# STUDIES ON $CU_2SNS_3$ THIN FILMS: REVIEW

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## ABSTRACT

This review emphasizes the preparation of Cu2SnS3 thin films using pulsed laser deposition, spray pyrolysis and successive ionic layer adsorption and reaction method. The advantages and limitations of these techniques were discussed. Some aspects of the characterization of the obtained films were presented also. X-ray diffraction patterns confirm that the growth of various structures of $Cu_2SnS_3$ films under different experimental conditions.

**Keywords:** pulsed laser deposition, spray pyrolysis, $Cu_2SnS_3$ thin films, SILAR method.

## INTRODUCTION

Copper-containing chalcogenides such as I-IV-VI groups have been considered as good absorber material in photo voltaic devices (Naoya *et al,* 2014; Aihara *et al,* 2013; Kuku and Fakolujo, 1987; Jakapan *et al*, 2017; Lee *et al*, 2017). Because of excellent properties such as high absorption coefficient of $10^4 cm^{-1}$ (Bouaziz *et al,* 2011) and appropriate band gap values in the range of 0.9-1.5 eV (Zhang *et al*, 2014; Wang *et al*, 2016; Reddy and Reddy, 2017). Previously, cadmium telluride thin films (Echendu *et al,* 2016; Wang et al, 2015; Shih and Qiu, 1985; Falcao *et al*, 2006;Shan *et al*, 2016) and $Cu(In,Ga)Se_2$ films (Lee *et al*, 2016; Witte *et al*, 2008; Choi, 2011; Roy *et al*, 2002) have been synthesized by many researchers. However, researchers aware that cadmium is a toxic metal, indium and gallium are expensive. Therefore, research works have been focused to low toxicity and abundant materials for thin film solar cells such as nickel sulphide (Ngai *et al*, 2010; Sonawane *et al,* 2015; Ho *et al*, 2011), copper sulfide (Saravanan *et al,* 2011; Sangamesha *et al,* 2013; Anuar *et al*, 2011), zinc sulfide (Tan *et al*, 2011; Wei *et al*, 2013; Tan *et al,* 2010), manganese sulfide (Sunil *et al,* 2017; Anuar *et al*, 2010), cobalt sulphide (Sartale and Lokhande, 2000; Mane *et al*, 2011; Kamble *et al,* 2015), iron sulphide (Dzulkefly *et al*, 2010; Kawai *et al,* 2014) and etc. Copper tin sulfide thin films such as $Cu_4SnS_4$, $Cu_3SnS_4$, and $Cu_4Sn_7S_{16}$ have been prepared using different deposition techniques including pulsed laser deposition, solvothermal (Kamalanathan *et al*, 2018), radio-frequency magnetron sputtering (Bodeux *et al*, 2015; Gong *et al*, 2015; He *et al,* 2017; In *et al*, 2016), chemical bath deposition (Manjulavalli and Kannan, 2015; Shelke *et al*, 2017a; Anuar *et al,* 2009), electro deposition (Kassim *et al*, 2008; Dominik *et al,* 2012; Ho *et al*, 2009; Kuang *et al*, 2009), spray pyrolysis method, sol gel spin coating (Yasar *et al,* 2015; Dahman *et al*, 2014), co-evaporation method (Jose *et al*, 2016) and successive ionic layer adsorption and reaction technique (Su *et al*, 2012; Pathan and Lokhande, 2004).

This work was done to review the synthesis of $Cu_2SnS_3$ (CTS) films using various deposition methods such as SILAR, spray pyrolysis and pulsed laser deposition. Here, we report results obtained by different tools. In general, the growth of various structures $Cu_2SnS_3$ films such as tetragonal (Tiwari *et al*, 2014; Devendra *et al*, 2013; Arindam et al 2017), monoclinic (Chalapathi *et al,* 2015; Berg *et al*, 2012), triclinic (Shelke *et al* 2017b), cubic (Bouaziz *et al,* 2009; Baranowski *et al*, 2014) could be obtained under various deposition parameters.

