One-step diffusion membrane assisted CBD synthesis and characterization of Cu$_2$SnS$_3$ thin films

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Abstract. This paper present a novel method for growing thin films of Cu$_2$SnS$_3$ (CTS) using a solution-based chemical route consisting of simultaneous precipitation of Cu$_{2-x}$S and SnS$_2$ performed by diffusion membranes assisted CBD technique. Diffusion membranes are used to optimize the kinetic growth through a moderate control of the releasing metal into the solution. The conditions in terms of concentration of metal species, sulfide anion and temperature required for the precipitation of the Cu$_2$SnS$_3$ compound were determined through a study of chemical equilibrium of the system SnCl$_2$, Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, CuCl$_2$ and Na$_2$S$_2$O$_3$·5H$_2$O. These conditions were obtained solving the equilibrium equations with the help of the Visual MINTEQ 3.0 package, supported on the program MINTEQA2. X-ray diffraction (XRD) and Raman spectroscopy were used to characterize the structural properties of the CTS films. Optical, morphological and electrical properties were also studied by spectral transmittance, atomic force microscopy (AFM) and resistivity vs temperature measurements. XRD and Raman measurements confirmed the formation of the Cu$_2$SnS$_3$ phase.

1. Introduction

Thin film photovoltaics is becoming a viable option for large-scale power generation. However, due to the limited availability of In, some concern exists that high material expenses restrict the capacity to lower production costs, especially in view of the desired industrial mass production. Cu$_2$ZnSnS$_4$ has been considered as the alternative absorber layer to Cu(In,Ga)Se$_2$ due to its earth abundant and environmental friendly constituents, optimal direct band gap of 1.45eV and high absorption coefficient in the visible range [1,2]. In recent years, great efforts have been focusing on the preparation of CZTS thin films and exploration their potential application in thin film solar cells [2-4].

A variety of routes have been undertaken for thin-film deposition. These include vacuum and solution based deposition approaches. For each of these deposition routes, the compositional control and growth of single phase CZTS films are the main barriers toward a reliable process. These barriers are attributed to the incompletely understood nature of the Cu–Zn–Sn– S phase diagram [5] and to the volatility upon heating of Sn materials [6]. Despite these limitations reasonably successful film deposition and device fabrication has been demonstrated for both vacuum and solution-based deposition approaches. Cu$_2$ZnSnSe$_4$ and Cu$_2$ZnSn(S,Se)$_4$-based solar cells using hydrazine-based solution process have already reached an energy conversion efficiency as high as 11.1 % [4], demonstrating the effectiveness of the solution process in CZTSe-based solar cells.

In this work, we propose a novel route for the preparation of Cu$_2$SnS$_3$ thin films used as precursor of Cu$_2$ZnSnS$_4$ films grown using a solution based method. The Cu$_2$SnS$_3$ films are formed by core-precipitation of Cu$_{2-x}$S and SnS$_2$ performed by diffusion membranes assisted CBD technique. Further, results are reported related to structural, optical and morphological properties determined from XRD,
Raman spectroscopy, transmission and AFM measurements. These are compared with those of reference CZTS films prepared by sequential evaporation of metallic precursors in presence of elemental sulfur.

2. Experimental Procedure

The Cu$_2$SnS$_3$ compound was prepared using a novel procedure consisted of simultaneous precipitation of Cu$_{2-x}$S and SnS. The co-precipitation of Cu$_{2-x}$S and SnS$_2$ was achieved introducing initially an aqueous solution of (SnCl$_2$·2H$_2$O + Na$_3$C$_6$H$_5$O$_7$·2H$_2$O) and (CuCl$_2$·2H$_2$O) into two spatially separate diffusion membranes and then, both membranes are introduced into a solution containing (Na$_2$S$_2$O$_3$·5H$_2$O + glucose) dissolved in water. The role of the diffusion membranes is to optimize the kinetic thin film growth through a moderate control of the releasing metal into the solution by osmosis, and glucose is added to promote the reduction of Cu$^{2+}$ to Cu$^+$. The sodium citrate act as complexing agent and as a pH regulator.

