



Spray Pyrolytic Deposition of CuInS_2 Thin Films: Properties and Applications

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Abstract

Spray pyrolysis (SP) method is simple and cost-effective method and is capable of depositing numerous metal oxide and composite thin films with precisely control over the chemical composition and morphology. The physico-chemical properties of the film can be controlled by adjusting the deposition parameters such as substrate temperature, concentration of precursor solution and spray rate, *etc.* In this paper an intensive review on spray pyrolytic deposition of CuInS_2 (CIS) thin films and its use as a light absorbing layer in solar cell have been presented. Due to fascinating optoelectronic properties, the CIS thin films are mostly suited for their application in solar cells. The CIS is one of the promising alternatives material to the first-generation solar cells. The advantages like non-toxic elements, suitable energy band gap, high absorption coefficient make it one of the promising candidates in the photovoltaic market. Here, we review studies conducted on the deposition, structural, optical and electrical properties of spray deposited CIS thin films. The performance of spray deposited CIS absorber layer in solar cell is also discussed. In addition, some strategies towards the enhancement of quality of CIS thin-film deliberated in detail.

Keywords: Spray deposition; CIS thin films; Physical properties; Solar cell.

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1. Introduction:

With the increase of global population and the improved standards of the living the world will need much more energy in future than the current consumptions. Right now, mainly the fossil fuels (~ 80%), petroleum, coal, hydrocarbon gas, natural gas and nuclear energy supplies the world energy requirements. These are non-renewable energy sources and are limited and eventually run out with time.^[1] The constant consumption of fossil fuel with the current rate, become extinct within 65 years.^[2-4] The burning of fossil fuel significantly emits air pollution gaseous and influence the earth's environment with waste product. Further, nuclear energy has always created

issues related to health and waste management. Therefore, in the view of limited availability of major energy resources (mainly nonrenewable energy resources) and considering their impact on environment, there is the need to find alternative and sustainable energy resources. It is essential to use renewable energy sources to fulfil the energy requirements and the improvement of human health.

Renewable energy comes from different sources that will never deplete, no matter how much is used. Renewable energy comes from sources with an unlimited supply such as water, wind, the sun, and biomass, *etc.* Many efforts have been made to develop new alternative energy sources over the last few decades.^[5-7] Solar energy is one of important categories of renewable energy and variable in the process of energy generation.

1.1 CIS light absorber layer

The light absorbing layer is one of the most important part of the solar cell. Many efforts have been made to develop high quality light absorber layer since last few decades. The solar cell fabricated using semiconductors such as cadmium sulfide/selenide (CdS/Se), lead sulfide/selenide (PbS/Se), Indium arsenide (InAs), bismuth sulfate (Bi_2S_3), copper indium sulfide/ selenide ($\text{CuInS}_2/\text{Se}_2 - \text{CIS/Se}$), copper zinc

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tin sulfide/ selenide ($\text{Cu}_2\text{ZnSnS}_4\text{-CZTS}$), copper indium gallium sulfide/selenide ($\text{Cu}_2\text{InGaS}_4/\text{Se}_4$ – CIGS/Se) have been prepared with various chemical and physical methods. These binary, ternary and quaternary semiconductor exhibits nontoxic and earth-abundant elements, sufficiently high light absorption coefficient in visible and near IR regions and the band gap close to the solar spectrum. Fig. 1 shows some of the important chalcopyrite materials which are used as a light absorber layer in solar cell.

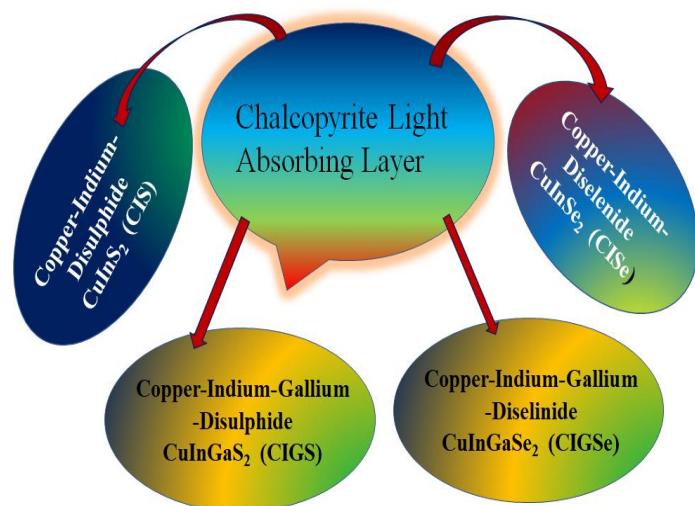


Fig. 1 Different chalcopyrite materials used as a light absorber layer in the solar cell.

Among different light-absorbing materials, CuInS_2 (CIS) has attracted much attention. It can be used for various optoelectronic applications like a solar cell, photoelectrochemical cell (PEC), photodetector and light-sensing transistors,^[8-12] *etc.* In thin film technology segment, CIS is mostly utilized as a solar absorber layer due to non-toxicity character, direct bandgap (1.3 - 1.5 eV) and high optical absorption coefficient (10^5 cm^{-1}). Theoretically, 27-32% solar energy conversion efficiency is possible for CIS.^[13] In laboratory-scale, polycrystalline CIS solar cell have shown up to 13% of power conversion efficiency.^[14]

Over the past few decades, various deposition techniques have established to deposit CIS materials both by chemical as well as physical method. Few of the chemical methods includes: chemical bath deposition (CBD),^[15,16] spray pyrolysis,^[17-20] electrodeposition,^[21,22] successive ionic layer adsorption and reaction SILAR,^[23,24] *etc.* and co-evaporation from elemental source,^[25] molecular beam epitaxy,^[26] Rf-sputtering,^[27] chemical vapor deposition (CVD),^[28] laser chemical vapor deposition (LCVD),^[29] atomic layer deposition,^[30] *etc.* are the physical methods.

The deposition of thin films via physical method mentioned above results in good-quality of thin films. However, physical methods are operated at relatively high temperature, high vacuum and are highly expensive and requires many material targets. Therefore, an alternative low-cost method is needed to produce good quality films. The

chemical method of deposition of thin films could be the best alternative because most of them do not require expensive equipment. The chemical method is strongly dependent on the deposition parameters such as solution chemistry, solution concentration, pH value, solution temperature, *etc.* Some of the physical and chemical method for the deposition of CIS thin films is shown in Fig. 2.

