Chemical Spray pyrolysis of Copper Indium Disulphide Thin Films for Solar Cell Application: Review

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Abstract: Chalcopyrite I-III-IV2 type Copper Indium Disulphide ($CuInS_2$) is an effective light absorbing material in thin film solar cells. Since last decade $CuInS_2$ has been emerged as credible alternative to other solar cell materials. Great efforts have been put in to the development of cheaper, relatively high efficient $CuInS_2$ thin films using different cost effective thin film deposition techniques. The chemical spray pyrolysis technique (SPT) has been, one of the low cost technique to deposit high quality $CuInS_2$ based absorber thin films for solar cell applications. This paper presents an extensive review on application of spray deposited $CuInS_2$ thin films in different $CuInS_2$ based solar cells modules.

Keywords: $CuInS_2$ thin films, Spray pyrolysis, chalcopyrite semiconductors, photovoltaics, thin films, Solar Cell, Solar cell parameters

1. Introduction:

The spray pyrolysis technique has been applied to deposit wide variety of thin films. The materials like simple oxides, mixed oxides, metallic spinal type oxides, group I-VI, II-VI, III-VI, IV-VI, V-VI, VIII-VI binary chalcogenides, group I-III-VI, II-II-VI, II-III-VI, II-VI-VI , ternary chalcogenides such as $CuInS_2$, $CuInSe_2$, $CuInTe_2$, adamantine copper compounds such as Cu_2ZnSnS_4/Se_4, Cu_2CdSnS_4/Se_4, $CuGaSnS_4/Se_4$, Cu_2InSnS_4/Se_4, $CuIn_5S_4/Se_4$ have been deposited , successfully applied in solar cells, sensors, fuel cells applications. A number of thin film deposition techniques have been examined for production of high quality thin films. These include co- evaporated of elemental metal, reactive, nonreactive sputtering, chemical vapour deposition etc., a number of solution growth methods, so-called chemical techniques.

Review articles pertaining to spray pyrolysis processing of variety of material have been reported in the literatures [1]. An extensive survey on physico-chemical properties , preparation conditions of deposition of thin films of transition metal oxides, metallic spinel type oxides, binary, ternary, quaternary chalcogenides , superconducting thin films are discussed by Patil [2]. However, a comprehensive review of all possible semiconductor chalcopyrite Copper Indium Disulphide ($CuInS_2$) thin film materials that could be deposited by spray pyrolysis technique for solar cell applications has not been undertaken so far. Currently $CuInS_2$ (CIS) based technology have been largely dominated by solar cell industry. $CuInS_2$ is a promising material for solar cell application because of its high optical absorption coefficient in the range of 10^5 cm^{-1}. It has a crystal bulk b, gap around 1.55 eV , for polycrystalline thin films; direct optical b, gap varies between 1.3 , 1.5 eV. This covers the maximum of Sol. Energy spectrum. $CuInS_2$ is an exceptional stable material for the solar cell applications. $CuInS_2$ can be obtained in both n-type, p-type since its conduction type depends on the intrinsic defects, such as cation vacancies , anti-site defects etc. Theoretically solar conversion efficiency of 27-32 % has been calculated with $CuInS_2$ as an absorber [3]. Laboratory solar cell efficiency of polycrystalline CIS as an absorber has been reported to be about 13% [4]. The preparation of $CuInS_2$ as an absorber layer in the solar cell is strongly dependent on the preparation conditions, the experimental conditions during the test. While reporting on CIS based solar cells, synthesis, preparative parameters, experimental conditions of copper $CuInS_2$ based absorber thin films, of are needed. In the present review we outlined properties of spray deposited CuInS2 based solar cell. The solar cell parameters of sprayed $CuInS_2$ absorber material in different $CuInS_2$ based solar cell module are discussed and summarized in table 2.