A possible reaction mechanism for the formation of the Cu$_2$SnS$_3$ compound is the following:

In the reaction medium must exist free species of S$^{2-}$, Sn$^{4+}$ and Cu$^+$ to precipitate sulfides. The S$^{2-}$ ion is generated as free specie in solution due to hydrolysis of sodium thiosulfate in basic medium, according to the following reaction [5]:

$$\text{S}_2\text{O}_3^{2-} + 2\text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{S}^{2-} + \text{H}_2\text{O} \quad (1)$$

The cation is obtained from the complex [SnCit]$^-$ content in one of the membranes, which diffuses slowly and in a controlled way toward the solution favoring the ion by ion growth and decreasing the cluster growth, because of the physical barrier provided by the membrane. In solution, the species [SnCit]$^- \beta \text{Sn-Cit} = 2 \times 10^{10}$ participate in an equilibrium releasing Sn$^{2+}$ in a controlled manner. The precipitation take place in two step, oxidation of Sn$^{2+}$ to Sn$^{4+}$ by thiosulfate, and in the second step the ions in solution (Sn$^{4+}$ and S$^{2-}$) must exceed the solubility product.

$$\text{Sn}^{2+} + \text{Cit}^3^- \rightarrow \text{[SnCit]}^- \quad \beta_{\text{Sn-Cit}} = 2 \times 10^{10} \quad (2)$$

$$4\text{Sn}^{2+} + 3\text{O}_3^{2-} + 8\text{H}^+ \rightarrow 4\text{Sn}^{4+} + 2\text{HS}^- + 3\text{H}_2\text{O} \quad (3)$$

$$\text{Sn}^{4+} + 2\text{HS}^- \rightarrow 2\text{H}^+ + \text{SnS}_2(s) \quad K_{sp} = 3.5 \times 10^{-58} \quad (4)$$

At the same time should be given co-precipitation of Cu$_{2-x}$S. For that, Cu$^{2+}$ contained within one membrane diffuses toward the solution containing glucose (C$_6$H$_{12}$O$_6$), reducing it to Cu$^+$. 

$$\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{Cu}^{2+} + 3\text{OH}^- \rightarrow \text{C}_6\text{H}_{11}\text{O}_7^- + 2\text{H}_2\text{O} + 2\text{Cu}^+ \quad (5)$$

As in the reaction medium there is a high concentration of free thiosulfate ions and Cu$^+$ species, the following complexes can be formed:

$$\text{Cu}^+ + \text{S}_2\text{O}_3^{2-} \rightarrow \text{[CuS}_2\text{O}_3^- \beta_{\text{Cu-S}_2\text{O}_3} = 10^{10.3} \quad (5)$$

$$\text{[CuS}_2\text{O}_3^- + \text{S}_2\text{O}_3^{2-} \rightarrow \text{[CuS}_2\text{O}_5]^{2-} \beta_{\text{Cu-S}_2\text{O}_5} = 10^{12.2} \quad (6)$$

$$\text{[CuS}_2\text{O}_5]^{2-} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{[CuS}_2\text{O}_6]^{5-} \beta_{\text{Cu-S}_2\text{O}_6} = 10^{13.8} \quad (7)$$

For precipitation to occur, the ionic product $[\text{Cu}^+][\text{S}^{2-}]$ must exceed the solubility product $K_{sp}$ of Cu$_2$S.

$$2\text{Cu}^+ + \text{HS}^- \rightarrow \text{H}^+ + \text{Cu}_2\text{S}(s) \quad K_{sp} = 1.2 \times 10^{-35} \quad (8)$$

Subsequent to the formation of sulfides binary, they react in solution to form the ternary compound Cu$_2$SnS$_3$, according to the following reaction:

$$\text{Cu}_2\text{S}(s) + \text{SnS}_2(s) \rightarrow \text{Cu}_2\text{SnS}_3(s) \quad (9)$$
Parameter values for the reagents constituting the work solution (concentration of metal species, sulfide anion and temperature), required to obtain the Cu$_2$SnS$_3$ compound from co-precipitation of Cu$_2$S and SnS$_2$ were found by means of a study of the equilibrium conditions of the systems SnCl$_2$ + Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, CuCl$_2$ + Na$_2$S$_2$O$_3$·5H$_2$O. The concentrations and equilibrium constants allow building chemical equilibrium equations present in the system which were solved using the Visual MINTEQ 3.0 package, supported on the program MINTEQA2.

Using as input data the values determined through the solution of the chemical equilibrium equation, a parameter study was done with the purpose of finding suitable conditions to grow the Cu$_2$SnS$_3$ compound. The following chemical bath composition led to good results: [CuCl$_2$]=50mM, [SnCl$_2$]=100mM, [Na$_2$S$_2$O$_3$]=250mM, [glucose]=345mM and [Na$_3$C$_6$H$_5$O$_7$]=237mM. During the deposition the bath temperature was maintained at 70 °C and the final solution pH was around 5.

