

Recent Advances in Spray-Pyrolysed $\text{Cu}_2\text{ZnSnS}_4$ Thin Films for Photovoltaic Applications Structure–Property Relationships, Phase Engineering, Surface Morphology and Device Optimization

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Research Article

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RECENT ADVANCES IN SPRAY-PYROLYSED $\text{Cu}_2\text{ZnSnS}_4$ THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

Structure–Property Relationships, Phase Engineering, Surface Morphology and Device Optimization

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Abstract

Copper zinc tin sulphide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS) is an earth-abundant, comparatively low-toxicity semiconductor with a direct band gap commonly reported around 1.4–1.6 eV and a high optical absorption coefficient. Spray pyrolysis is an attractive non-vacuum deposition route because of its relatively simple equipment, compositional flexibility and potential for large-area coating. Nevertheless, the properties of spray-pyrolysed CZTS depend strongly on precursor chemistry, substrate temperature, droplet transport, sulphur availability, post-deposition treatment and cation stoichiometry. These variables determine kesterite-phase formation, crystallite development, secondary-phase segregation, morphology, optical absorption, electrical transport and photovoltaic performance. This review examines processing mechanisms and recent advances, with emphasis on structural characterization by X-ray diffraction and Raman spectroscopy, optical band-gap determination, electrical transport, surface morphology, thermal treatment and photovoltaic device integration. Particular attention is given to distinguishing kesterite CZTS from related secondary phases, including ZnS and copper–tin sulphides. Building on the earlier review by Raj, Sebastian and Rajendran on spray-pyrolysis-deposited CZTS, the present manuscript emphasizes critical structure–property relationships and the need to connect absorber measurements to validated device performance.

Keywords: CZTS; spray pyrolysis; kesterite; thin films; Raman spectroscopy; X-ray diffraction; surface morphology; optical band gap; electrical properties; photovoltaic applications.

1. Introduction

The development of sustainable photovoltaic technologies requires semiconductors that combine high optical absorption, suitable band-gap energy, long-term stability, affordable processing and availability of constituent elements. CZTS is attractive because it contains copper, zinc, tin and sulphur. Its direct band gap and strong absorption make it a candidate for thin-film solar absorbers. However, these intrinsic advantages do not automatically translate into high device efficiency: native defects, compositional inhomogeneity, secondary phases, grain-boundary recombination and interface-related losses can limit performance.

Spray pyrolysis offers a practical route to CZTS fabrication by atomizing a precursor solution and transporting droplets towards a heated substrate. Solvent evaporation, precursor decomposition and chemical reactions lead to solid-film formation. The technique can support large-area processing without requiring expensive vacuum deposition equipment. The earlier review by C. S. A. Raj, S. Sebastian and S. Rajendran specifically addressed spray-pyrolysis-deposited CZTS thin films for solar-cell applications. The present review extends that foundation by focusing on recent processing strategies, phase verification, structure–property relationships and device-oriented optimization.