The spray pyrolysis method has been attracted considerable interest because of the advantages like versatile nature, low operating temperatures, large-area deposition, flexibility in the selection of substrate and low cost, *etc.*^[31] However, there is no such review available, which address the deposition, properties and applications of CIS using spray pyrolysis technique. Therefore, in this review, deposition parameters, structural, morphological, electrical properties are thoroughly discussed. The application of spray deposited CIS layer as a light absorber in solar cell is also discussed. Furthermore, the challenges and future scope of CIS are highlighted.

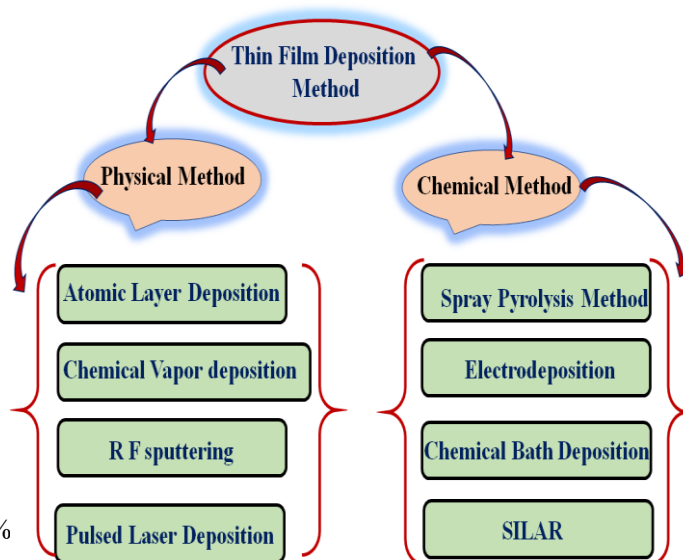


Fig. 2 Deposition of CIS thin film by various Chemical and Physical method.

2. Basics of spray pyrolysis method

A variety of methods have applied for the deposition of the CIS thin-films which includes chemical and physical methods. Among all chemical methods spray pyrolysis technique is most famous because of its applicability to produce a variety of conducting and semiconducting materials.^[17-20, 31-37] Using a spray pyrolysis deposition technique, different kind of thin and thick films, ceramic coatings, and powders can be deposited. Unlike many other film deposition techniques, spray pyrolysis represents a straight forward and relatively cost-effective processing method.

From the last three decades, the chemical spray pyrolysis (SP) method has been one of the major methods to deposit a wide variety of oxides in thin film form. The prime requisite for obtaining good quality thin film is the optimization of

deposition conditions such as substrate temperature, spray rate, the concentration of solution, *etc.* Metal oxide films have been deposited using several deposition methods. Among these, spray pyrolysis is one of the promising methods for the production of metal oxide films. The spray pyrolysis method is based on spraying the gas and solution (aerosol) and to direct the mixture onto the heated surface of the substrate where a chemical reaction leaves a desired solid film. This method has been employed to prepare several types of materials, like transparent conductive contacts,^[38] semiconductors,^[39] luminescent materials,^[40] sulfides,^[41] selenides.^[42]

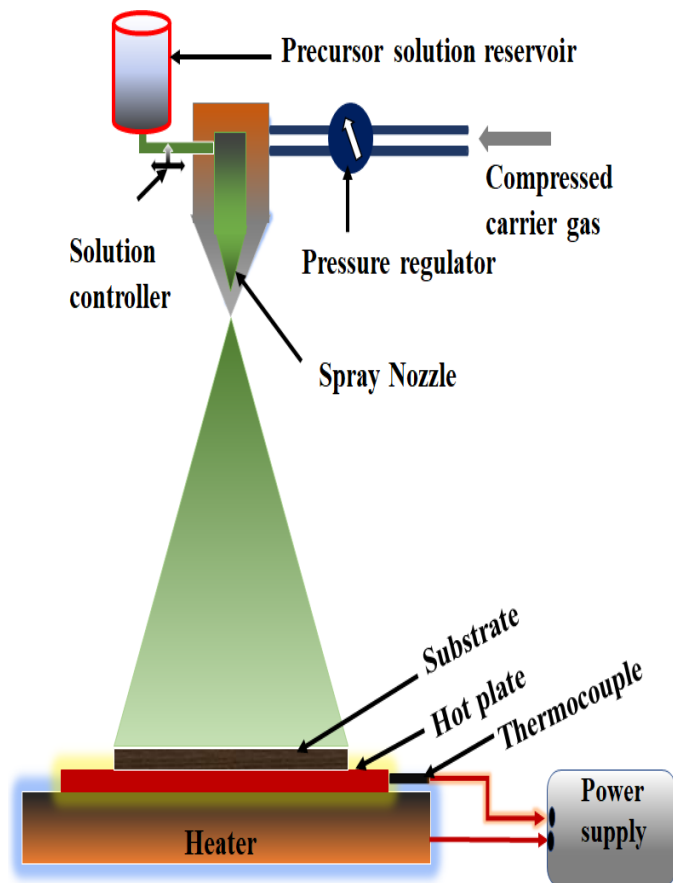


Fig. 3 The schematics of the experimental set up for spray pyrolysis.

2.1 Mechanism of thin films formation by spray pyrolysis method:

The scheme of pyrolysis and the formation of thin films by the spray pyrolysis method was described in detail.^[43] In the spray pyrolysis method, thin film formation is based on a thermally stimulated chemical reaction between clusters of liquid or vapor atoms of different chemical species. In this process, the precursor solution is atomized through a glass nozzle. The nozzle converts the solution into small droplets, known as aerosols. These aerosols are allowed to incident onto preheated substrates. The pyrolysis decomposition of the aerosols and formation of thin films with desired properties depends on the optimum substrate temperature.

The properties of the film depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also the cooling rate after deposition. The film thickness depends upon the distance between the spray nozzle and substrate, substrate temperature, the concentration of the precursor solution and the quantity of the precursor solution sprayed. The film formation depends on the process of droplet landing, reaction and solvent evaporation, which are related to droplet size and momentum. An ideal deposition condition is when the droplet approaches the substrate just as the solvent is completely removed. Lampkin^[44] showed that, depending on droplet velocity and flow direction, a droplet will flatten, skip along the surface or hover motionless. The schematics of the experimental set up of the spray pyrolysis method is shown in Fig. 3.

2.2 Advantages of spray pyrolysis method

The spray pyrolysis method has a number of advantages.^[43]

1. It offers an extremely easy way to dope films with virtually any element in any proportion by merely adding it in some form to the spray solution.
2. Unlike closed vapour deposition methods, spray pyrolysis neither requires high-quality targets and/or substrates nor it requires vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.
3. The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol-gel which produces films of limited thickness.
4. Operating at moderate temperatures (373-773 K), spray pyrolysis can produce films on less robust materials.
5. Unlike high-power methods, such as radio frequency magnetron sputtering (RFMS), it does not cause local overheating that can be detrimental for materials to be deposited. There are virtually no restrictions on the substrate material, dimension or its surface profile.
6. By changing the composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.
7. It is believed that reliable fundamental kinetic data are more likely to be obtained on particularly well-characterized film surfaces, provided the films are quite compact, uniform and that no side effects from the substrate occur.