## LITERATURE SURVEY

### CTS thin films via PLD technique

Pulsed laser deposition abbreviated as PLD is a physical technique used to deposit a high quality of thin films, including oxides, nitrides, chalcogenides, etc. In PLD technique, a high-power pulsed laser beam is focused onto a target of the material that is to be deposited on the film inside a vacuum chamber. The laser pulse is incident on the target, then the energy of laser is converted to electronic excitation followed by the thermal, chemical and mechanical energy. The process resulted in the evaporation of target material, ablation, plasma formation and even exfoliation [Chrisey and Hubler, 1994]. In short, the target/material is vaporized in the form of a plasma plume and deposited on the suitable substrate as a thin film. Usually, this process can occur in a vacuum or inert atmosphere or even in the presence of a background gas. The simplistic basic setup as compared to other vacuum based deposition techniques, uncomplicated in terms of operation, flexibility in the engineering design and apparatus, enrichment in crystallinity of the product, clean deposition, very precise transfer of species from the target to substrate makes the PLD as a superior deposition technique. The deposition parameters, such as laser pulse energy, pulse repetition rate, target-to-substrate distance, target material, substrate temperature, orientation of the substrate, pressure in the chamber and type of gas have a strong influence on the film properties which exhibits the huge versatility of PLD technique [Vanalakar *et al,* 2015a]. In addition, the conductivity of the target is also plays the key role in the PLD deposition [Vanalakar *et al*, 2014]. However, the high cost of equipments, requirement of vacuum and time for depositions are some of the limitations of the PLD system which hurdle its common use. Apart from this, a part of the volatile fraction may be lost during the deposition of materials with volatile components such as oxygen or sulphur [Schou, 2009].

The basic requirement for the deposition of thin film via PLD technique is the formation of solid target by using different powders. The single or multi-component targets can be purchased or made in the laboratory prior to the deposition. Generally, the target is in the form of pellet which is composed by mechano-chemically processed desired powders in appropriate quantities. Further the mechno-chemically processed powder was shaped in pellet and sintered for a particular temperature. Ettlinger *et al*. (2015) prepared the $Cu_2SnS_3$ (CTS) target by mixing $Cu_2S$ and $SnS_2$ powder in 1:1 M ratio followed by solid state reaction at 750°C. Similarly, Vanalakar et al., (2015a) used CTS pellet as a target by hot-pressing of commercial available $Cu_2S$ and $SnS_2$ powders with a 1:1 molar ratio.

The proper stoichiometric transfer is the main advantage of PLD which is very essential for the formation of multinary chalcogenides. However, this technique has rarely been used to deposit to deposit multinary chalcogenides such as $Cu_2SnS_3$ thin films. Ettlinger *et al*. (2015) first reported the synthesis of CTS thin films by using the PLD method on the silica substrate. The thickness of the CTS thin films was about 400 and 600 nm. In the report, authors have investigated the effect of fluence and deposition temperature on physico-chemical properties of CTS and deposition rate of CTS and ZnS films. Ettlinger *et al.* (2015) in their report, not only deposited CTS but ZnS thin films also and they observed that the deposition rate measurements of CTS under similar conditions are significantly lower than the deposition rate of ZnS. The one reason for different deposition rate might be the lower heat conduction of sintered ZnS-target than for the metals. Second reason might be sintered target may have a high amount of defects at the grain boundaries which absorb photons at the laser energy 3.49 eV, which is slightly below the direct band gap energy of 3.54 eV for a perfect cubic-phase ZnS crystal. Meanwhile, authors do not able to deposit cubic phase pure CTS even at higher deposition temperature. In addition, the elemental analysis indicated lower sulphur (S) and tin (Sn) content in $Cu_2SnS_3$ films produced at higher fluence. Figure-1 shows the X-ray diffraction (XRD) pattern and scanning electron microscopy (SEM) images of CTS thin films deposited at various temperatures. However, the authors have successfully used PLD technique to deposit CTS thin films in the tetragonal phase, though they highlighted more work is needed to confirm that the films are stoichiometric. Due to the presence of secondary phases, Ettlinger *et al*. not reported the solar cell performance of CTS thin films.

