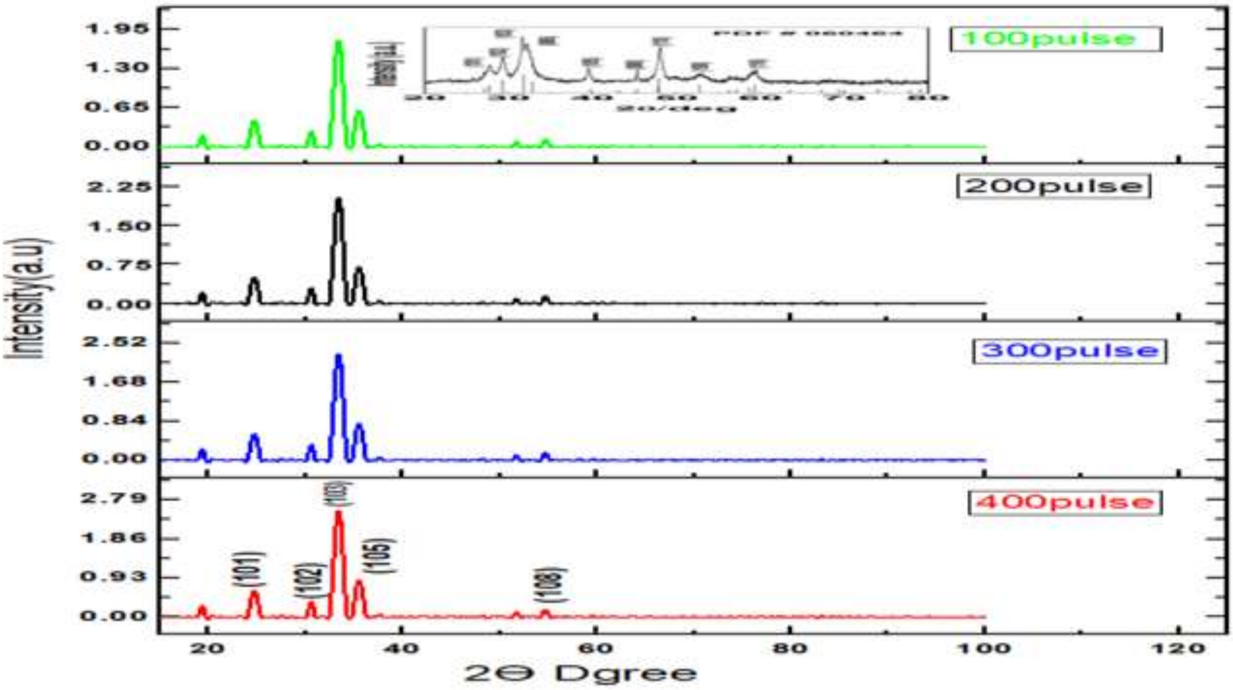

Figure 5. *XRD patternof the CuS prepared films.*

Table1. *Phases of different thicknesses CuS thinfilms*

CuS-sample	2Ө (Deg.)	hkl	Phase	Card no.
100 pulses	26.7800	(101)	Orthorhombic	00-042-1278
200 pulses	27.2902	(102)	Hexagonal	00-006-0464
300 pulses	24.3119	(101)	Orthorhombic	00-042-1278
400 pulses	33.1233	(103)	Hexagonal	00-006-0464