Spray pyrolysis Process containing the following stages, (1) solvent evaporation, (2) drying, (3) thermolysis, (4) formation of microporous particles, (5) formation of solid particles, and (6) sintering of solid particles.^[45] The deposition of a uniform thin film is one of the advantages of this method. Its simple experimental arrangement and user-friendly approach make this a unique in all the deposition methods. Quality of the film will be easily maintained by controlling the deposition parameters like flow rate, nature of additives,

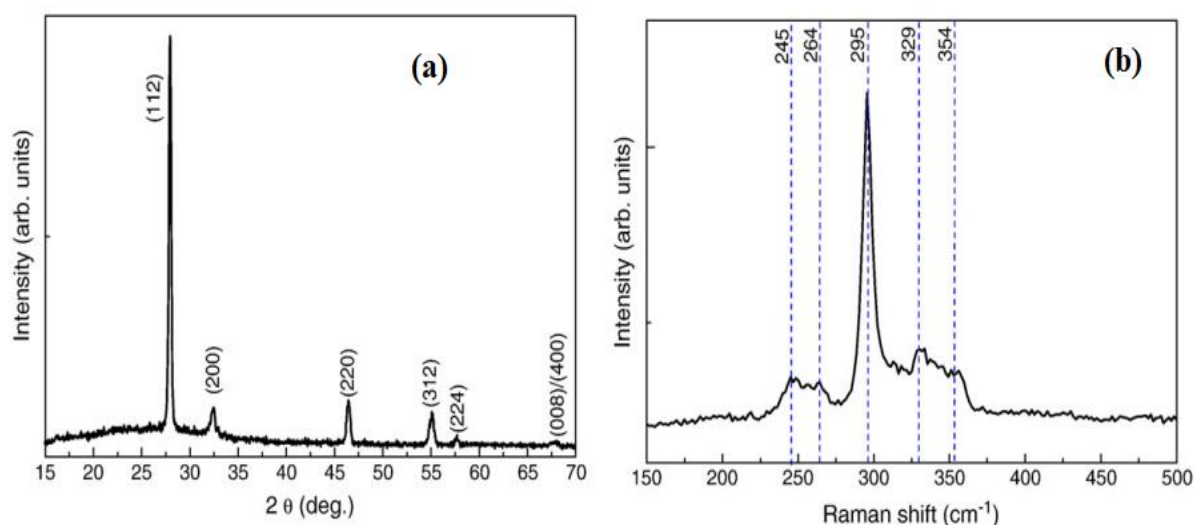


Fig. 4 a) XRD pattern, b) Raman scattering of CIS film deposited by spray pyrolysis method (Reprinted with permission from Ref. [48], Copyright 2010 Elsevier).

the concentration of reactants in the precursor solution and deposition temperature *etc.* porous and high-density and high uniform film can be deposited by using this method. An atomizer, precursor solution, substrate heater, and temperature controller are the main part of the spray pyrolysis system.

3. Properties of CuInS₂ thin films deposited using spray pyrolysis method

3.1 Structural properties of CIS thin-film

Valdes *et al.*^[46] synthesized CuInS₂ thin films on compact and porous ZnO substrate and reported the structural properties. The spray deposited CIS thin film showed orientation along (112) plane with secondary CuS phase. The composition analysis showed Cu rich films with a direct bandgap of 1.42 eV. An acceptor density (N_A) of $5 \times 10^{18} \text{ cm}^{-3}$ and flat band potential of 0.42 V was reported. The nanocrystalline CIS thin films were deposited on the glass substrate and the effect of acetonitrile on the physical properties of thin films was studied.^[47] The acetonitrile converts the aqueous solutions of cations and anions into a colloidal solution with very fine particles. Nanocrystalline CIS films of average crystal size was about 8-15 nm were obtained at substrate temperature in the range 275-325 °C with a colloidal solution.

Lee *et al.*^[48] synthesize the CIS thin film and performed studies on XRD pattern and Raman spectra of CIS thin films deposited at 460 °C (Fig. 4 (a,b)). The XRD study revealed the sulfurized Cu-rich CIS film showed good crystallinity without any impurity. The Raman spectra of CIS films after post-sulfurization showed the most dominant CH ordered scattering (295 cm^{-1}). The Raman spectrum helps to confirm the phase purity of the compound. The CIS has three possible metastable states i.e., Cu–Pt (CP)-ordered phase, Cu–Au (CA)-ordered phase (305 cm^{-1}), and chalcopyrite (CH) phase (295 cm^{-1}).^[48] The CA and CH ordered phases are stable at room temperature.^[48,49] The CA order phase is related to the increased defects in the compound and affects the efficiency

of the photovoltaic cell.^[50, 51] Kotabi *et al.*^[52] deposited CIS thin films and reported that Raman study showed the chalcopyrite structure of CIS film with CH-ordering.

3.2 Effect of substrate temperature

In the spray pyrolysis process, substrate temperature plays a vital role in thin film formation. The variation greatly influenced optoelectronic, compositional and structural properties of the CIS thin films. Mahendran *et al.*^[53] studied the effect of substrate temperature on structural, optical and photoluminescence properties for CIS thin films. The XRD study showed all CIS films deposited at substrate temperature range 300 to 400 °C exhibited a chalcopyrite structure. The bandgap was reported to be reduced from 1.66 to 1.58 eV as temperature increased. The photoluminescence study showed about 6 emission peaks in the wavelength range 450 to 720 nm for the substrate temperature at 300 °C. At higher substrate temperature, these peaks shift towards a shorter wavelength of 440 to 540 nm. Sebastian *et al.*^[54] studied the effect of substrate (300, 350 and 400 °C) temperature on structural and compositional properties of CIS thin films. The compositional study revealed that at higher substrate temperature, the film grown showed sulfur deficiency and copper-rich. The average grain size of the sample prepared at 300 °C substrate temperature was observed to be 8 nm. The heat treatment of CIS film after deposition resulted in the better crystallinity.^[55] Mere *et al.*^[56] employed the spray deposited CIS absorber layer in superstrate configuration ZnO/CdS/CuInS₂. With spray deposited columnar-microstructure CIS layer, the cell fabricated showed open-circuit voltage (V_{oc}) around 443 mV and the short-circuit current density (J_{sc}) around 5.5 mA/cm². Oja *et al.*^[57] reported that the CIS films annealed in the H₂S atmosphere above 500 °C result in good crystalline CIS thin films about 90 nm of crystallite size. Theresa *et al.*^[58] fabricated cells with a CuInS₂ and a double layer of In₂S₃ using the CSP technique with the Ag electrode showed 9.5%

efficiency. Guezmir *et al.*^[59] reported that deposited films have a polycrystalline structure, with a (112) preferential orientation. The deposits have a columnar structure with many cracks and grain boundaries. Krunk *et al.*^[60-64] have investigated a detailed study of CIS thin films using a spray pyrolysis method. The CuCl_2 , InCl_3 and $(\text{NH}_2)_2\text{CS}$ (thiourea) was used starting material in aqueous solution to deposit the CIS thin film at various substrate temperature from 350 to 400 °C. The Cu and In rich thin films were exhibited band gap energy 1.45 and 1.53 eV, respectively.