The transmittance measurements were done using a Varian – Cary 5000 spectrophotometer and the film thickness was determined using a Veeco Dektak 150 surface profiler. Further characterization involved X-ray diffraction on a Shimadzu-6000 diffractometer and Raman spectroscopy on a Horiba JobinYvon micro-Raman Spectrometer LabRamHR in backscattering configuration with a laser of 780nm, 20 mW focused with a 50X objective. Morphological studies were also done through AFM measurements carried out with a PSI AP-0100 Scanning Probe Microscope.

3. Results and discussion

3.1. Optical properties

Figure 1 displays transmission and reflection spectra of a typical Cu$_2$SnS$_3$ thin film of approximately 450nm thick. This result shows that the sum of the transmittance and reflectance is significantly less than 100%, indicating that in addition to the fundamental absorption this material contains absorption centers in the gap that significantly contribute to the absorption of photons of lower energies than the corresponding energy gap (E$_g$). This behavior is apparently caused by the presence of a high density of native defects (vacancies, interstitial and anti-site), which generate absorption centers within the energy gap that contribute to the photon absorption mainly in the VIS and NIR region.

![Figure 1](image)

**Figure 1.** a) Transmission and reflection spectra of a typical Cu$_2$SnS$_3$ thin films deposited in one-step using diffusion membrane assisted CBD method b) curve of $\alpha$ vs $\lambda$ and c) curve of $(\alpha h \nu)^2$ vs $h \nu$ obtained from transmittance and reflectance measurements.

In Fig. 1 are also displayed curves of $\alpha$ vs $\lambda$ and $(\alpha h \nu)^2$ vs $h \nu$. The absorption coefficient $\alpha$ was determined from measurements of spectral transmittance and reflectance and using the following relationship:

$$T(\lambda) = [1 - R(\lambda)]e^{-\alpha d}$$

(10)

Where $T(\lambda)$ is the spectral transmittance, $R(\lambda)$ the spectral reflectance and $d$ the sample thickness.
The Cu\textsubscript{2}SnS\textsubscript{3} thin films we have grown in this work have a value of $E_g = 2.15$ eV and an absorption coefficient in the high absorption region ($\lambda < 500$ nm) greater than $10^4$ cm\textsuperscript{-1}. The value of $E_g$ was determined from the intercept with the axis $h\nu$ of a curve of $(\alpha h\nu)^2$ vs $h\nu$.

3.2. Structural characterization

In Fig. 2 is compared the diffractogram of a typical Cu\textsubscript{2}SnS\textsubscript{3} thin film prepared by diffusion membrane assisted CBD method with the diffractogram taken to the material precipitated during its growth. It is observed that the CTS thin film present reflections corresponding only to the Cu\textsubscript{2}SnS\textsubscript{3} phase (PDF cart #00-019-0412), whereas the diffractogram corresponding to the precipitated powder, show reflexions associated to the Cu\textsubscript{2}SnS\textsubscript{3} phase as well as to the Cu\textsubscript{3}SnS\textsubscript{4} (PDF cart #00-036-0217)) and CuS (PDF cart #03-065-7111) phases.

![Figure 2. Comparison of XRD pattern of a CTS thin film prepared by One-step diffusion membrane assisted CBD method with that of the material which precipitates during its growth.](image)

Besides X-ray analysis, Raman spectroscopy measurements were done on thin films of Cu\textsubscript{2}SnS\textsubscript{3}. In Fig. 3 the Raman spectrum of a typical Cu\textsubscript{2}SnS\textsubscript{3} film is depicted. Deconvolution of this spectrum, allows identify three peaks around 292, 320 and 352 cm\textsuperscript{-1} respectively.