1.1 Structure of $CuInS_2$:

Compound $CuInS_2$ semiconductors often simply referred as chalcopyrites because of their tetragonal crystal structure. $CuInS_2$ is a chalcogenide material belonging to I-III-VI_2 ternary semiconductor with molecular formula ABX_2. Crystal structure of $CuInS_2$ can be changed between two polymorph forms: chalcopyrite, sphalerite. These materials are easily prepared in a wide range of compositions, their corresponding phase diagrams have been intensively investigated. The crystal structure parameters, the physical properties are summarized in the table 1.

Table1: Physical properties of the bulk $CuInS_2$ material.

Sr.No.	Physical Properties	Specification/ Value	Ref.
1	Crystal Structure	Tetragonal (Chalcopyrite)	[5]
		a=b= 0.5517,	[6]
		c= 1.11, c/a = 2.01	
Transport Properties (n-$CuInS_2$), T=300 K			
2	Resistivity	1Ωcm	[7]
3	Carrier concentration	3×10^{16} cm^{-3}	
4	Motilities	15 $cm^2V^{-1}S^{-1}$	
Transport Properties (p-$CuInS_2$), at Room Temperature.			
5	Carrier concentration (p)	6×10^{17} to 2×10^{18}	
6	Mobility (μ_b)	4-12 $cm^2V^{-1}s^{-1}$	[8]
7	Conductivity (σ)	11/ Ωcm	
8	Seeback Coefficient(s)	$2.7\times10^{-1}VK^{-1}$	
9	Refractive Index	2.83(ħw = 0.5ev)	[9]
10	Melting Point	1140 K	[10]
Electronic Properties			
11	Energy B, Gap	153 eV (T=300K)	
12	Splitting Energies,	> - 0.005 eV, - 0.02 eV	
	$\Delta_{cf}(\Gamma)$, $\Delta_{Sg}(\Gamma)$,		[11]
13	D like Character	45%	
14	Excitoinic Energy Gap	(A) 1.536 eV (T=2K);	[10]
		(B) 1.554 eV	
15	Effective Mass(m_p)	$1.3m_0$	[9]
Impurities , Defects			
16	Acceptor, donor binding energy	0.15 eV,0.35 eV	[7]
17		$\tau = 0.1\text{-}2.4\times10^{-3}$s	
		$\tau_n = 1.2\times10^{-10}$ s;	
	Decay times , diffusion lengths	$L_n = 2.5\times10^{-5}$ cm	[12,13]
		$\tau_p = 6.5\times10^{-7}$ s;	

$$L_p = 2.5 \times 10^{-4} \text{ cm}$$

2. Thin films synthesis by Chemical Spray Pyrolysis technique:

Spray pyrolysis is a process in which thin films are deposited by spraying a solution on a heated surface. The schematic of spray pyrolysis processing is shown in figure 1. Droplets impact on the substrate surface, spread into a disk shaped structure, undergo thermal decomposition, where the constituents react to form a chemical compound. Chemical spray deposition processes can be classified according to the type of reaction taking place during the formation of compound. In process A, the droplet resides on the surface as the solvent evaporates, leaving behind a solid that may further react in the dry state. In process B, the solvent evaporates before the droplet reaches the surface , the dry solid impinges on the surface, where decomposition occurs. In process C, the solvent vaporizes as the droplet approaches the substrate; the solid then melts , vaporizes, , the vapor diffuses to the substrate, there to undergo a heterogeneous reaction. In process D, the entire reaction takes place in the vapor state. In all processes, the significant variables are the ambient temperature, carrier gas flow rate, nozzle-to-substrate distance, droplet radius, solution concentration, solution flow rate,- for continuous processes substrate motion.