The Sebastian *et al.*^[65] employed spray deposition method to fabricate the FTO/CIS/ In_2S_3 p-n junction and studied the photoactivity of the junction by changing the thickness of absorber layer. The CIS film deposited at 350 °C showed a better photocurrent. Sharma *et al.*^[66] prepared the single phase of nanocrystalline CIS thin films in the temperature range of 275–325 °C. The calculated average grain size was found to be 8 to 15 nm. The SEM surface morphological study showed the particle size in between 10–25 nm to all substrate temperature. The optical gap estimated was 1.48 eV to 1.54 eV for all CuInS_2 films. Hussain *et al.*^[67] reported the deposition of CuInS_2 by spray pyrolysis, the structural characterization presented the films having tetragonal structure and good crystallinity. The optical band gap energy value was observed at 1.48 eV. Khan *et al.*^[68] prepared the CIS thin films by spray method and characterized by XRD, SEM and TEM. The XRD study shows the films were polycrystalline with crystallite size 10-13 nm. The SEM and TEM micrographs show that the particle size of the films is in the range of 12-15 nm. Suhail *et*

al.^[69] synthesized the CIS thin film at various substrate temperature and studied the structural, chemical composition and optical properties. The study demonstrated that properties like uniformity, growth rate and adhesion of the CIS films strongly depend on the substrate temperature and spray rate. Sankir *et al.*^[70] prepared the CIS thin films and reported the impact of an ultrasonic nozzle on various deposition parameters. The electrical mobility was observed 48 cm^2/Vs for 51 ml/cm^2 mass loading film at 48 kHz nozzle frequency. Oja *et al.*^[57] studied the effect of H_2S treatment on the CIS thin films. The films treated at 500 °C temperature showed good crystallinity. The XRD pattern showed an addition CuIn_5S_8 a spinal phase, which was vanished after heat treatment with the formation of better-quality CIS film. Hou *et al.*^[71] have deposited uniform CIS films with well-controlled stoichiometry by novel electrostatic spray assisted vapor deposition (ESAVD) method at different deposition temperatures 300 to 400 °C. The as-prepared CIS films was polycrystalline in nature and the average grain size was found to be 24 nm with 1.43 eV of the energy band gap. Guezmir *et al.*^[72] have studied the optical properties of CIS thin film and confirmed the high absorbing characteristics, which is favorable in the photovoltaic application. The effect pH of deposition solution on the growth of CIS thin films have been investigated.^[73] The deposited thin film revealed a good single-phase stoichiometric in acidic medium (pH-3.5). The measured optical band gap values were 1.34 and 1.27 for pH-3.5, 4.5 respectively.

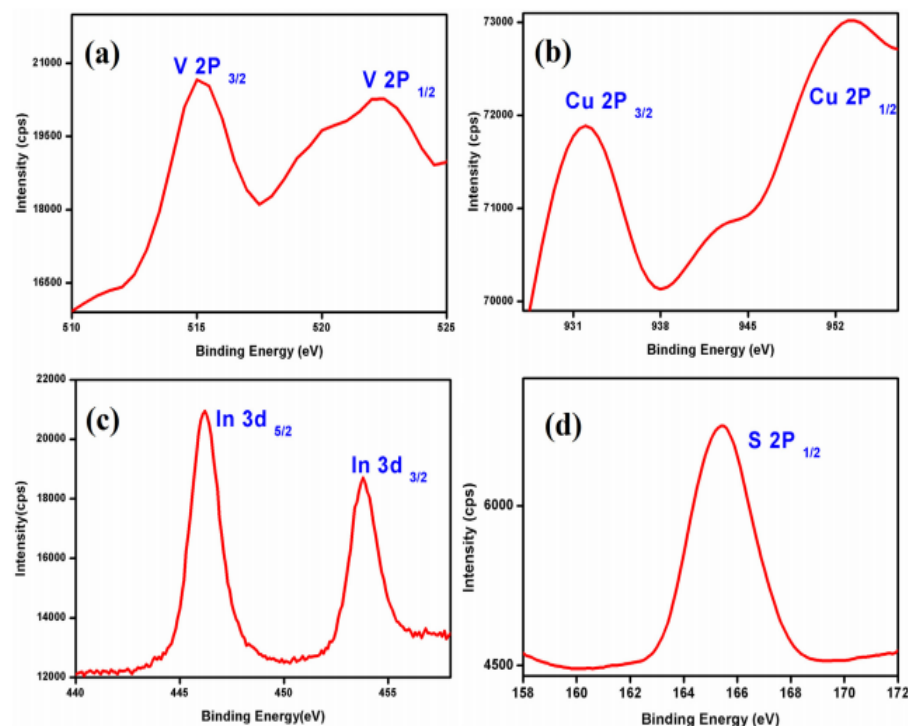


Fig. 5 The X-ray photoelectron spectroscopy (XPS) of spray deposited CIS thin films (Reprinted with the permission from Ref. [75], Copyright 2016 Elsevier).

Jayaraj *et al.*^[74] reported the deposition of polycrystalline CIS thin films using a nebulized spray pyrolysis method at a 350 °C substrate temperature. The film annealed at 200 °C showed Cu rich composition and a band gap of 1.41 eV. From the electrochemical impedance spectroscopy study, the charge transfer resistance under illumination was found to be 81.97 Ω . From the Mott-Schottky plot, the flat band potential and the acceptor density was found to 0.53 V and $9.25 \times 10^{21} \text{ cm}^{-3}$ respectively.

