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Synthesis and characterization of CZTS films

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ABSTRACT

Multilayerfilms with kesterite are often used for energy conversion, such as photoanode for hydrogen production and manufacture of photovoltaic solar cells. It is due to the fact that they are efficient and use small amounts of material. Cu_2ZnSnS_4, known as CZTS, is a semiconductor belonging to the kesterite group, which can be obtained in powder or film form. Copper, zinc, tin and sulfide are precursors commonly used in the synthesis of the CZTS. The methodology used to synthesize films is crucial for the success of the final product. It is essential to develop methods which can lower synthesis costs, which can also lower the solar cell costs, for example. Besides the costs, the method must be efficient and increase the efficiency of the devices in which they are employed, and must not be harmful to the environment. This study developed a methodology to synthesize CZTS. It was used in this work dimethyl sulfoxide, copper acetate, tin chloride, zinc chloride and thiourea as precursors. The layers of the film above the glass substrate were characterized with X-ray diffraction, ultraviolet and visible analyses, scanning electron microscopy, fourier transform infrared spectroscopy and X-ray fluorescence spectroscopy. The results absorbance peaks between 300 and 400 nm, in the ultraviolet range, reflectance around 40% in the visible, transmittance reaching above 50% and 50%, and direct band gap about 1.42 ± 0.02 eV associated with the kesterite. The characterization methods proved to be efficient to identify the presence of the kesterite phase at films produced by overlapping layers.

Keywords: Kesterite; Synthesis; Characterization.

1. INTRODUCTION

Solar energy is one of the most widely used renewable energy sources in the world, in particular solar photovoltaic energy. The most used element in commercial photovoltaic solar cells is monocrystalline and polycrystalline silicon (Si) [1], because it has the most equilibrium between efficiency and cost production compared to other elements. Due to the reduction of environmental impacts, there is an increase in the demand and incentive in transition of fossil energy generation to a more renewable energy generation [2, 3]. There are several ways to utilize solar energy, including the use of photovoltaic solar cells, devices that convert sunlight into electricity through the photovoltaic effect. But, the process to make silicon solar cells has high cost because, to make it, it needs high temperatures to process the quartz dust. Besides, alternatives to silicon have been explored. In recent years, one material is gaining increasing attention, precisely for the production of silicon-free photovoltaic solar cells, this material is kesterite [4–7].

The kesterite is an example for multinary semiconductor with the general chemical form of $Cu_2M^{II}M^{IV}X_4$ (X = O, S, Se, Te) [4]. Some examples of kesterite, a p-type semiconductor, include Cu_2ZnSnS_4, Cu_2FeSnS_4, Cu_2CdSnS_4 , Cu_2ZnGeS_4 and their selenium-based counterparts [5]. The characteristics of ketereite include, but are not limited to, the use of materials abundant in the earth's crust, band gap around 1,5 eV, high light absorption, and long-term stability [8–15]. Beyond the use in photovoltaic areas, kesterite has been researched for hydrogen production by water electrolysis [16, 17].

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Several techniques have been explored in the search to obtain kesterite. Spin coating was used to successive layers deposition of kesterite precursor solution obtain films with eight layers, where from the characterization by XRD, Raman Spectroscopy and XRF was observed the presence of kesterite of $(Ag,Cu)_2Zn(Sn,Ge)(S,Se)_4$ [18]. Researchers obtained $(Ag,Cu)_2Zn(Sn,Ge)(S,Se)_4$ from precursor salts mixed with thiourea and chloridric acid in Dimethylformamide (DMF) solvent and thermal treatment, consecutive by selenization in argon atmosphere with 340°C and 560°C of temperature . In another work, using a solution with precursor salts of copper, tin, zinc and thiourea in ethylene glycol, Cu_2ZnSnS_4 (CZTS) films were obtained from the conversion of deposited layers in substrate with heating to 473K in air atmosphere for 1 hour [19]. Furthermore, the synthesis of Cu_2ZnSnS_4 (CZTS) particles from heat treatment at different temperatures and application of the vacuum process of the kesterite precursor solution has been explored [20].