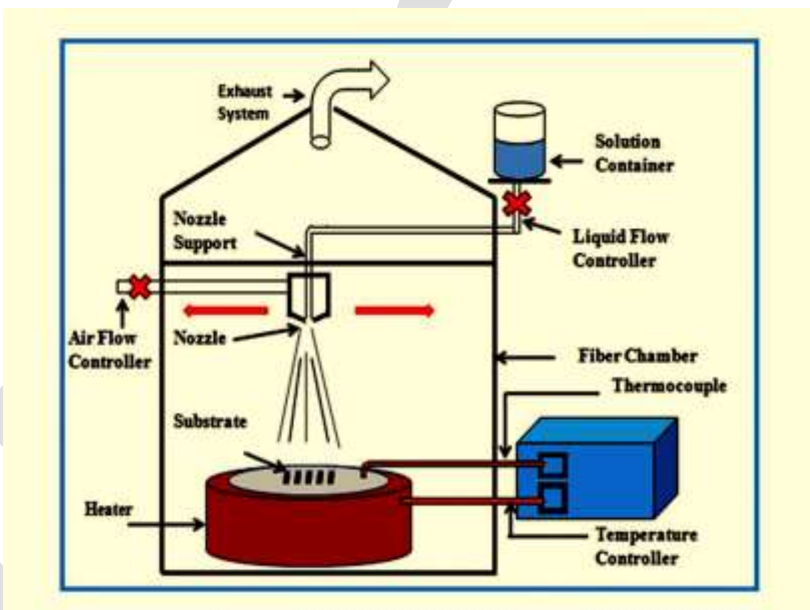

Figure1: The schematic experimental setup of the spray pyrolysis method.

3 $CuInS_2$ Based solar cells:

Solar cell is a junction device obtained by placing different electronically dissimilar materials together with a thin electronic barrier in between to ensure high conversion efficiency of solar photons, high collection efficiency of excited charge carriers. The efficiency of the cell can be expressed in terms of the short circuit current (I_{SC}), the open circuit voltage (V_{OC}) of the device, once the fill factor is defined:

$$FF = \frac{V_m \cdot I_m}{V_{oc} I_{sc}} \quad (1)$$

Here, V_M , I_M represent the voltage , the current intensity for the conditions of maximum output power of the device. Therefore, the cell efficiency (Ƞ) defined as the ratio of the generated power with respect to the power of the incident radiation (P_{in}), may be written as:

$$\eta = \frac{FF\ V_{oc}\ .\ I_{sc}}{P_{in}} \qquad (2)$$

The quantum efficiency of solar cell device is an important parameter. It is related to number of electrons collected per incident photon. The quantum efficiency can be the device quantum efficiency which includes reflection, absorption losses, or the internal quantum efficiency (per photon absorbed).

3.1 Structure of $CuInS_2$ based solar cell:

The basic structure of heterojunction CIS based thin film solar cell consists of substrate, back contact, absorber, buffer layer, window layer, top contact grid, antireflection coating is shown in figure 2.

Figure 2: Schematic representation of CIS based chalcopyrite solar cell (not to the scale).

3.1.1 Absorber Layer:

The main function of absorber layer is to absorb light , 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. Energy b, gap of chalcopyrite materials usually correlated with the lattice constant for isovalent isostructural materials using the formula ((2/3) a + (1/6) c) ^{O}A, 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.

3.1.2 Buffer Layer:

The role of the buffer layer is to produce an optimal transparent front junction to the absorber. Buffer layer should have large energy b, gap for high optical transmission in the visible region. In CIS module with wide b, gap materials (CdS, In_2S_3) separation of electron , hole pairs across the junction can be achieved when the energy b, discontinuity between the wide b, gap buffer layer , the absorber material is distributed in such a way, that there is no b, offset for the majority carriers, but there is a large barrier for the minority carriers . If there is a b, offset for the majority carriers in the buffer layer, then it may lead to a formation of a 'spike', or cliff'. If the b, offset produces a cliff, the probability of the interface cross-recombination is increased, , the flat b, condition is achieved at a bias smaller than E_g/q of the absorber. The sufficiently large doping density in the buffer layer than that in the absorber is essential, in order to confine the space charge region in the absorber.

3.1.3 Window layer:

Window layer should be highly transparent, conductive. This leads to the optical absorption in the infrared region. Therefore, it is necessary to increase the mobility in the window material in order to get larger conductivity while keeping the carrier concentration low. The b, gap of the materials should be large enough (ZnO) to show a large transmission of light photon.