3.3 XPS study of spray deposited CIS thin films

The X-ray photoelectron spectroscopy (XPS) study is an important tool to verify the valence state of the elements in the compound. In the CIS compound, the core level of Cu2p has peaks of Cu2p_{1/2} and Cu2p_{3/2} corresponding to the binding energies 951.3 eV and 931.4eV and the peak separation is 19.9 eV.^[75,76] The Cu in CIS exist in the Cu⁺ state which is largely different from Cu²⁺ (942 eV).^[76] The In3d_{3/2} and In3d_{5/2} peaks are located 452.3 eV and 444.7 eV with a peak splitting of 7.6 eV, which corresponds to In³⁺ state. Two peaks of Sulfur S2p_{1/2} and S2p_{3/2} are located at 162.8 eV and 161.7 eV corresponds to S²⁻ state. Fig. 5 depicts the XPS spectra of CIS thin films doped with Vanadium.^[75]

3.4 Effect of doping on the properties of CIS thin films

The highest efficiency of CIS based absorber layer reported is nearly 13%,^[14] however, the theoretical efficiency (32%)^[13] is much larger than the highest efficiency reported so far. One of the reasons for the large difference from the theoretical value is the presence of atomic level defects in the compound. The defect level problems can be solved by depositing highly crystalline films by controlling the deposition strategies and adding the appropriate impurity (doping). In order to enhance

the structural, electrical and optical properties several impurity ions doped with CIS has been reported using different deposition technique. The following are the few reports that demonstrate the importance of spray deposition method for deposition of doped CIS thin films. Tapia *et al.*^[77] reported the Na-doped CuInS₂ thin films were prepared by spray pyrolysis. The films were In-rich and crystallized in the sphalerite structure of CuInS₂, showing traces of In₆S₇, In₂S₃ and CuIn₅S₈ as secondary phases. All the films showed p-type conductivity with a magnitude in the 10^{-2} - $10^{-5} \Omega/\text{cm}$. The structural and optical properties of Al-doped CIS thin films were studied on In₂S₃/glass, ZnO/glass, SnO₂/glass substrate at 340 °C substrate temperature.^[78] The Al-doping concentration increased the crystalline nature of the film. The optical band gap was observed to be increased with an increase in Al concentration.

Mahendran *et al.*^[79,80] have reported on the effect of zinc doping on the structural, optical and electrical properties of spray deposited CIS thin films. The Zn incorporation in CIS film improves the crystallinity and facilitates the growth of CIS along (112) orientation. The optical band gap was observed to be increased from 1.66 to 1.78 eV as substrate temperature increased from 300 to 400 °C. The photoluminescence (PL) spectra of undoped CIS film showed more no emission peaks than the doped CIS film. The broad emission peak centered around 500 nm in the PL is indicative of donor-acceptor pair transition between sulfur vacancy and indium vacancy or Cu or Zn vacancy. The effect of Bi-doping as a function concentration of a salt solution in the precursor was studied.^[81,82] The Bi doped CIS films were amorphous in nature. The band gap of Bi doped CIS thin film was reported to be 1.62 to 1.82 eV.

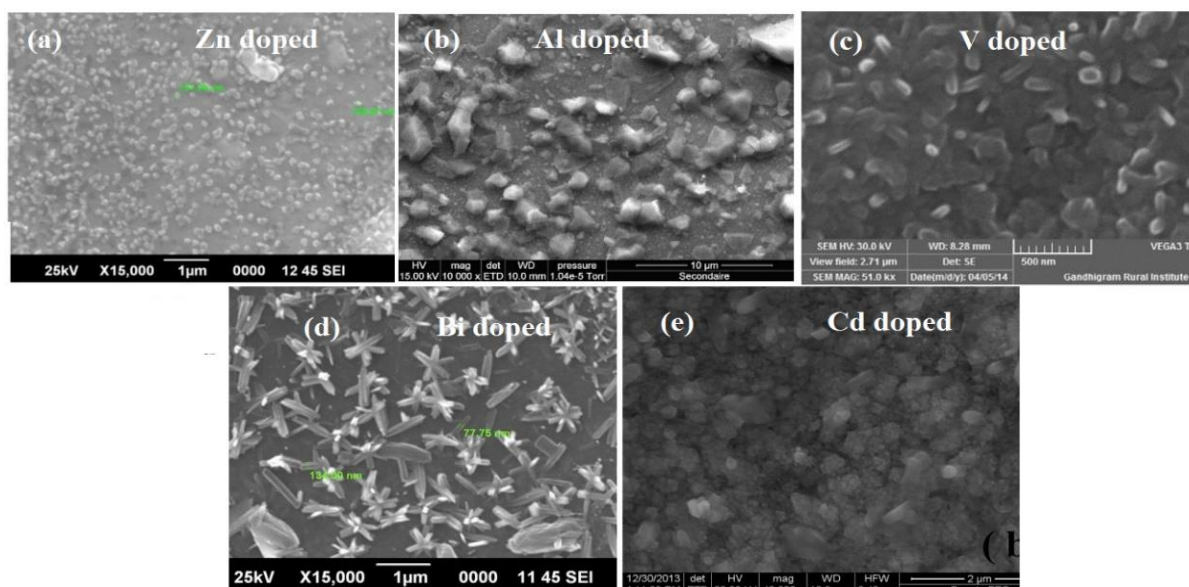


Fig. 6. The SEM images a) Zn-CIS (Reprinted with the permission from Ref. [79], Copyright 2012 Elsevier), b) Al-CIS (Reprinted with the permission from Ref. [78], Copyright 2010 Elsevier) c) V-CIS (Reprinted with the permission from Ref. [75], Copyright 2016 Elsevier), d) Bi-CIS (Reprinted with the permission from Ref. [81], Copyright 2012 Elsevier), e) Cd-CIS (Reprinted with the permission from Ref. [82], Copyright 2015 Elsevier), doped-CIS thin films deposited using spray pyrolysis.