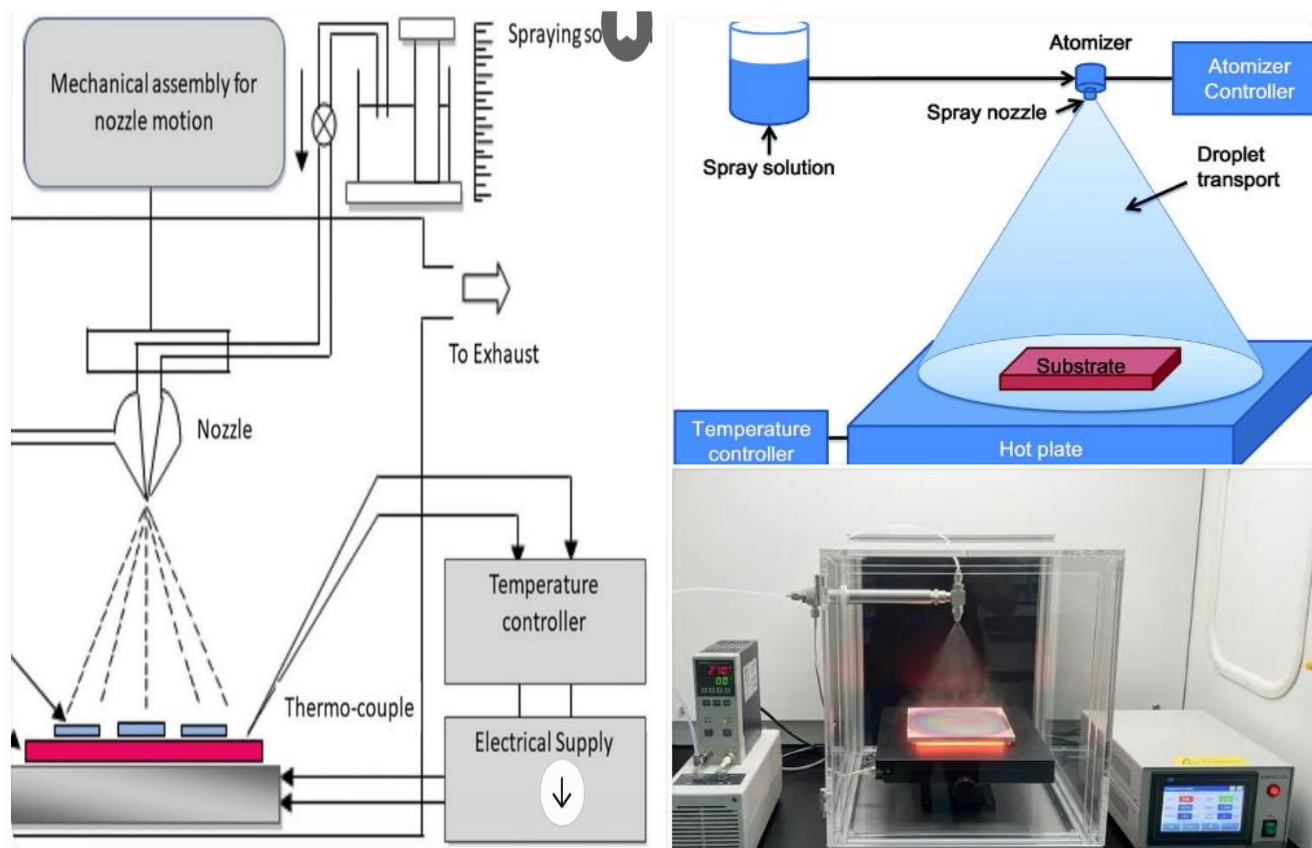
1.1 Scope and objectives

- Explain mechanisms and process variables governing spray-pyrolysed CZTS growth.
- Evaluate phase formation, crystallinity, lattice disorder and secondary-phase identification.
- Compare optical band gaps, absorption characteristics and electrical transport reported in the literature.
- Relate surface morphology and grain development to absorber-layer performance.
- Examine thermal treatment, sulphurization and compositional engineering.
- Discuss photovoltaic architectures, performance limitations and future research opportunities.

2. Fundamentals of spray pyrolysis

2.1 Deposition mechanism

Spray pyrolysis converts a solution containing suitable metal and sulphur precursors into a solid semiconductor coating. The process comprises (i) atomization of the precursor solution, (ii) droplet transport and solvent evaporation, (iii) precursor decomposition and reaction, and (iv) film nucleation, growth and densification.



Deposition mechanism

Spray pyrolysis involves the conversion of a solution containing suitable metal and sulphur precursors into a solid semiconductor coating. The process can be divided into four stages.

Stage I — Atomization: The precursor solution is converted into droplets using a pneumatic, ultrasonic or other atomization system.

Stage II — Droplet transport and solvent evaporation: Droplets travel towards the heated substrate while undergoing solvent evaporation and changes in solute concentration.

Stage III — Precursor decomposition and reaction: Metal-containing species react with the sulphur source to form intermediate compounds and, under suitable conditions, the CZTS phase.

Stage IV — Film growth and densification: Nucleation, crystallite growth and thermal decomposition govern the film's microstructure. Subsequent annealing or sulphurization may improve crystallinity and composition.

The actual pathway depends on the droplet-size distribution, solvent, precursor stability, substrate temperature, spray distance and ambient atmosphere. Consequently, nominally similar spray-pyrolysis recipes can yield substantially different films.