The most popularized methods to deposit the material is spray coating, spray pyrolysis, a method that uses spray to create material clouds in high temperature, it is possible to make large films with this method [8]. Sol Gel method is the methodology that produces the film through hydrolysis, has low cost and high efficiency [21]. Sputtering method is the methodology that uses a high vacuum chamber with Argon (Ar), using a cathode to deposit the desired material through a high voltage [22]. Techniques that have been applied to obtain kesterite films include chemical bath deposition, sulphuration, selenium atmospheric annealing, sol-gel, spin coating, spray pyrolysis, sputtering, reactive sintering, hot treatment, pulsed laser deposition, direct fusion, successive ionic layer adsorption and reaction, thermal decomposition, wet chemical heating up, and solvothermal process [23].

The obtention of kesterite films is based by two strategies, vacuum deposition, whose commonly used techniques are pulsed laser deposition, sputtering, and evaporation, while in non-vacuum deposition the most used techniques are spin coating, dip coating, blade coating, spray coating, printing, and electrodeposition [24]. The most synthesis kesterite film methods involves the fabrication of a precursor film at low temperature, followed by a high-temperature heat treatment process using a short process time, but since there is a great challenge involving the controllable growth of the film, many studies seek to discover the most suitable growth process [25].

In the Kesterite literature reviews published by [23–25] observed that the Drop Casting method was not approached as a kesterite films production method. Drop Casting deposition methodology is a method in which a small amount is placed on top of the substrate using a pipette [26]. The method focuses on low cost and overlapping layers of material to reduce layer thickness. Besides it is not widely used compared to other deposition methods for producing thin films, with a focus on studies related to CZTS. In fact, the obtained films with kesterite precursor applying the Drop Casting present limited information or have not been studied in depth. Therefore, this work addresses the use of the Drop Casting technique to obtain films using a solution with kesterite precursors.

One of the main factors that impede the improvement of kesterite solar cells is the low quality of the thin absorber films made using kesterite precursors caused by secondary phases, such as Sn(S)Se, Zn(S)Se, and Cu(S)Se, which are formed during, as well as the loss of Sn and decomposition of kesterite during the synthesis process, which can affect the carrier transport and reduce the open circuit voltage in the cell [25]. With this problem in mind, to lower the costs and increase the efficiency of the current photovoltaic solar cells, in this work is shown a method to synthesize, deposit and characterize films from kesterite precursors and, after that, was analyzed the potential for solar or optical device production. The analysis of film layers with multilayers deposited from subtract by overlapping susceptible layers by Drop Casting method using kesterite precursor solution is exploited. The objective is analyse the effect of overlapping layers from kesterite precursor solution through films production on through characterizations by X- Ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), ultraviolet and visible analyses, scanning electron microscopy (SEM) and fourier transform infrared spectroscopy (FTIR). The studied films contain 1 layer, 2 layers, 3 layers and 4 layers.

2. MATERIALS AND METHODS

All reagents were used without further purification.

A solution was mixed at room temperature with the following reagents: 20 mL of dimethyl sulfoxide (DMSO); 20 MM of copper II acetate ($C_4H_6CuO_4.H_2O$);13.7 MM tin chloride ($SnCl_2$); 14 MM MM zinc chloride ($ZnCl_2$) and 66 MM thiourea (CH_4N_2S), according to the Figure1 it’s possible to see the color change in solubilization process due to the addition of reagents. The mixed solution was then placed over the microscopy plate, using the drop casting method, and treated in a muffle furnace at 500°C for 1 hour in the air atmosphere. Different layers of solution on glass were tested. For one layer the procedure described above was done once, for two layers the same procedure was repeated twice, and so forth.

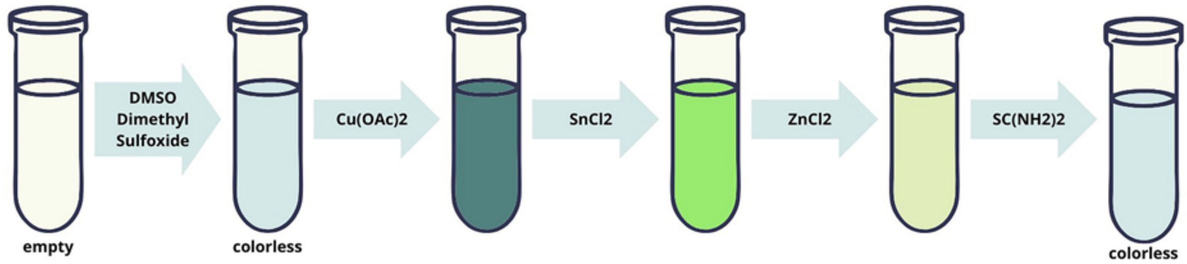

Figure 1: Scheme of the kesterite precursor solution synthesis.