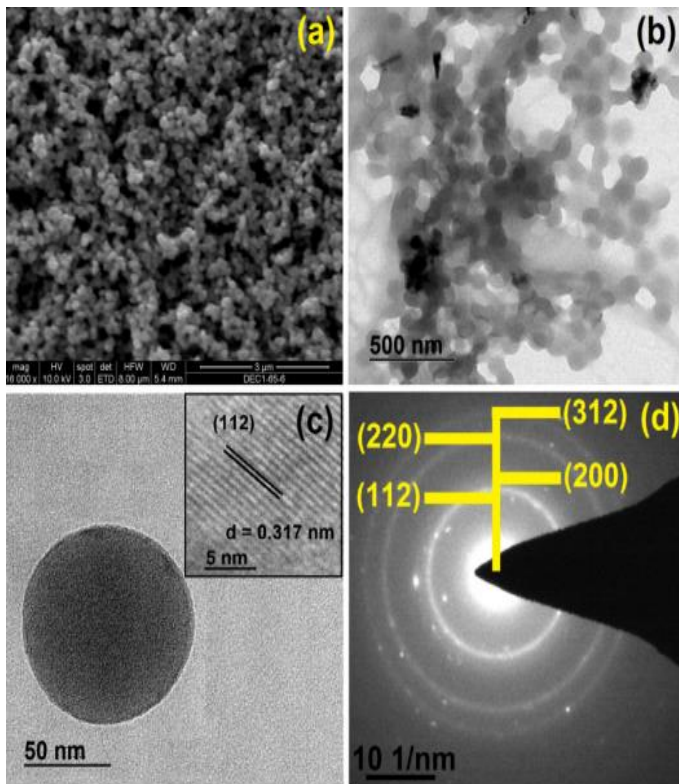


Fig. 7 a) SEM image, b) and c) TEM image (inset- c) HRTEM and d) SAED pattern of CIS thin film deposited using electro spray chemical aerosol deposition technique (ESCAD) deposition technique (Reprinted with the permission from Ref. [82], Copyright 2015 Elsevier).

The effect of doping of pristine and vanadium (V) on the physical properties of CIS thin films have been reported.^[75] The XRD study revealed the body-centered tetragonal crystal structure of V-CIS thin films without any impurity phases.

However, a decrease in crystallite size was observed with an increase of V content. The surface morphology was changed from elongated nanoparticle like one-dimensional structure to the randomly aligned CIS nano-rods. The composition of In in CIS film was observed to be decreased with an increase of V doping. Doping with V also changed the conductivity from p-type to n-type in V-CIS. A similar kind of transformation in the conductivity was observed in Cd doped CIS thin films.^[83] The SEM images of CIS thin films doped with different dopant is shown in Fig. 6.

Logu *et al.*^[84] employed an electro spray chemical aerosol deposition technique (ESCAD) to deposit CIS thin films on the FTO substrate. The film deposited at 350 °C was good crystalline. The average crystallite size estimated is about 18 nm. Two Raman peak centered at 294 and 305 cm⁻¹ were observed, which are characteristics peak of A1-CH mode of CIS. The spherical shaped CIS nanoparticles with 1.47 eV band gap was formed. The SEM and HRTEM images of CIS thin films deposited using spray pyrolysis method is depicted in Fig. 7. Dube *et al.*^[85] studied the dispersive optical properties of spray deposited CIS thin films. The CIS thin films were deposited at 150 °C substrate temperature and annealed for 2 hr at 250, 300 and 350 °C temperature. The film annealed at 250 °C showed chalcopyrite structure whereas the transformation was observed from chalcopyrite to wurtzite structure at 350 °C annealing temperature. Fig. 8 shows the spectral dependence of imaginary (ϵ_i) and the real dielectric constant (ϵ_r). The slight variation in the optical properties at 350 °C is attributed to the transformation of structure from chalcopyrite to wurtzite structure. The preparative parameters of CIS thin-film deposited using the spray pyrolysis deposition technique are summarized in Table. 1.

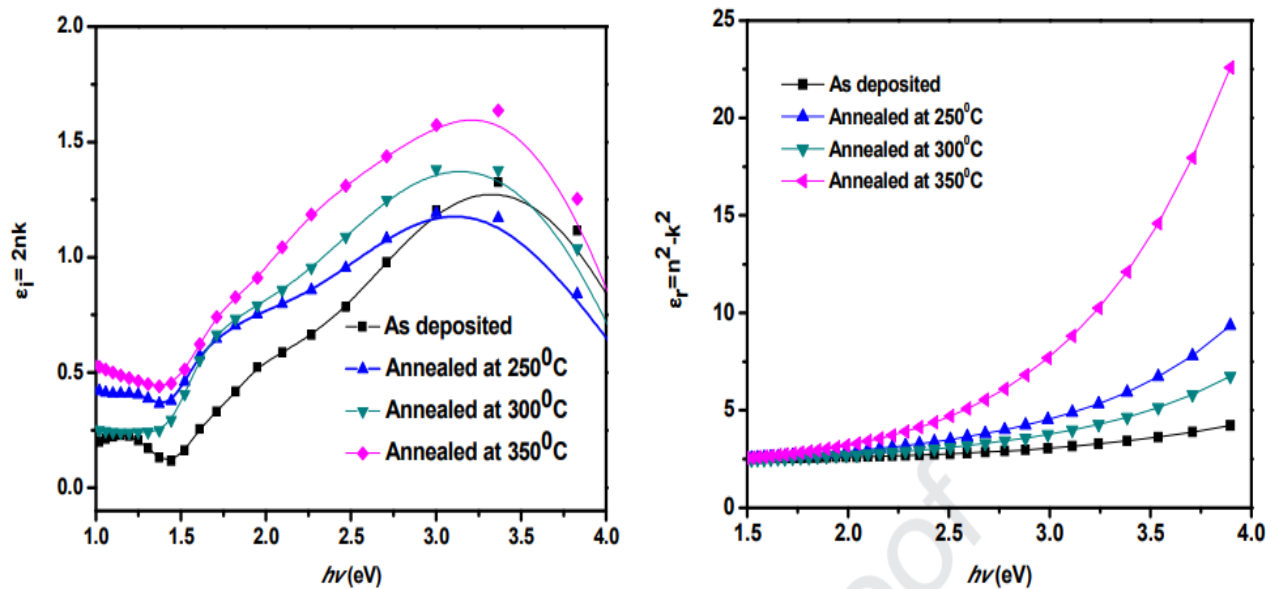


Fig. 8. a) Plot of the imaginary (ϵ_i) and b) real dielectric (ϵ_r) constant of the as deposited and annealed CuInS₂ (Reprinted with the permission from Ref. [85], Copyright 2019 Elsevier).

Table 1 The deposition parameters of CIS thin-film deposited using the spray pyrolysis deposition technique.