2.2 Important process parameters

Parameter	Primary influence	Potential consequence of poor optimization
Substrate temperature	Pyrolysis, nucleation and crystallization	Incomplete decomposition or excessive material loss
Precursor concentration	Film thickness and deposition rate	Precipitation, non-uniformity or rough surfaces
Cu:Zn:Sn ratio	Defect chemistry and phase stability	Secondary phases or non-ideal stoichiometry
Sulphur precursor concentration	Sulphur availability and reaction chemistry	Incomplete sulphidation or unwanted sulphur-rich phases
Spray rate and droplet size	Material flux and solvent evaporation	Powder formation, porosity or non-uniform growth
Nozzle-to-substrate distance	Droplet drying and arrival conditions	Inhomogeneous deposition
Annealing atmosphere	Sulphur retention and phase development	Sulphur loss, oxidation or decomposition
Post-deposition treatment	Grain growth and defect redistribution	Grain coarsening or secondary-phase formation

3. Structural properties and phase formation

3.1 Crystal structure

CZTS typically adopts a tetragonal kesterite structure. Its relationship to stannite and the presence of secondary phases make definitive phase identification challenging. X-ray diffraction (XRD) is essential but should not be used alone to claim phase purity. The commonly discussed diffraction features include reflections indexed to (112), (220) and (312), with exact positions and intensities depending on composition, strain, crystallinity and instrumental conditions.

3.2 Crystallite size and lattice strain

The Scherrer equation is commonly used to estimate coherent diffraction-domain size: $D = K\lambda/(\beta \cos \theta)$, where D is the apparent crystallite size, K is a shape factor, λ is the X-ray wavelength, β is the instrument-corrected full width at half maximum in radians, and θ is the Bragg angle. This value is not necessarily equal to the grain size observed by SEM. Instrumental broadening and microstrain should be considered.

The Williamson–Hall relationship, $\beta \cos \theta = K\lambda/D + 4\epsilon \sin \theta$, can provide an approximate separation of size and strain contributions under the assumptions of the model, where ϵ is the estimated microstrain.

3.3 Secondary phases and Raman confirmation

Potential secondary phases include ZnS, Cu₂SnS₃, Cu₂S, SnS and SnS₂. They can alter optical response, carrier transport and interface recombination. Raman spectroscopy is a valuable complement to XRD because several secondary phases produce diffraction features that overlap with CZTS. A Raman feature around 330–338 cm⁻¹ is often associated with CZTS modes, but assignment should consider the complete spectrum and likely competing phases.

A robust workflow combines XRD, Raman spectra collected at multiple sample positions, SEM–EDS or other composition-sensitive analysis, and XPS when chemical bonding or oxidation states require confirmation.

3.4 Temperature-dependent crystallization

Increasing substrate temperature can improve precursor decomposition and crystallite growth, but excessive heating may promote sulphur loss, tin-containing species volatilization and secondary-phase formation. A spray-deposition study by Deokate and co-workers reported optical band gaps of 1.42–1.58 eV and absorption coefficients of approximately 10^5 cm^{-1} under its reported conditions. Research using ultrasonic spray pyrolysis also found that deposition temperature influenced phase disorder and apparent band gap. These are study-specific observations, not universal values for all spray-pyrolysed films.

4. Optical properties

4.1 Absorption coefficient

In a simplified model neglecting reflection and interference, the absorption coefficient can be estimated from $\alpha = (1/t) \ln(1/T)$, where α is the absorption coefficient, t is film thickness and T is fractional transmittance. This approximation is unsuitable without correction for strongly reflecting, rough, scattering or multilayer samples; a more complete optical model may be required.

4.2 Optical band-gap determination

For a direct allowed transition, the Tauc-type relation is commonly written $(\alpha h\nu)^2 = A(h\nu - E_g)$, where $h\nu$ is photon energy, A is a proportionality constant and E_g is the estimated optical band gap. The result depends on the selected fitting interval, film thickness, baseline correction and scattering. Reported values should be compared only after measurement and fitting differences are considered.

Study / processing	Reported optical result	Interpretation
Deokate et al. (2022), one-step spray deposition	$E_g = 1.42\text{--}1.58 \text{ eV}$; absorption coefficient approximately 10^5 cm^{-1}	Promising absorber characteristics
Ultrasonic-spray study (2022), temperature varied	Reported band gap range 1.42–1.89 eV	Optical response sensitive to processing and disorder
Spray deposition with combined thermal treatment (2023)	Reported band gap approximately 1.5–1.6 eV	Post-treatment investigated to improve absorber properties