![Figure 3. Raman spectrum corresponding to a typical CTS thin film prepared by One-step diffusion membrane assisted CBD method.](image)

The shoulder in the region between 280 cm\textsuperscript{-1} and 300 cm\textsuperscript{-1} with a maximum around 292 cm\textsuperscript{-1} (see deconvolution) has been assigned to the Cu\textsubscript{3}SnS\textsubscript{4} compound grown with tetragonal structure [6]. The vibrational mode corresponding to the band b has been attributed to the A‘ symmetry of the Orthorhombic Cu\textsubscript{3}SnS\textsubscript{4} phase [6] and the peak at 352 cm\textsuperscript{-1} to the A’ symmetry vibrational modes from the monoclinic Cu\textsubscript{2}SnS\textsubscript{3} phase [7].
3.3. Electrical characterization
Electric conductivity measurements carried out as a function of temperature in a range of -80 to 700 K were used to identify scattering processes affecting the transport mechanisms of the CTS films. The conductivity ($\sigma$) was measured using electrical contacts of molybdenum deposited by sputtering, arranged to get the resistance through the standard four-stripe method; the film thickness was obtained using an $\alpha$-step profiler. Fig. 4 shows a typical curve of $\sigma$ vs T, obtained with a CTS films prepared by CBD.

![Figure 4](image-url)  
*Figure 4. Curve of $\sigma$ vs T corresponding to a CTS film deposited by CBD.*

The $\sigma$ vs T curves show two negative slopes and one positive, indicating that the conductivity is affected by different transport mechanisms, each one predominating in a different temperature range.

The results of Fig. 4 were analyzed assuming predominance of one determined transport mechanism in the temperature ranges denoted as I, II and III respectively. The curve of Ln $\sigma$ vs 1000/T displayed in inset of Fig. 4 shows that in the region II (between 350 and 570K) the conductivity can be expressed by the relation: $\sigma = \sigma_0 \exp[-(E_C - E_F)/(kT)]$, indicating that in this range of temperature the conductivity is predominantly affected by free carrier transport in extended states of the conduction band. Since the prefactor $\sigma_0$ varies slowly with temperature and the term $\exp[-(E_C - E_F)/kT]$ depends strongly on T, $\sigma_0$ can be assumed as approximately constant. Under this approximation, the slope of the graph ln$\sigma$ vs 1/T gives the activation energy $E_a = E_C - E_F$.

In the range of low temperatures (region I), the curve of $\sigma$ vs T can be expressed by a relation of the form: $\sigma = \sigma_0 \exp[(Q\phi)/(kT)]$. Since in this temperature range the free carrier density is not significantly affected by the temperature, the conductivity in the region I seems mainly affected by the carrier mobility, which in its turn is affected by the height of the potential barrier $\phi$ that the carrier must overcome in the grain boundary regions; the high barrier $\phi$ can be estimated from the slope of the $\sigma$ vs. 1000/T curve.

In the highest temperature region (region III), the conductivity decreases as the temperature increases. This behavior could be caused by phase change of the CTS compound (verified through XRD measurements) or mobility decrease induced by interaction of free carriers with lattice phonons.

3.4. Morphological characterization

Fig. 4 shows the AFM image of a Cu$_2$SnS$_3$ thin films prepared by One-step diffusion membrane assisted CBD method. It is observed that these type of samples have an unusual morphology characterized by sheet-shaped grains grouped together in big clusters with sizes varying in the range of
1X0.4 µm and 2.5x1.4 µm. Similar results were observed with Cu₂SnS₃ films prepared by co-evaporation of elemental precursors at 250°C followed by annealing at 550°C in sulfur atmosphere.

![AFM image of a Typical Cu₂SnS₃ thin film.](image)

**Figure 5.** AFM image of a Typical Cu₂SnS₃ thin film.

### 4. Conclusions

Cu₂SnS₃ thin films were grown using a novel chemical route consisting of simultaneous precipitation of Cu₂S and SnS₂ performed by diffusion membranes assisted CBD technique. The conditions in terms of concentration of metal species, sulphide anion and temperature required for the precipitation of the Cu₂SnS₃ compound were determined through a simulation of the chemical equilibrium of the systems (SnCl₂ + Na₃C₆H₅O₇·2H₂O), CuCl₂ and Na₂S₂O₃·5H₂O performed with the help of the Visual MINTEQ 3.0 package, supported on the program MINTEQA2.

XRD measurements gave evidence of the formation of single phase Cu₂SnS₃ films grown with tetragonal structure. Raman spectroscopy confirmed this result and additionally revealed the presence of the Cu₄SnS₄ phase grown with both tetragonal and orthorhombic structure. Transmittance and reflectance measurements indicated that in addition to the fundamental absorption the CTS films contains absorption centers in the gap that significantly contribute to the absorption of photons of lower energies than the corresponding energy gap, mainly in the VIS and NIR region. AFM studies revealed that the morphology of CTS thin films prepared by One-step diffusion membrane assisted CBD method have an unusual morphology characterized by sheet-shaped grains grouped together in big clusters.

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