Sr. No.	Precursors	Deposition parameters					Remark	Ref.
		Substrate temp.	Substrate used	Solution quantity	Spray rate	Nozzle to substrate distance		
1	CuCl ₂ + InCl ₃ + SC(NH ₂) ₂	200 °C	TiO ₂ , ZnO	-	-	-	CIS films were grown on different flat electrodes (ITO, TiO ₂ , ZnO). The Cu rich solutions lead to the (112) direction orientated films with larger crystallites. The I–V characteristics of ITO/CIS, ZnO/CIS showed linear behavior, whereas the I–V characteristic of TiO ₂ /CIS showed a diode like behavior in the dark.	[46]
2	CuCl ₂ + InCl ₃ + SC(NH ₂) ₂	200 – 400 °C	Glass	-	-	-	The CIS nanoparticles of size 8-15 nm were synthesized. The acetonitrile was used as a solvent. The AFM micrographs showed that the particle size of the films is around 10–25 nm. Resistivity was found to be increased from 2.5×10 ⁴ Ωcm to 9×10 ⁴ Ωcm as the substrate temperature increased from 275 °C to 325 °C.	[52]
3	CuCl ₂ + InCl ₃ , SC(NH ₂) ₂ Nitrogen - carrier gas	460 °C	Glass	-	1 ml/min	30 cm	The post sulfurization of Cu-In films resulted in good quality CIS thin films as evident from XRD study. The Raman study reveals Cu _{2-x} S phase in sulfurization films and weak intensity for peak 478 cm ⁻¹ due to the inhomogeneous coverage of the CuS over the surface.	[53]
4	0.1M CuCl ₂ + 0.1 M InCl ₃ , + 0.1M SC(NH ₂) ₂ (Cu/In=1.25 and S/Cu = 1)	300- 400 °C,	Glass	40 ml	1 ml/min,	20 cm	The crystallite size was observed to be reduced in the substrate temperature range increased from 375 – 400 °C. Reductions in bandgap energies from 1.66 to 1.58 eV in the was observed as temperature increased from 300 – 400 °C. Photoluminescence study showed 6 emission peaks in the wavelength range 450 – 720 nm. For the higher temperature, these peaks shift towards a shorter wavelength of 440– 540 nm.	[54]

5	CuCl ₂ , + InCl ₃ + SC(NH ₂) ₂ . (Carrier Gas: N ₂ Cu/In=1 and S/Cu= 5 0.5 mol/L KCN)	300 °C	Glass	-	-	-	The XRD pattern showed (112) peak along with (204/220) and (116/312). A secondary phase CuS was observed. After KCN treatment, CuS phase disappeared. Cu rich film was confirmed by the EDAX analysis. A direct bandgap of 1.42 eV was reported from the optical absorption study. An acceptor density of 5×10 ¹⁸ cm ⁻³ and a flat band potential of 0.42 V reported. [60-64]
6	0.1 M of CuCl ₂ + InCl ₃ SC(NH ₂) ₂ Vanadium (III) chloride (aqueous solution)	350 °C	Glass	45 ml	3.5 ml/min	24 cm	The effect of doping of pristine and vanadium (V) on the physical properties of CIS thin films have been reported. The decrease in crystallite size was observed with an increase of V content. The surface morphology was changed from elongated nanoparticle like one-dimensional structure to the randomly aligned CIS nano-rods. The composition of In in CIS film was observed to be decreased with an increase of V doping. Doping with V also changed the conductivity from p-type to n-type in V-CIS. [75]
7	CuCl ₂ .2H ₂ O + InCl ₃ +(CS(NH ₂) ₂ , (aqueous solution)	350 °C	Glass	56 ml	0.5 ml/min	5 cm	Polycrystalline CIS films were deposited on the glass substrate at 350 °C substrate temperature. The films annealed at 200 °C showed Cu rich composition. From the Mott-Schottky plot, the flat band potential and the acceptor density was found to 0.53 V and 9.25 x 10 ²¹ cm ⁻³ respectively. [70]
8	CuCl ₂ + InCl ₃ + SC(NH ₂) ₂	340 °C	Glass, In ₂ S ₃ /glass, ZnO/glass, SnO ₂ /glass	25 ml	5 ml/ min	25 cm	Structural and optical properties of Al-doped CIS thin films were studied on In ₂ S ₃ /glass, ZnO/glass, SnO ₂ /glass substrate at 340 °C substrate temperature. The Al doping concentration increased the crystalline nature of the film. The optical band gap was observed to be increased with an increase in Al concentration. [78]

9	0.1 M CuCl ₂ + InCl ₃ + SC(NH ₂) ₂ + ZnCl ₂	300-400 °C	Glass	-	2 ml/min	-	The effect of substrate temperature on Zn-CIS was studied. The Zn incorporation in CIS film improves the crystallinity and facilitates the growth of CIS along (112) orientation. The optical band gap was observed to be increased from 1.66 to 1.78 eV as substrate temperature increased from 300 to 400 °C. The broad emission peak centered around 500 nm in the PL is indicative of donor-acceptor pair transition between sulfur vacancy and indium vacancy or Cu or Zn vacancy.	[79]
10	0.1 M of CuCl ₂ + InCl ₃ + (CS (NH ₂) ₂ , (aqueous solution)	350 °C	FTO	10 ml	1.5 ml/min	-	The film deposited at 350 °C was good crystalline. The average crystallite size estimated is about 18 nm. Two Raman peak centered at 294 and 305 cm ⁻¹ were observed, which are characteristics peak of A1 CH mode of CIS. The spherical shaped CIS nanoparticles with 1.47 eV direct band gap was reported.	[84]
11	0.05 M CuCl ₂ + 0.05 M InCl ₃ + 0.2 M (SC(NH ₂) ₂) (aqueous solution)	150 °C	Glass	30 ml	1.5 ml/min	40 cm	Transformation of CIS from chalcopyrite to wurtzite structure were observed after annealing from 250 -350 °C substrate temperature. The optical properties was found to be structure dependent.	[85]
12	0.005 M CuCl ₂ + InCl ₃ + SC(NH ₂) ₂	297-397 °C	Glass	-	5 ml/min	-	The CIS films were deposited by varying Cu/In ratio in the solution. The XRD showed the chalcopyrite structure of CIS, however, for large Cu/In ratio, the additional impurity phases were observed. The Hall mobility around 12 cm ² /Vs was observed for Cu/In =1. The sulfur-rich precursor solution showed single phase CIS thin films.	[13, 86]
13	0.05 M Cu(CO ₂ CH ₃) ₂ + InCl ₃ + SC(NH ₂) ₂	200-500 °C	Glass	-	-	-	The XRD pf CIS thin films deposited using 30 % of excess sulfur showed good crystalline nature with major (112) orientation diffraction pattern. The band gap estimated was 1.5 eV.	[87]

From the above discussion, it is seen that the spray pyrolysis process is a sensitive and important method to prepare the CIS thin films. Not only the physical, electronic properties of the film differ with deposition temperature, but also the deposition efficiency contrast. The average grain size in many reported work was small which is a weakness for solar cell applications. Despite these difficulties, spray pyrolysis is an excellent method for the deposition of large-area thin films. The deposition parameters of the CIS thin film deposited using the spray pyrolysis technique are summarized in Table 1.