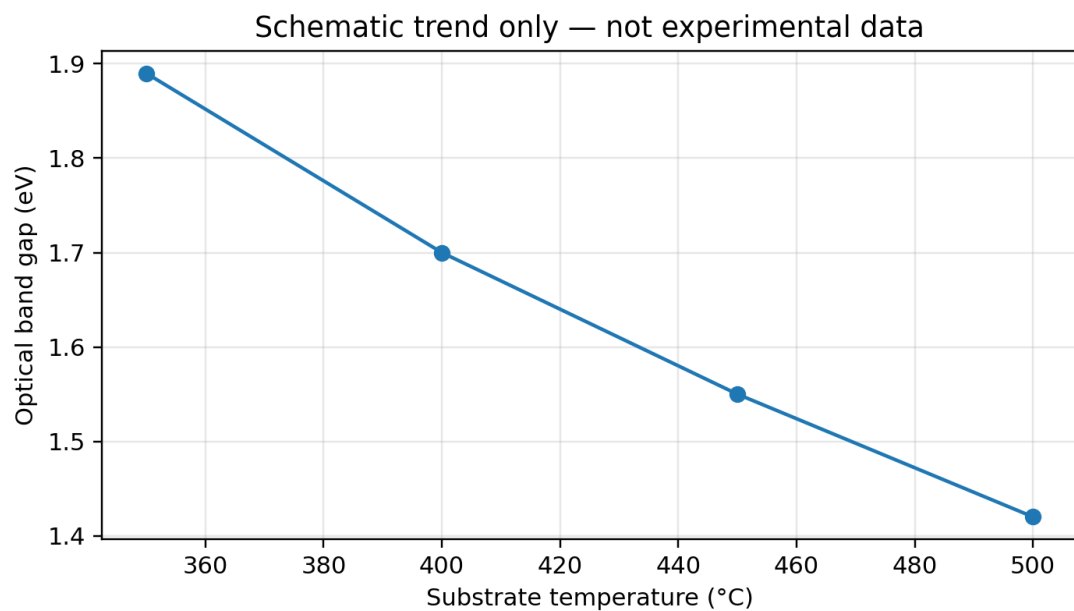


Figure 1. Schematic trend only; the plotted points are illustrative and are not experimental measurements from a cited study.

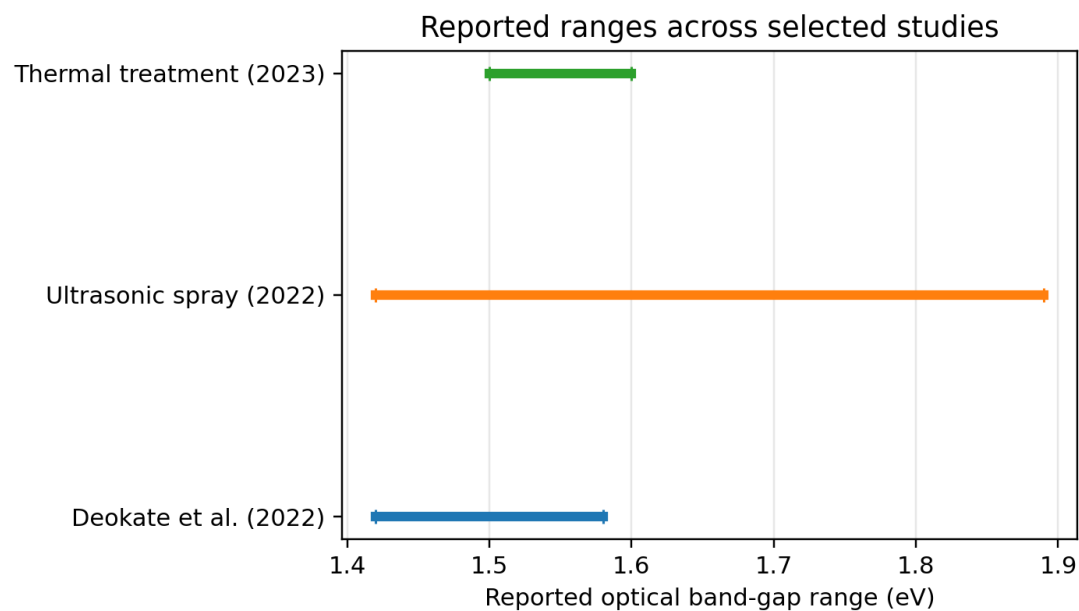


Figure 2. Comparison of optical band-gap intervals reported for selected studies. The ranges summarize different studies and do not represent a controlled head-to-head experiment.

5. Electrical properties

5.1 Electrical resistivity

Resistivity can be evaluated using four-point-probe measurements or other appropriate electrical configurations. For a uniform conducting film, $\rho = R_s t$, where ρ is resistivity, R_s is sheet resistance and t is film thickness; geometrical

corrections may be required. Lower resistivity can improve lateral conductivity, but it is not an independent measure of photovoltaic quality.