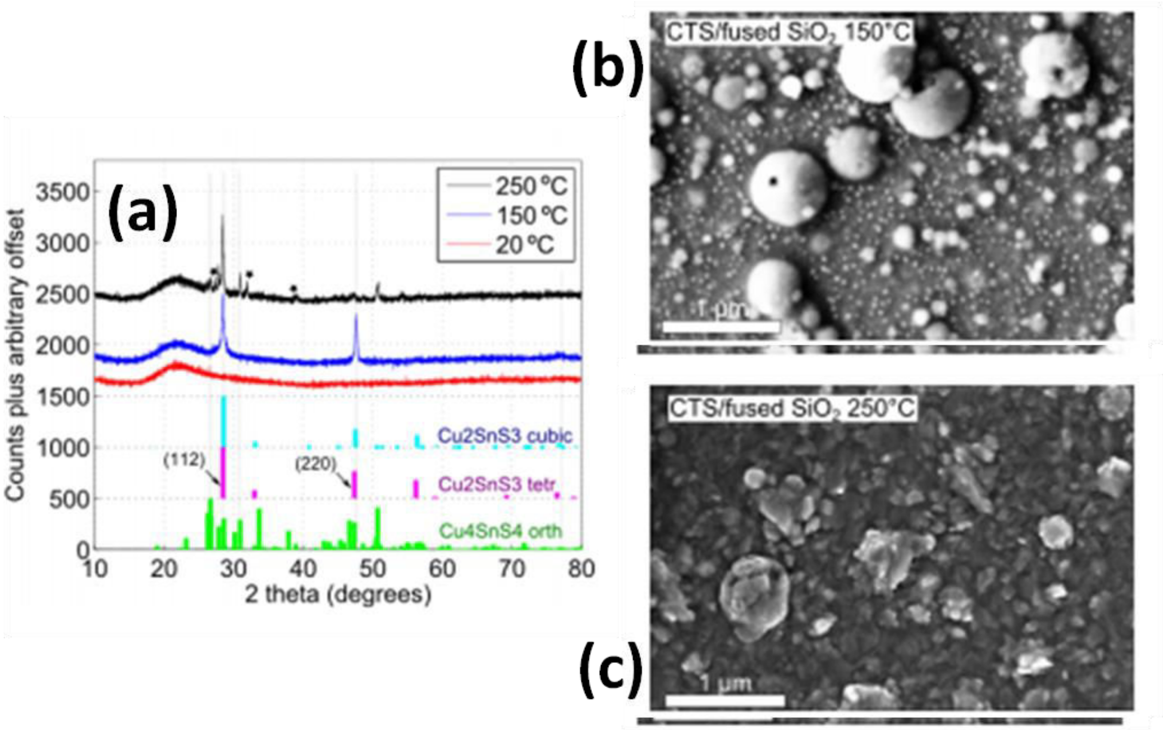


**Figure-1.** (a) XRD pattern of CTS thin films deposited at various temperatures such as 20, 150 and 250 $^0$C, (b and c) SEM images of CTS thin films deposited at 150 and 250 $^0$C, respectively. The SEM images shows the uneven surface morphology of the product. (Reproduced with the permission from Elsevier).

Vanalakar *et al.* (2015b) first reported the CTS thin films based solar cells fabricated via the PLD technique. They studied the effect of post-annealing temperature on the formation of CTS thin films. They annealed as synthesized CTS thin films in the sulphur atmosphere at different temperatures, such as 200, 300 and 400 °C for 1 h, immediately after removing from the PLD system. Vanalakar *et al*. (2015) observed that annealed

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CTS thin films become more crystalline and phase pure as the annealing temperature goes on increasing. Particularly, the CTS film annealed at 400 $^{0}$C was compact in nature and showed void free and highly crystallized morphology. Even the films have no secondary phases and have optimal band gap energy of 1.01 eV. Finally, a thin film based solar cell was fabricated with a SLG/Mo/CTS/CdS/i-ZnO/AZO/Al structure. Figure-2 shows the XRD pattern, SEM images and solar cell performance of CTS thin films annealed at various temperatures. The fabricated solar cell showed photo-electric conversion efficiency of 0.82 % with short circuit current density ($J_{SC}$) of 11.90 mA/cm$^2$ and open circuit voltage ($V_{OC}$) of 0.26 V. The low Voc value was attributed due to the recombination, small grain size, defects and poor *p–n* junction contact. Hence, studying and improving these factors can enhance the PCE of solar cells.