4. Application of spray deposited CIS thin films as a light absorber layer in the solar cell

The main function of absorber layer is to absorb light and to convert photon energy in to energy of electron-hole pairs. The energy gap of the absorber material should match the spectral region where the cell is expected to operate. For CuInS_2 the direct energy gap is sufficiently wide (1.5 eV) to absorbs most of photons in visible region so that large absorption coefficients can be achieved. Because of a high absorption coefficient, a 2- μm -thick layer is sufficient for absorption of maximum incident radiation. The quality of CuInS_2 absorber layer is mostly depends depend on the deposition technique used for its fabrication. The schematic of the of CIS-based solar cell is depicted in Fig. 9.

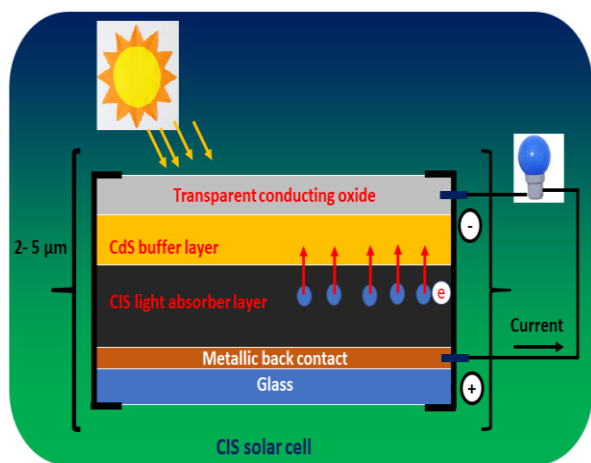


Fig. 9 Schematic of CIS solar cell.

4.1 Performance of CIS absorber layer in solar cell

Kazmerski *et al.*^[88] have fabricated first CuInS_2 homojunction solar cell with an efficiency around 3.62% using dual-source deposition technique. The maximum efficiency reported so far with dc-magnetron sputtered CIS absorber layer is around 12.5%.^[14] The highest efficient CIS solar cell are fabricated using sophisticated and high vacuum methods. However, it is fairly advantageous to employ fairly reliable, nano vacuum and low-cost method instead of highly expensive vacuum method for the deposition of absorber layer of the solar cell. Among all the non-vacuum method spray pyrolysis method is one of an attractive method for the deposition of CIS thin film. In the following discussion we have described on performance solar cell based on CIS light

absorber layer prepared using spray pyrolysis technique.

Ikeda *et al.*^[89] investigated the effect of annealing temperature of sprayed CuInS_2 films on solar cell performance. The CuInS_2 thin films annealed with 600 °C used in Al: $\text{ZnO}/\text{CdS}/\text{CIS}/\text{Mo}/\text{glass}$ cell showed 5.1% of photoconversion efficiency. However, the Ga doped Ga-CIS absorber layer in Al: $\text{ZnO}/\text{CdS}/\text{Ga: CIS}/\text{Mo}/\text{glass}$ showed greater efficiency of about 5.8%. Hou *et al.*^[90] fabricated CdS/CIS heterojunction on ITO coated glass and reported 0.65% efficiency at 1.5 A.M. Khan *et al.*^[91] reported 7.2 % photo conversion efficiency from CdS/CIS heterojunction onto ITO coated glass. 3D CIS/ TiO_2 solar cell was prepared by Hayre *et al.*^[92] and the effect of cell thickness, buffer layer thickness, and the morphology of the TiO_2 nanoparticulate matrix were studied. Efficiency of about 3.0% was reported for 500 nm thick TiO_2 , above and below this thickness the cell performance was not good. Use of CdS as buffer layer in solar cell has demonstrated excellent potential for cost-effective production of solar electricity. However, element Cd, which is a stable compound in thin-film modules therefore issues raised includes the hazards associated with this materials in fabrication of CIS based solar cells. So, the quest for an alternative buffer layer is being pursued. Serious efforts are made to replace CdS as a buffer layer by other wide band gap materials such as ZnS, ZnSe, ZnO, InxSey , Inx(OH,S)y , In_2S_3 etc. with considerable conversion efficiencies.

Effect of In_2S_3 on the performance of $\text{CuInS}_2/\text{In}_2\text{S}_3/\text{TiO}_2$ was investigated by Goossens *et al.*^[93] and reported 7% of efficiency of the solar cell. In such type of device Cu diffusion from absorber CuInS_2 in In_2S_3 becomes the serious problem. Cherian, *et al.* reported^[94] double layer of CuInS_2 by spray deposition with In_2S_3 as a buffer layer could be more advantageous for stability of the device. Photo conversion efficiency of 5.87% was reported from CIS/ In_2S_3 cell and investigated that the efficiency could be improved by precise control of the thickness of the absorber CuInS_2 and buffer layer In_2S_3 and their atomic concentrations. A record 9.5 % efficiency was reported by John *et al.*^[95] with oxygen free In_2S_3 as a buffer layer and investigated that the diffusion of Cu from absorber to In_2S_3 layer creates Cu-deficiency at the surface of the CuInS_2 layer and makes the interface more photosensitive responsible for resulting high efficiency. Nanu *et al.*^[96] fabricated 3D solar cell based on $\text{TiO}_2/\text{In}_2\text{S}_3/\text{CuInS}_2$ nanocomposite resulted in 5% efficiency.

5. Conclusion and future scope

The present review outlines the preparative parameters and the physical properties of the CIS absorber layer deposited via the spray pyrolysis method. The CIS absorbing layer can be obtained by using simple non-vacuum and economically cheap spray pyrolysis method. However, proper optimization of preparative parameters and understanding of suitable solution chemistry is needed.

Spray pyrolysis technique is widely used for the deposition of large-area CIS thin films. The CIS films grown on different

flat electrodes (ITO, TiO₂, ZnO) showed dense structure, good adhesion, and flat surface. The thin film crystallinity can be enhanced by annealing the film at optimized annealing temperature. Further, the structural, morphological and electrical parameters can be improved by treating the films in inert gas or H₂S atmosphere during annealing procedure. Post sulfurization of CIS thin film resulted in good quality CIS thin films. As an absorber material in solar cell application, the required grain size of CIS film must have a value of around 1-2 μm. However, it is found easy to obtain the required grain size of CIS material using spray pyrolysis. The CIS absorber layer is an attractive material for solar energy conversion. Despite the major industrial ventures to produce CIS-based cells on a megawatt-scale, progress has been slow because of reliability problems with the manufacturing. A simple and cheaper spray pyrolysis manufacturing process onto cheaper and flexible substrate could revive the commercial fortunes of these cells.

Supporting information

Not applicable

Conflict of interest

There are no conflicts to declare.

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