5.2 Carrier concentration and mobility

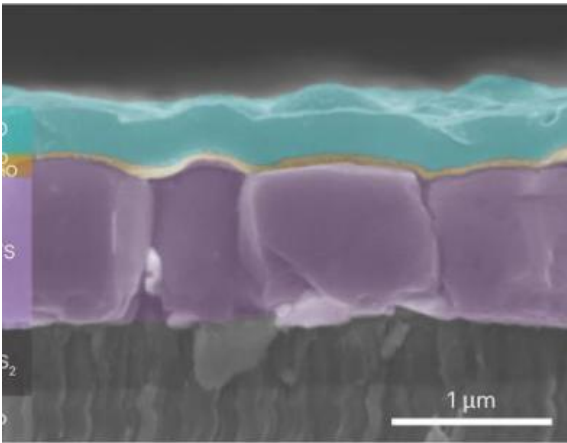
For a simple single-carrier approximation, conductivity is $\sigma = qn\mu$, where q is the elementary charge, n is carrier concentration and μ is mobility. Polycrystalline CZTS can depart from this model because of multiple defect populations, grain-boundary barriers and inhomogeneous conduction. Electrical results should therefore be interpreted alongside structural and compositional characterization.

5.3 Defect chemistry and cation disorder

Copper vacancies and copper-on-zinc antisite defects are among the defect configurations discussed in kesterite materials. Defect complexes can compensate charge carriers or create recombination pathways. The objective is to control defect populations, reduce non-radiative recombination and preserve favourable p-type transport, rather than to assume that every native defect is detrimental.

6. Surface morphology and microstructure

SEM analysis is useful for evaluating grain size, surface coverage, porosity, cracks and compositional inhomogeneity. Spray-pyrolysed films may exhibit granular, clustered, porous or compact morphologies depending on deposition conditions. Continuous surface coverage is generally desirable because pinholes can facilitate shunting and reduce junction uniformity. Larger grains may reduce the relative contribution of grain boundaries, but grain size alone does not establish electronic quality.



Morphological feature	Possible beneficial effect	Potential adverse effect
Larger grains	Reduced grain-boundary density	Abnormal growth or compositional segregation
Compact coverage	Fewer pinholes and improved junction continuity	Stress or cracking
Controlled roughness	May improve contact in selected architectures	Increased interface recombination in others
High porosity	May benefit selected functional coatings	Poor absorber continuity and enhanced recombination
Uniform thickness	More consistent absorption and junction behaviour	Difficult to maintain with uncontrolled droplet delivery

A complete assessment should combine plan-view SEM, cross-sectional SEM, thickness measurements and elemental mapping. AFM can provide quantitative surface-roughness data.

7. Recent advances in spray-pyrolysed CZTS

7.1 One-step deposition

One-step spray pyrolysis offers a route to deposit the absorber directly without necessarily requiring a separate sulphurization step. Published work demonstrates that promising optical characteristics can be obtained under optimized conditions. However, a promising thin film is not equivalent to a high-efficiency solar cell; device fabrication and full current–voltage characterization are essential.

7.2 Sulphurization and rapid thermal annealing

Post-deposition treatments can promote phase formation, improve crystallinity and modify secondary-phase distributions. Combined sulphurization and rapid thermal annealing have been investigated for spray-deposited CZTS. The treatment window must balance grain development against sulphur loss, tin volatilization and unwanted phase transformations. Reproducible reporting should include atmosphere, heating rate, dwell time, cooling conditions and sulphur-source geometry.

7.3 Ultrasonic spray pyrolysis

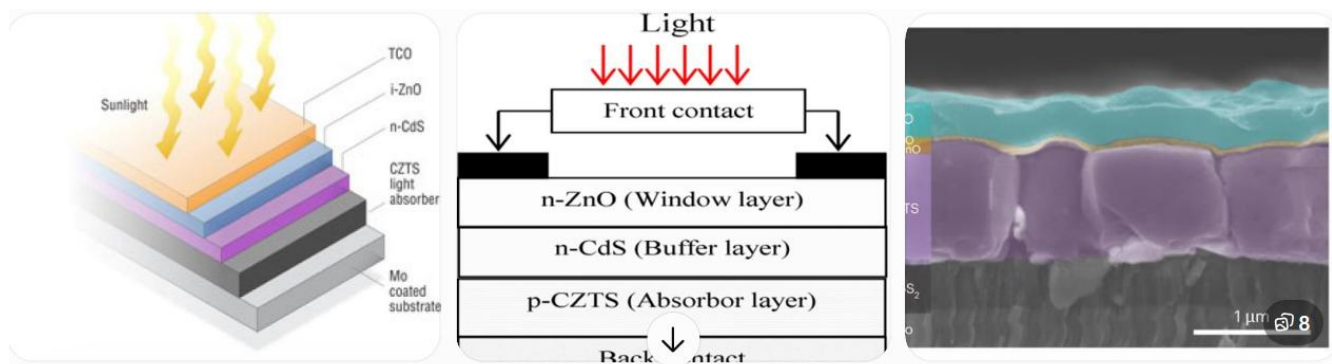
Ultrasonic atomization can offer control over droplet generation and material delivery. Its influence on CZTS formation includes both morphology and phase disorder. Comparative studies should separate atomization effects from precursor chemistry, substrate temperature and post-deposition treatment.