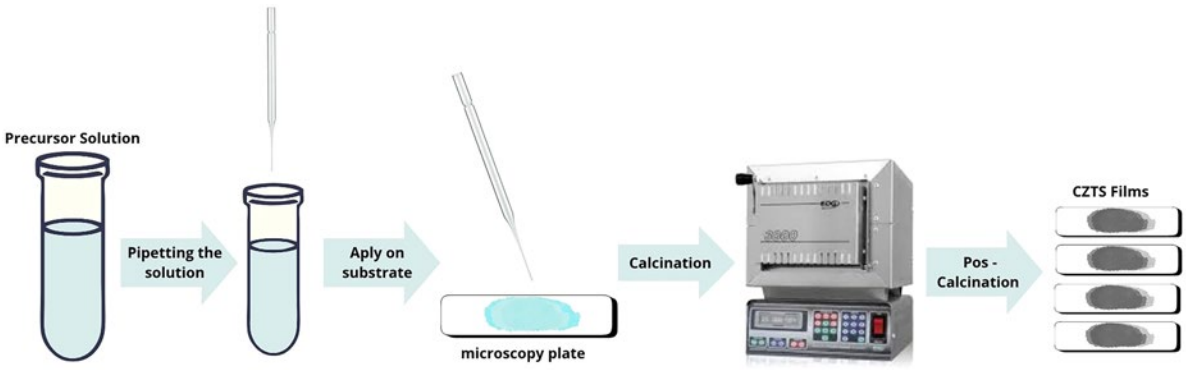

Figure 2: Scheme of the synthesis method.

The layers on glass were characterized by X-Ray (XRD, DMAXB, Rigaku); UV-Visible (spectrophotometer Shimadzu UV-2600 if integrating sphere ISR-2600Plus); SEM (Quanta 450 FEG, FEI); Infrared (Thermo Scientific; Nicolet IS5) and XRF analysis, performed on Olympus VCR. Figure 2 describes the methodology used in this work.

3. RESULTS

3.1. X-Ray diffraction (XRD)

The XRD is one of the instrumental techniques commonly used to identify the existence of secondary phases and evaluate the crystalline quality of materials [23]. Crystallinity can be studied using different techniques, such as X-ray diffraction and electron microscopy, in which the term crystallinity is associated with ordered arrangements, that is, materials that have a repetitive arrangement of their atoms or molecules, which are called crystalline materials, while amorphous materials have a more random arrangement of their particles [27]. In XRD the crystalline materials present diffraction peaks or characteristic peaks with a defined shape, while for amorphous materials there are no diffraction peaks. Figure 3 has the DRX spectra for the four layers, from 20° to 100°.

The peaks are dispersed for 1 layer formed on the microscopy plate, and it becomes more defined as the layers add on. Figure 2 (C) has the peaks formed for the CZTS, where the three layers presented higher crystallinity quality out of the four. The 1-layer film the formation of random arrangements of atoms tends to be dominant, which is reflected by the absence of a distribution of peaks with defined aspects. From this it is possible to infer that a film formed by only one layer has low crystallinity compared to the other films produced. The layer had tin (Sn) (110) at 45.270° and copper sulfide (CuS_2) (210) at 41.410°. The grain size for this sample was 50.1398 nm. The 2-layers film had copper-tin (Cu_xSn) (200) at 38.036° ,(211) at 50.902° and zinc sulfide (ZnS) (222) at 70.035°, (111) at 33.346°. The grain size was 53.7727 nm.