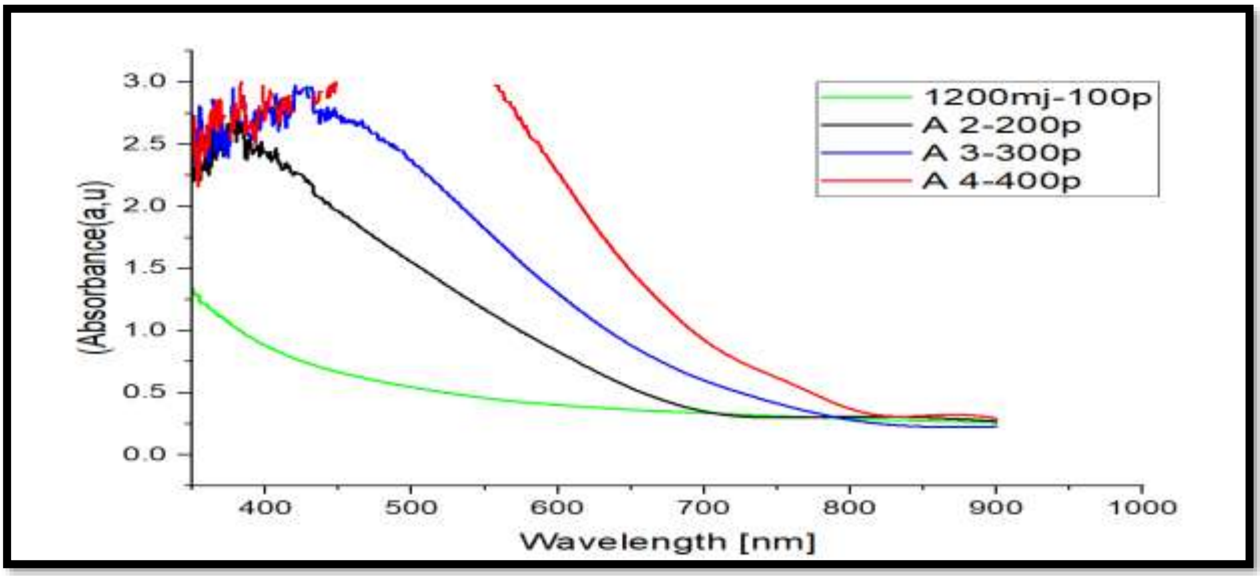

Figure 6. *Absorbance of CuS thin films for different thicknesses.*

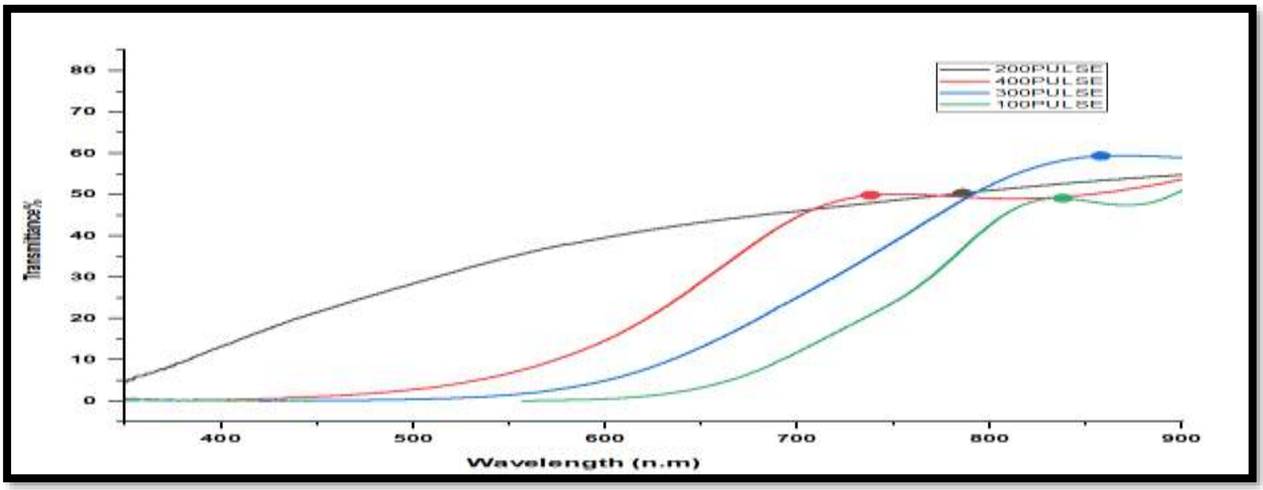

Figure 7. *Transmittance of CuS thin films for different thicknesses.*

Table 2. *Values bandgaps,no. of pulses, gap effect.*

Number of Pulses	Bandgab	Gap (eV) Effect
100 pulses	~2.3–2.4 eV	Strong quantum confinement
200 pulses	~2.3 eV	Moderate reduction in Eg.
300 pulses	~2.2 eV	Increased grain size, reduced
400 pulses	~2.16 eV	Bulk-like behavior, minimal confinement