3.1.4 Substrate:

Solar cell substrate should be stable at the cell production temperature. Another important issue is a good adhesion to the layers of the cell. Depending on the application, it may be cheap like a soda lime glass, or light like a polyimide film.

3.1.5 Top Contact:

The top layer of the grid has to be a good electrical conductor, , it has to be readily connectable. Aluminum is often used as the top layer.

3.1.6 Back Contact:

Wider b, gap material should be used for the back contact in order to increase the carrier type selectivity, to reduce the interface recombination. Since this contact is not transparent, an appropriate metal–semiconductor junction will generally perform well at a bias close to zero.

4 Chemical Spray Deposited $CuInS_2$ Based Solar cells:

First photovoltaic device, using $CuInS_2$ as an absorber material, was fabricated by Kazmerski et al. [14]. They employed dual-source deposition technique for the fabrication of n, p $CuInS_2$homojunction solar cell. They reported 3.62 % conversion efficiency for 0.124 cm^2 device. The maximum efficiency reported for CIS based solar cell is 12.5% by Klaer et al. [15]. They employed dc magnetron sputtering of the metals , sulfurisation in elemental sulfur vapour. Siemer et al. [16] obtained efficiency of 11.4% by using rapid thermal process for the preparation of $CuInS_2$ absorbers. $CuInS_2$ absorber thin films with Cu rich phases were prepared using thermal evaporation method, employed in the device that could achieve efficiency of 10.2%. Chemical bath deposited (CBD) CdS buffer layer were used in the device. The cell structure In_2O_3/CdS/$CuInS_2$ with conversion efficiency of 9.7% was fabricated by Ogawa et al. [17]. They employed atom beam sputtering to deposit In_2O_3 films.

However from the selenide based devices conversion efficiency of 15.7% has been achieved with cadmium-free $In_x(OH,S)_y$ as buffer layer for a Cu(In,Ga)Se_2- based solar cell. The conversion efficiency of 19.2% has been achieved for the cell structure ZnO/CdS/CuInGaSe_2. Co-evaporation technique was used to deposit absorber layer, which is the maximum efficiency reported for CIS based thin film solar cells. Naghavi et al. [18] used Indium sulfide as a buffer layer deposited by atomic layer chemical vapour deposition(ALCVD) for copper-indium-gallium-diselenide (coevaporation) solar cells yielded an efficiency 16.4%.

Highest efficient CIS-based solar cells were prepared using sophisticated high vacuum instruments. It is fairly advantageous to fabricate reliable, efficient non-vacuum processes instead of the expensive vacuum technique for solar cells based on the $CuInS_2$ absorber. Among a variety of non-vacuum processes, spray pyrolysis is an attractive method for deposition of $CuInS_2$thin films as discussed in article 2. Because of easiness to deposit the high quality $CuInS_2$ films over a large area spray pyrolysis technique has emerging tool for the thin film deposition process. Spray pyrolysis technique has been employed for deposition of variety of materials.

The spray deposited $CuInS_2$ films have been employed in the $CuInS_2$ based modules. In the following discussion we have made review on solar cell modules fabricated from chemical spay deposited $CuInS_2$ as an absorber material, the solar cell parameters from different literature are presented in table 3. Naciri et al. [19] investigated effect of thickness of chemical bath deposited CdS on the performance of $ZnO/CdS/CuInS_2$ module. For the module 3.24 % efficiency were reported for 60 nm thickness of CdS buffer layer. Presence of CdS produces favorable condition for b, alignment between $CuInS_2$, ZnO layer. Mere et al. [20] reported superstrate $ZnO/CdS/CuInS_2$ configuration from Indium rich solution composition (0.9 –1.1). The carrier concentration of absorber $CuInS_2$ was $10^{17}/cm^3$, which enhanced the short circuit current in the device. Ikeda et al. [21] investigated the effect of annealing temperature of sprayed $CuInS_2$ films on solar cell performance. The $CuInS_2$ thin films annealed with 600 ^{O}C showed larger open circuit voltage, short circuit current, 5.1% conversion efficiency was reported with these films as an absorber layer in Al: ZnO/CdS/CIS/Mo/glass device. However the Ga dopped CIS absorber showed greater efficiency of about 5.8%. CdS/CIS heterojunction on ITO coated glass were synthesized by Hou et al. [22].They employed Electrostatic Spray Assisted Vapor Deposition (ESAVD) method, 0.65% efficiency reported for 1.5 A.M. Light absorption in the CdS layer (Eg ∼ 2.4 eV) reduces the spectral response in the blue region, which results in the reduced photocurrent. This has been identified as a major problem in the total photocurrent loss. Khan et al. [23] reported 7.2 % conversion efficiency from CdS/CIS heterojunction onto ITO coated glass.