The 3-layers film identified the kesterite phase, with COD 9004750 and peaks (024) at 55.59° and (112) at 33.16°. According to [28], it can be hard to single out the different phases of CZTS. The minor phases presents in 3-layer sample were tin (Sn) (110) at 45,270°, sulfur (S) (111) at 33.373°, zinc sulfide (ZnS) (002) at 31.241°, CTS (Cu_xSnS_x) (208) at 40.184° and tin sulfide (Sn_xS_x) (103) at 37.358°. The grain size was 30.7490 nm. For 4 layers, it was identified tin sulfide (SnS) (10-1) at 39.183°, (100) at 33.722°, (040) at 36.505°, (151) and at

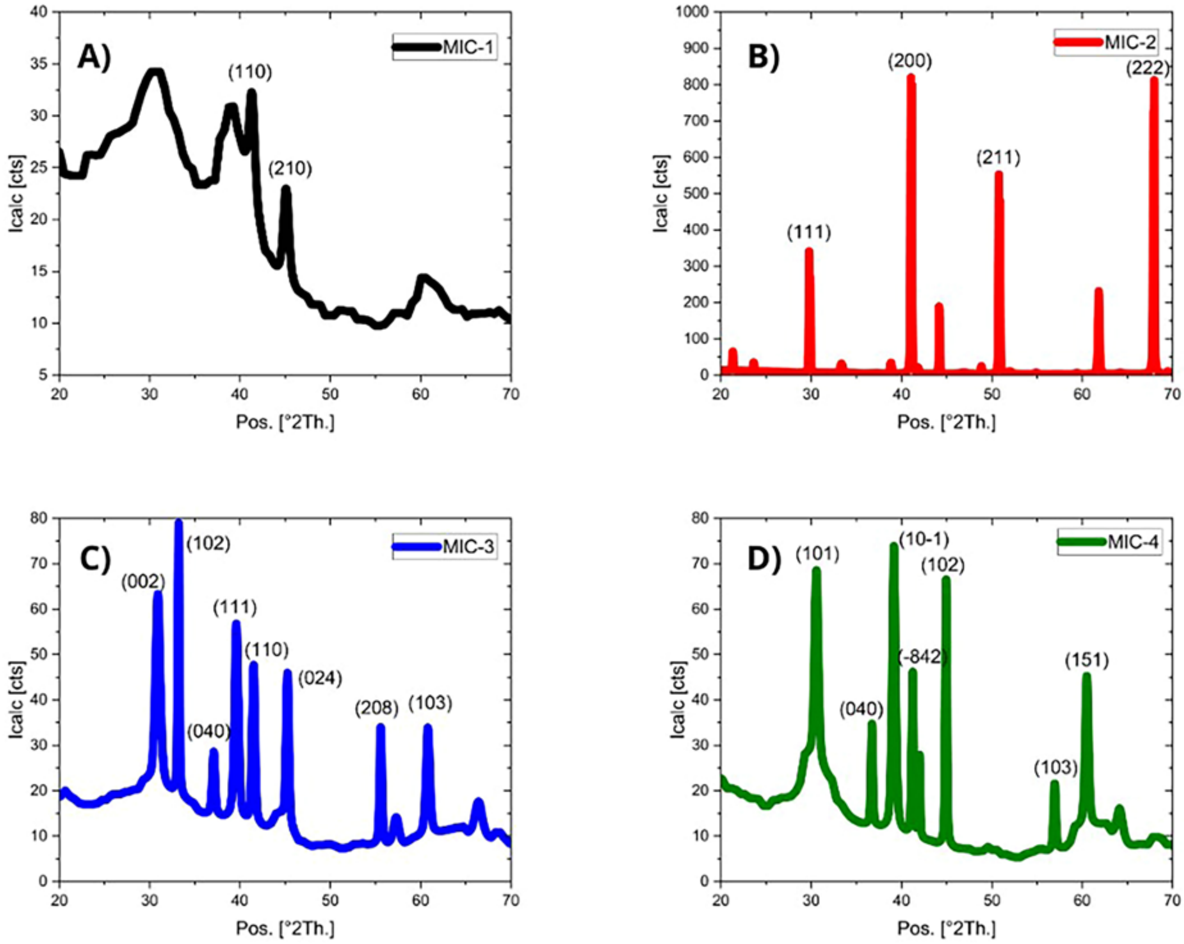

Figure 3: XRD spectra analysis of the layers (A)1 (B) 2 (C) 3 and (D) 4.