7.4 Compositional and defect engineering

Compositional tuning, controlled non-stoichiometry, alkali incorporation and defect passivation are promising directions. Their success depends on improving absorber quality without introducing electrically harmful phases. Results from CZTSSe, sputtered, evaporated or otherwise deposited kesterite materials should not automatically be attributed to spray-pyrolysed pure CZTS.

8. Solar-cell applications

A conventional CZTS thin-film solar cell may use a glass/Mo/CZTS/buffer/window/front-contact architecture, although the exact stack varies. The absorber must combine adequate absorption, favourable band alignment, low recombination, good carrier transport and a stable interface with the buffer layer.



8.1 Photovoltaic performance metrics

The principal parameters are open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and power-conversion efficiency (η). Efficiency is $\eta = (V_{oc} \times J_{sc} \times FF / P_{in}) \times 100\%$, using consistent units for current density and incident power density.

8.2 Efficiency benchmarks and interpretation

Certified kesterite-cell benchmarks vary by publication date and by whether the absorber is pure CZTS or the selenium-containing alloy CZTSSe. Device records are not necessarily based on spray pyrolysis. A review must distinguish the best reported kesterite efficiency from the best efficiency demonstrated specifically with spray-pyrolysed pure CZTS. Verify the latest applicable Solar Cell Efficiency Tables before submission.

8.3 Main performance limitations

- Voltage deficit associated with non-radiative recombination and defects.
- Current limitations arising from incomplete absorption, poor collection or transport barriers.
- Fill-factor losses caused by shunts, series resistance and non-ideal junction behaviour.
- Reproducibility problems due to composition, thickness and phase variation.
- Scale-up challenges in maintaining uniform droplet delivery, temperature and sulphur chemical potential.

9. Research gaps and future directions

1. Use Raman and XRD together to verify phase purity and identify secondary phases.
2. Optimize Cu-poor and Zn-rich precursor compositions while monitoring sulphur and tin content.
3. Report nozzle characteristics, droplet conditions, solution chemistry and substrate temperature for reproducibility.
4. Balance crystallinity improvement against sulphur and tin losses during thermal treatment.
5. Quantify grain-boundary density and porosity and connect them to carrier collection.
6. Report complete device parameters, active area, illumination conditions and measurement protocol.
7. Assess stability under relevant thermal, optical and environmental stresses.
8. Demonstrate uniformity and reproducibility over larger substrate areas.

10. Conclusion

Spray pyrolysis is a promising route for developing earth-abundant CZTS thin films, offering flexibility in precursor selection, relatively simple equipment and potential compatibility with scalable manufacturing. Published studies demonstrate that suitable processing can produce films with strong optical absorption and band-gap energies appropriate for photovoltaic absorbers. Nevertheless, high-quality CZTS requires more than a favourable optical spectrum. Phase purity, cation disorder, defect populations, electrical transport, surface continuity and heterojunction quality must be optimized together. Raman spectroscopy is valuable for distinguishing kesterite from related compounds, while SEM and composition-sensitive techniques provide information about uniformity and microstructure. Future progress depends on reproducible process–structure–property relationships that connect spray parameters to validated device performance.

The following figures support the structural, spectroscopic, morphological, process–property and photovoltaic discussions. Figures 3–5 are schematic or synthetic illustrations, not raw experimental measurements or published micrographs. Figure 7 summarizes reported device values from distinct studies and conditions; it is contextual, not a controlled ranking.