3D CIS/TiO_2 solar cell were prepared by Hayre et al. [24] , the effect of cell thickness, buffer layer thickness, , the morphology of the TiO_2 nanoparticulate matrix were studied. Efficiency of about 3.0% was reported for 500 nm thick TiO_2, above, 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 b, gap materials such as ZnS, ZnSe, ZnO, In_xSe_y, $In_x(OH,S)_y$, In_2S_3 etc. with considerable conversion efficiencies.

Effect of In_2S_3 on the performance of $CuInS_2/In_2S_3/TiO_2$ was investigated by Goossens et al. [25] , reported 7.00% 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 [26] 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. Conversion efficiency of 5.87 % was reported from CIS/In_2S_3 module, investigated that the efficiency could be improved by precise control of the thickness of the absorber $CuInS_2$ buffer layer In_2S_3 , their atomic concentrations. A record 9.5 % efficiency of were reported by John et al. [27] with oxygen free In_2S_3 as a buffer layer investigated that diffusion of Cu from absorber to In_2S_3 layer creates Cu-deficiency at the surface of the $CuInS_2$ layer , makes the interface more photosensitive responsible for resulting high efficiency. Nanu et al. [28] fabricated 3D solar cell based on $TiO_2/In_2S_3/CuInS_2$ nanocomposite resulted in 5% efficiency. I-V characteristics of the module are shown in the figure 3. Table 2 summarizes the efficiencies of different solar cell module. In all modules absorber layer $CuInS_2$ is synthesized using spray pyrolysis technique.

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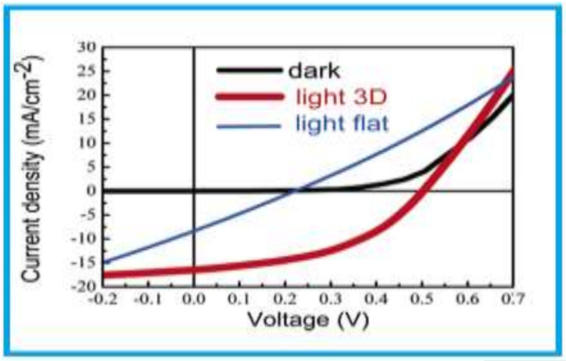

Figure 3: I-V characteristics of 5 % efficient 3D solar cell based on $TiO_2/In_2S_3/CuInS_2$ nanocomposite (Figure adapted from 28).

Table 3: Spray deposited $CuInS_2$ based solar cell modules, solar cell parameters. (*for spray deposited layer)

o.	Substrate	CIS($CuInS_2$) based module	Thickness of layer	Voc (mV)	Jsc (A/cm^2)	FF (%)	Efficiency	Ref.
	Glass/ITO	ZnO^*/CdS/ $CuInS_2^*$	1-2µm /60nm/1-2µm	270	2.8	43	3.24	[19]
	Glass/Mo	Al:ZnO/CdS/ $CuInS_2$ *	-	590	18.1	48	5.1 (AM-1.5)	[21]
	Glass/ ITO	CdS*/ $CuInS_2$ *	300nm/ 2um	205	10.4	30	0.65	[22]
	Glass/ ITO	CdS/ $CuInS_2$*	300nm/500nm	650 0.567 7.60	21.5	56.7	7.60 (AM-1.5) 100 mW/cm^2	[23]
	TCO/LOF Glass	3D $CuInS_2$*/TiO_2*	500 nm/ 150nm	460	13.2	46	2.8	[24]
	TCO/LOF Glass	TiO_2*/In_2S_3*/$CuInS_2$*	150nm/60nm/500nm	400	19.8	38	3 (AM-1.5)	[24]
	Quartz Glass	$CuInS_2$*/In_2S_3*/TiO_2*	-	710	23	43	7 (AM-1.5)	[25]