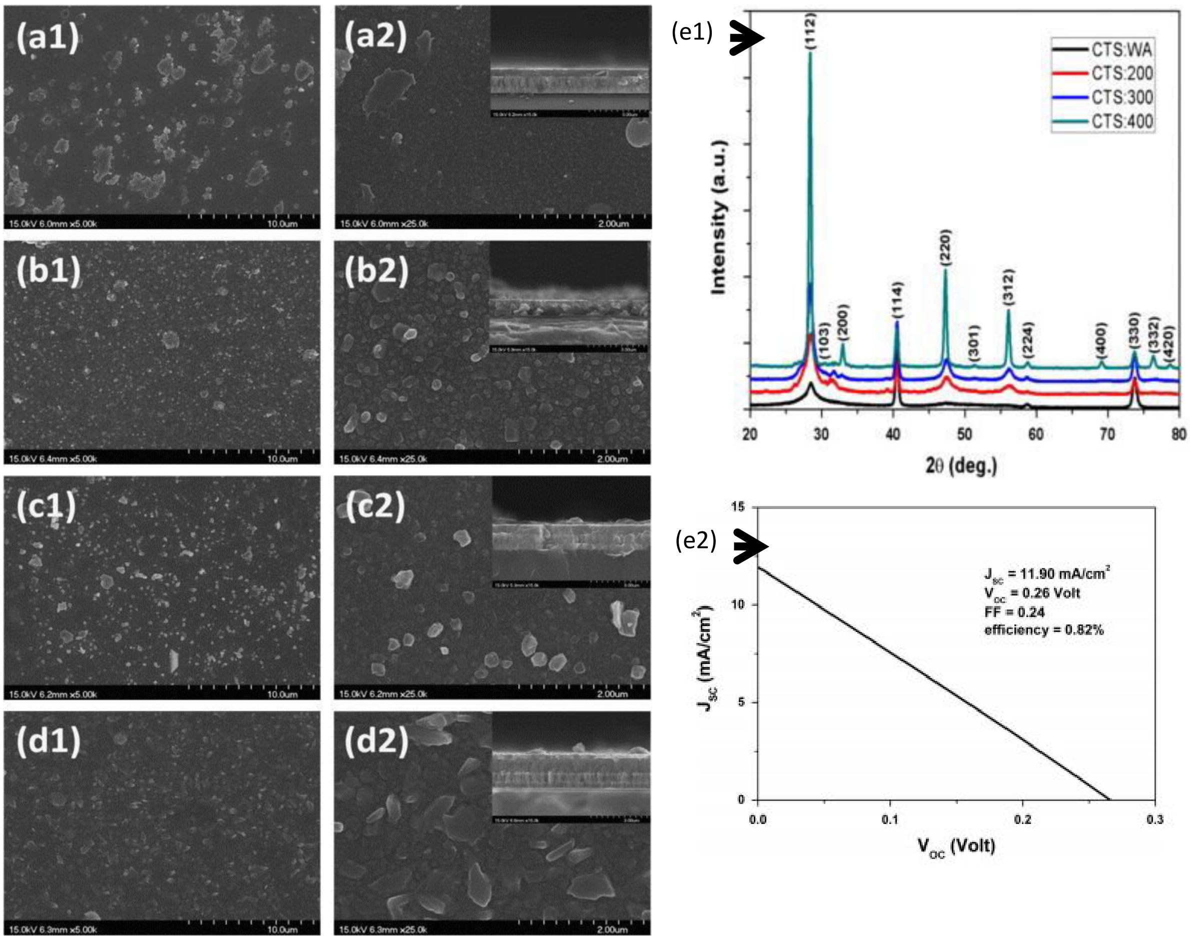


**Figure-2.** (a to d) FESEM images of CTS thin films annealed at various temperature. The FESEM images shows the enhancement in the grain growth as a function of annealed temperature, (e1) XRD pattern of CTS thin films annealed at various temperatures, and (e2) The solar cell performance of PLD deposited CTS thin film. (Reproduced with the permission from Elsevier).