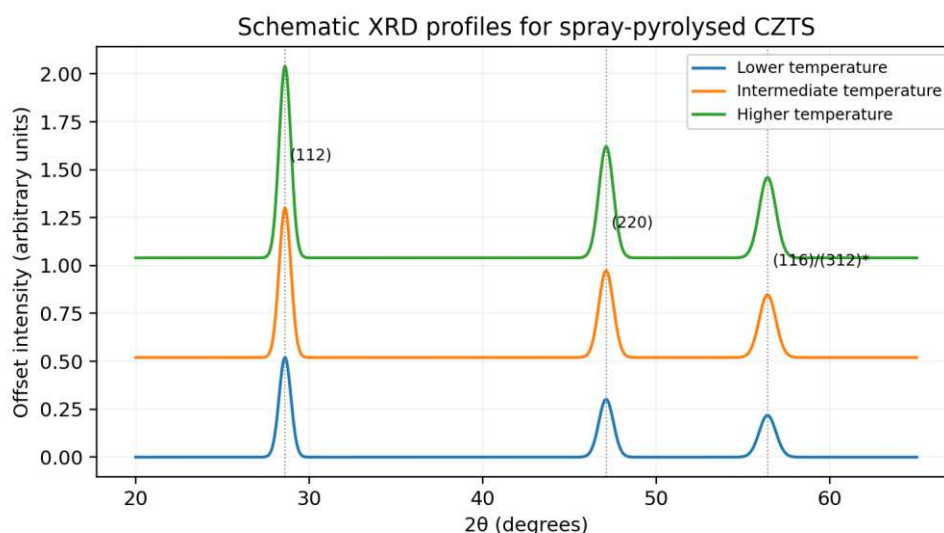


Figure 3. Schematic XRD profiles for CZTS films deposited at different substrate temperatures. Peak positions near 28.6° , 47.1° and 56.4° are based on reported CZTS reflections; intensities and widths are illustrative, not digitized experimental data. For source context, see Thiruvankadam et al., *Solar Energy* 106 (2014), DOI: 10.1016/j.solener.2014.02.041.

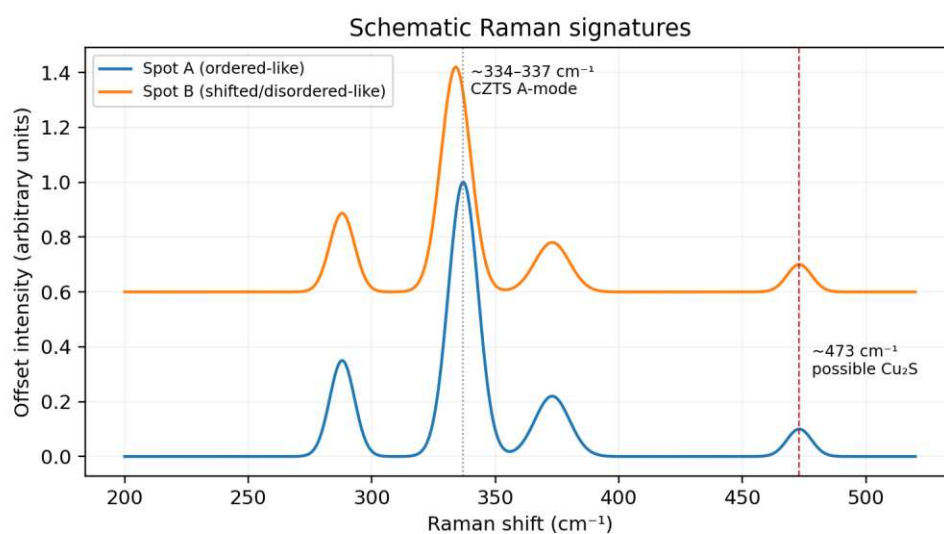


Figure 4. Schematic Raman signatures showing representative CZTS modes near 288 and $334\text{--}337\text{ cm}^{-1}$ and a possible secondary-phase marker near 473 cm^{-1} . Curves are illustrative, not measured spectra. Peak assignments depend on sample and excitation conditions; see DOI: 10.1016/j.physleta.2022.128331.