Glass/ ITO	$CuInS_2$*/In_2S_3*/Ag,	-/1µm/0.5µm/-	450	44.03	29.5	5.87	[27]
Glass/ ITO	$CuInS_2$*/In_2S_3*/Ag	1 µm/0.85µm/45nm	588	48.2	33.5	9.5	[28]
Glass/ ITO	TiO_2/In_2S_3/ $CuInS_2$		503	17	55	5 (AM-1.5)	[29]
Glass/ITO	ZnO*/CdS*/ $CuInS_2$*	-/500nm/-	443	5.5	37	-	[30]
Glass	$CuInS_2$*/ZnO/ (0.03 cm^2)	0.9 µ/ -/ -	280	13.3	38	2	[31]
Glass/ ITO	ZnO/TiO_2/In_2S_3/ $CuInS_2$*	-	425	12.0	43	2.2	[32]

5 Results and discussions:

Chacopyrite $CuInS_2$ thin films can be deposited with low cost spray pyrolysis technique. According to the analysis of the result outlined above it reveals that the properties of the $CuInS_2$ thin films prepared by spray pyrolysis technique mainly influenced by substrate temperature, chemical composition of the precursor solution , pH, spray rate ambient atmosphere, carrier gas, droplet size , post-deposition cooling rate etc. To improve the quality , thickness of $CuInS_2$ absorber (µm range), many thin layers may be deployed sequentially. Annealing plays a vital role to remove organic residuals from the solution, to increase film density, , crystallize of the film. Unfortunately film treated at high temperature can still contain structural defects that lead to limited carrier lifetime , mobility. Substrate material is observed to be one of the constraints to the high temperature treatments in the solar cell device fabrication process. In terms of solar cell applications, the title compound $CuInS_2$ prepared by low cost chemical spray pyrolysis technique, contributes to the novel absorbing materials (efficiency up to 10%) with precisely controlled absorber properties. However the design of appropriate hetero-structures with $CuInS_2$ absorber, suitable wide b, gap buffer , window layer material is great challenge to $CuInS_2$ based solar cell modules.

6 Conclusions:

This review has described the non vacuum based, low cost , versatile chemical spray pyrolysis method for preparation of $CuInS_2$ absorber thin films for solar cell application. $CuInS_2$ thin films prepared by spray pyrolysis technique mainly influenced by substrate temperature, chemical composition of the precursor solution , pH, spray rate ambient atmosphere, carrier gas, droplet size , post-deposition cooling rate etc. To improve the quality , thickness of $CuInS_2$ absorber (µm range), many thin layers may be deployed sequentially. Annealing plays a vital role to remove organic residuals from the solution, to increase film density, crystallize of the film. Unfortunately film treated at high temperature can still contain structural defects that lead to limited carrier lifetime, mobility. Substrate material is observed to be one of the constraints to the high temperature treatments in the solar cell device fabrication process. In terms of solar cell applications, the title compound $CuInS_2$ prepared by low cost chemical spray pyrolysis technique, contributes to the novel absorbing materials (efficiency up to 10%) with precisely controlled absorber properties. However the design of appropriate hetero-structures with $CuInS_2$ absorber, suitable wide b, gap buffer, window layer material is great challenge to $CuInS_2$ based solar cell modules. Low coast chemical spray pyrolysis technique for deposition of $CuInS_2$ absorber thin film is one of the suitable alternative to sophisticated, vacuum based techniques. Chemical spray pyrolysis of $CuInS_2$ thin-films as an absorber material for solar cells has high potential in the photovoltaic industries.

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