**CTS thin films via spray pyrolysis technique**

Chemical Spray Pyrolysis (CSP) technique was first introduced by Chamberlin and co-workers in 1966. In CSP technique metal, salt solutions are sprayed onto the preheated substrate surface; the optimum substrate temperature will result in pyrolysis of the solution and the constituents in the solution react to form the required chemical compound, which is coated on the substrate surface. Comparing with other deposition technique spray pyrolysis has some advantages such as simplicity of technique and good reproducibility; again, this is vacuum-free technique and scalable for industrial applications. In spite of these advantages, CSP technique has some disadvantages too. Precise substrate temperature measurement during the film deposition process is difficult. The selection of chemical salt and solvent should be in such a way that the undesired chemical compounds formed during the deposition are volatile at the deposition temperature. Moreover, selection of substrate is important; it should be able to withstand the deposition temperature and should not react with spray solution. In spite of these problems, there has been always great interest in adapting this simple technique for depositing compound semiconductor thin films. Recently there are efforts from many researcher groups throughout the world, for the deposition of $Cu_2SnS_3$ thin films using this technique.

In 2009, for the first time, Bouaziz *et al*. (2009) reported deposition of CTS thin film using CSP technique. $SnS_2$ and $Cu_xS$ thin films were sequentially deposited on glass substrates, and afterwards the deposited bi-sprayed films ($SnS_2/Cu_xS$) were annealed in sulfur atmosphere at 550 $^0$C for 2 h. $SnS_2$ film was deposited using spraying solution (a mixture of water and methanol) containing thiourea and stannic chloride at substrate temperature of 280 $^0$C. $Cu_xS$ is deposited over the $SnS_2$ film again through spraying solution containing thiourea and copper chloride at substrate temperature of 300$^0$C. Characterizations studies indicated formation of $Cu_2SnS_3$ having cubic structure with $E_g$(bandgap) of 1.15 eV. Amlouk *et al*. (2010) prepared $SnS_2$ film using the same condition as that used by Bouaziz et al., however here copper was evaporated in sulfur atmosphere at 550 $^0$C, resulting in cubic structured $Cu_2SnS_3$ films with $E_g$ of 1.75 eV.

Adelifard *et al*. (2012) fabricated $Cu_2SnS_3$ by single spray pyrolysis, using precursor solution containing copper acetate, stannous chloride and thiourea. Deposition temperatures was 285 $^0$C. Here various Sn/Cu molar ratios were used characterization studies indicated that, with the increase in Sn/Cu ratio, sulfur and tin deficiency improved while the copper content in the layers decreased; in this work $Cu_2SnS_3$ having dominant triclinic phase was formed with ($E_g$) 1.58 eV and resistivity 8.5 Ωcm. Chalapathi *et al.* (2013) prepared the samples using precursors cupric chloride, stannic chloride and thiourea dissolved in double distilled water. The substrate temperature was 360 $^0$C and the deposited films were annealed in sulphur atmosphere at different temperatures. From the structural analysis, both tetragonal and monoclinic CTS phases were found to be present; however, on increasing annealing temperature, monoclinic phase dominated, shifting the $E_g$ from 1.65 to 0.93 eV (as deposited to anneal at 500 $^0$C).

Jia *et al* (2015) prepared CTS films using the precursors copper chloride, stannous chloride and thiourea varying Cu/Sn ratio and substrate temperature. The samples prepared with varied Cu/Sn ratios (at 350 $^0$C) showed tetragonal phase only. After fixing Cu/Sn ratio, variation in substrate temperature resulted in increase in Cu/Sn ratio up to 375 $^0$C, and then decreased. Again these films had tetragonal structure up to 350 $^0$ C; on further increasing the temperature (375 $^0$C) it changes to cubic. However, at 400 $^0$C the structure again changed to monoclinic phase. The band gap varied from 1.37 to 1.59 eV with temperature and lowest resistivity was around $11.6\times10^{-2}$ Ω•cm. Brus *et al.* (2016) reported CTS thin film deposition on bare and molybdenum (Mo) coated glass substrates at temperature of 288 $^0$C with same precursor as that used by Chalapathi and co-workers. Films were deposited with different sulfur concentrations and thicknesses. Structural analysis proved presence of both $Cu_2SnS_3$ and $Cu_3SnS_4$ phases; with increase in the thickness, $Cu_{2-x}S$ phase increased ($E_g$ 1.89 eV). Electrical analysis showed two shallow acceptor levels- Ev~ 0.07 eV at T < 334 K and Ev~ 0.1 eV at T > 334 K.