Synthetic morphology classes — not experimental SEM micrographs

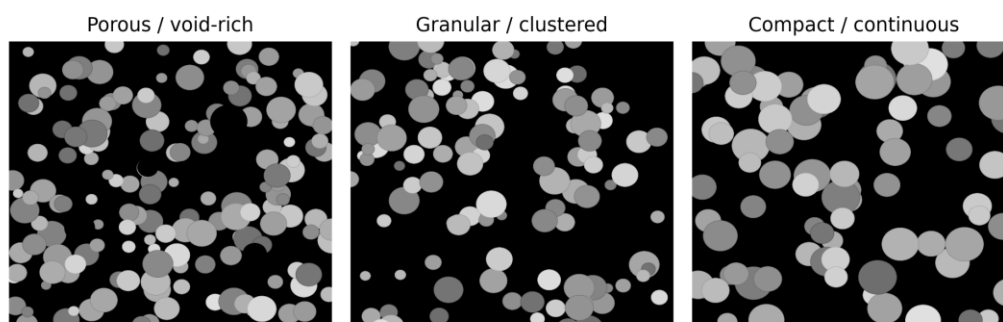
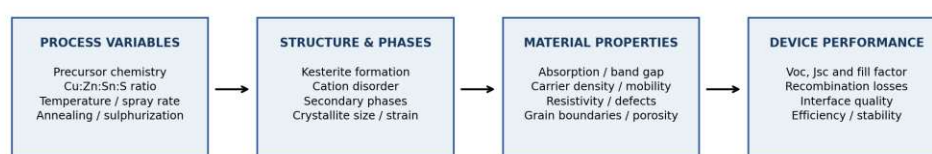


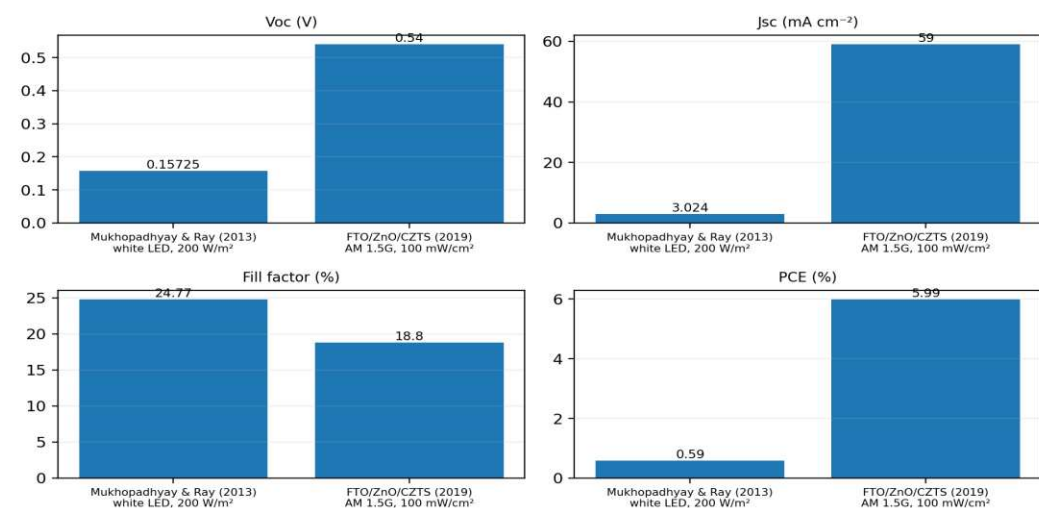
Figure 5. Synthetic illustrations of porous, granular and compact surface morphologies. These are conceptual visual aids, not actual SEM images. For publication, replace with original SEM data or properly licensed images from a cited source.



Feedback: device diagnostics guide further process and composition optimization

Figure 6. Process–structure–property–device relationship for spray-pyrolysed CZTS. This original schematic summarizes how deposition parameters affect phase formation and microstructure, which influence transport, recombination and photovoltaic performance.

Reported photovoltaic parameters for selected spray-deposited CZTS devices



Conditions and architectures differ; 2013 PCE calculated from reported Voc, Jsc and FF at 200 W/m². 2019 source reports Jsc = 59 mA cm⁻² and PCE = 5.99%; verify original units/data before publication.

Figure 7. Comparison of reported photovoltaic parameters for selected spray-deposited CZTS devices. Mukhopadhyay and Ray reported Voc = 157.25 mV, Jsc = 3.024 mA cm⁻² and FF = 24.77% under diffused white LED illumination at 200 W m⁻² (DOI: 10.1088/0268-1242/28/5/055001); PCE shown is calculated from those values and stated irradiance. A separate 2019 study reported PCE = 5.99%, Voc = 0.54 V, FF = 18.8% and Jsc = 59 mA cm⁻² for an FTO/ZnO/CZTS device under AM 1.5G illumination (DOI: 10.11648/j.ajmsp.20190401.11). Device architecture and test conditions differ; verify current-density units and values against the original article before publication.

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