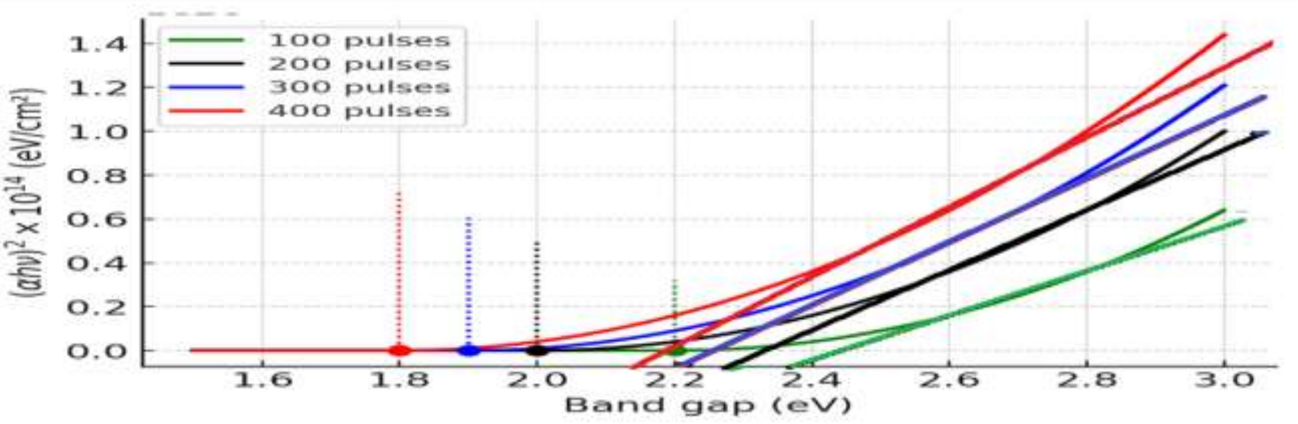

***Figure* 6.** *Bandgaps of CuS thin films for different thicknesses.*

and crystalline structure. The transmission variance of thin films is contingent upon the preparation methodology and conditions, as indicated in [10]. The thickness of the films produced by the PLD technology significantly influences optical transmission, and this effect can be stated as follows: Augmenting the thickness results in a reduction in permeability. As the number of pulses rises (from 100 to 400), the thickness of the films formed on the substrate also increases.. The increase in thickness leads to more absorption and scattering of light, which reduces light transmittance. Thin films often exhibit nonlinear behaviour; the effect may not be perfectly proportional to the number of pulses. Changes in crystal structure and roughness: Increasing the number of pulses can improve crystallisation, which may indirectly affect permeability. A rougher surface may lead to light scattering, which also reduces permeability. The wavelength of the light used in the measurement is important: Usually, permeability is higher at longer wavelengths (near-infrared) and decreases in the ultraviolet range. When the thickness increases, the optical absorption edge may shift to different wavelengths due to changes in the band gap.

4.9 Bandgap:

The band gap of thin films prepared by the (PLD) method is significantly influenced by the number of laser pulses (100–400 pulses) due to several key factors:

1. **Effect of Film Thickness on Band Gap**

- Increasing the number of pulses from 100 to 400 leads to thicker films, which can reduce the band gap due to:
    - Quantum confinement effects: Thin films deposited with fewer pulses (e.g., 100 pulses) tend to exhibit a wider band gap due to the size confinement of the nanostructures.
    - Reduced defects and improved crystallinity: More pulses typically enhance crystallinity, reducing localised states and narrowing the band gap.

2. **Structural and Morphological Influence**

- Low pulse numbers (100–200 pulses):
    - May result in nanostructured films with small grains and increased quantum confinement, leading to a higher band gap (~2.1 eV or more).
- High pulse numbers (300–400 pulses):
    - Produce thicker films with better crystallinity, reducing the band gap to values closer to bulk CuS (~1.8–2.0 eV) due to reduced confinement effects.

3. **Oxygen and Sulfur Deficiency Effects**

- PLD films can exhibit stoichiometry variations, particularly sulfur vacancies, which may introduce defect states and slightly shift the band gap.

4. **Optical Absorption Analysis**

- Measured using UV-Vis spectroscopy, the band gap can be estimated via Tauc plots

where **Eg (band gap)** depends on film thickness and deposition parameters.

“$(\alpha h\nu)^n = A(h\nu - E_g)$”, where:

- “α = Absorption coeff., hν is photon Energy”, n = material-dependent constant,
- n depends on the nature of the transition (for CuS, it is typically **n = 2** for a direct band gap)

4. Conclusions

The study confirms that CuS film thickness plays a crucial role in determining structural and optical properties. Thicker films demonstrate improved crystallinity and lower bandgap energies, making them suitable for integration into optoelectronic devices. These findings contribute to a better understanding of film-thickness engineering and serve as a guideline for device-oriented film synthesis.

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper
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- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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