Guo *et al.* (2016) deposited CTS thin films with different Cu/Sn precursor ratios and substrate temperatures using same precursor as that used by Chalapathi and co-workers. Dominant phase of CTS film changed from tetragonal phase to monoclinic phase on reducing Cu/Sn ratio or increasing substrate temperature. With increasing Cu/Sn ratio the $E_g$ of the CTS films changed from 1.87 to 1.03 eV, making the resistivity minimum ($\sim3.5\times10^{-3}$ Ω•cm). Annealing in sulfur atmosphere increased the crystallinity and sulfur content of the film. Chalapathi et al. (2016) prepared CTS film with different Cu/Sn ratio, using the deposition condition same as that of Chalapathi *et al*. (2013) structural characterization reveals formation of monoclinic phase with $E_g$ around ~0.90 eV.

This survey proved that so far only one group viz., Sunny and co-workers (2017) reported the fabrication of solar cells using sprayed CTS films. Unlike in all earlier cases this work reports the preparation of CTS thin films using precursors copper chloride, thiourea for copper (Cu) and Sulphur (S) while two different precursors were used for tin viz., stannous chloride and stannic chloride. The films deposited at substrate temperature of 325 $^0$C. The samples were having tetragonal structure with $E_g$ of 1.2 eV and 1.5 eV for stannous and stannic chloride precursors, respectively. For cell fabrication, CTS films were deposited over ITO ($In_2O_3$: Sn) followed by the deposition of $In_2S_3$ buffer layer using spray pyrolysis technique itself. The solar cells fabricated with stannic chloride showed better cell parameters (efficiency of 0.84% with $V_{oc}$~0.36V, $J_{sc}$~5.9mA/cm$^2$ and FF ~ 40%) in comparison with the other set fabricated using stannous chloride.

**CTS thin films via SILAR technique**

Binary, ternary and quaternary thin films have been successfully deposited via successive ionic layer adsorption and reaction (SILAR) technique as reported by many scientists. It is simple, less expensive technique if compared to other physical deposition techniques. Generally, experimental conditions such as deposition cycle and dipping time will influence the quality of thin films. During the deposition process, substrate is dipped into solution (containing cation and anion) in order to get pure phase films without secondary phase.

Harshad *et al* (2017) have synthesized *p*-type semiconductor of $Cu_2SnS_3$ using SILAR method. They highlighted some important findings such as surface area (2.1 m$^2$/g), morphology (spherical grains) and structure (formation of triclinic). The influence of annealing treatment was studied by Aykut (2017). The structure (from amorphous to polycrystalline) and morphology of films were changed after annealing. Also, band gap value reduced (1.27 to 1.21 eV) with annealing. On the other hand, the effect of film thickness on the obtained samples was investigated by Harshad *et al* (2017). They conclude that band gap value increased (0.98 to 1.4 eV) with reduce in film thickness. The power conversion of SILAR deposition of $Cu_2SnS_3$ films was tested by Shelke *et al* (2017c). Solar cell (ITO/CTS/$LiClO_4$/graphite) was fabricated and the highest value of photo conversion efficiency (0.11 %) with fill factor (30 %) was obtained.

Suleyman *et al* (2013) have reported the influence of copper content on the thin films deposited on soda lime glass substrate. Large grains could be observed as shown in SEM results. Band gap value increased (1.35 -1.45 eV) with increasing copper content.

## CONCLUSIONS

$Cu_2SnS_3$ thin films have been prepared using various deposition techniques such as pulsed laser deposition, spray pyrolysis and successive ionic layer adsorption and reaction method. The band gap values obtained in the range of 0.98-1.87 eV. The solar cell was fabricated and the power conversion efficiency around 0.11 to 0.84 %.

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