59.560°, copper sulfide (CuS) (−842) at 43.889°, (102) at 43.747°, (103) and at 56.958°. The grain size was 25.6031 nm [27].

Strong and well-defined diffraction peaks are observed for films formed with two, three and four layers, while for films formed with only the first layer there are no well-defined peaks. As previously mentioned, films with only one layer tend to present random arrangements of their atoms and this is reflected in low crystallinity, that is, in the family of diffraction peaks. However, it is worth noting that the positions of the experimental peaks of the films produced tend to be different from the references contained in the COD database, this is possibly due to variations in the arrangements of the atoms in the materials. In addition, peaks with low intensity could not be identified due to the fact that it is not possible to distinguish them from the low signal-to-noise ratio of the background. It is worth noting that the presence of the identified secondary phases indicates that the process still needs improvement to ensure a final product containing 100% kesterite. Secondary phases that arise during the synthesis process seriously affect the quality of the kesterite absorber film, which affects the carrier transport and reduces the open circuit voltage of the kesterite solar cell [25].

3.2. X-Ray Fluorescence (XRF)

The XRF analysis detected S, Cu, Zn, Sn and other contaminating elements, such as Si, Sc, Fe, Sr, Ti and Al, as the number of layers increases, the amount of contaminant becomes less evident. It is plausible to assume that this was a contamination problem, mainly due to the use of percussion solution, which can easily become contaminated, and the low purity of the microscopy plate used as, which is the substrate. Table 1 follows with the XRF analysis for the films deposited on glass plates using the Drop Casting method, where from information provided it is possible to observe the presence of S, Cu, Zn, Sn on the films without substrate effect. During the thermal synthesis process of kesterite precursors, loss of Sn and decomposition of kesterite may occur, as well as rapid diffusion of Cu and Sn elements, which may lead to both uneven distribution of the components and an incomplete reaction [25]. This is possibly one of the possible causes of the variation in the amounts of the elements in the deposited films.

Table 1: XRF analysis for the samples.

ELEMENT (%)	1 LAYER	2 LAYERS	3 LAYERS	4 LAYERS
S	68.21	33.52	62.73	73.60
Cu	14.52	49.32	21.94	15.78
Zn	16.20	10.22	11.81	7.90
Sn	1.07	6.94	3.52	2.72

3.3. UV-Vis analysis

The Uv-Vis analysis is important to characterize and study the behavior of the material in infrared, above 700 nm of wavelength, visible, above 400 nm and under 700 nm, and UV, under 400 nm. The transmittance describes and quantifies the percentage of light crossing through the material. Figure 4 analyzed the transmittance percentage, and the high transmittance is from 1 layer of material, and with more layers the transmittance decreases. Materials with high transmittance can be used to make transparent glass which can be used in decoration and energy generation at the same time.

Figure 5 analyzes the absorbance of the material. The absorbance peaks are similar to [29]. This phenomenon it's extremely important to solar application, because in photovoltaic solar cells the high absorbance can increase the efficiency of energy production and in solar thermal energy the high absorbance can be an increase factor to a good solar heater and more efficiency. Figure 6 showed the graphic of reflectance. In solar thermal energy, the reflectance is not good, because the reflected light does not cause absorption of heat by the panel. In solar photovoltaic, the reflectance helps the solar panel to not overheat and reflect part of the excess solar beams.

Transmittance is an optical property that depends on the layer and material of the film. The loss of transmittance in the infrared region observed in films (Fig. 4) as layers are added is possibly due to the effect of overlapping layers, while in the ultraviolet region it may be due to the influence of secondary phases. In the visible region, the loss of transmittance is attributed to both the effect of overlapping layers and the optical characteristics of the materials contained in the films. Similar behavior can be attributed to the absorbance and reflectance profiles. In addition, the effect of the material is analyzed through the calculation of the band gap illustrated in Figure 7.

For kesterite Cu_2ZnSnS_4 (CZTS) films the directed band gap is 1 eV unti1.5 eV [23]. Direct band gap for films obtained with different layers was determined from Kubelka-Munk analysis (Figure7). Direct band gap values for layers were 1.42 *e*V for 1 layer; 1.44 *e*V fot 2 layers; 1.44 *e*V for 3 layers and 1.40 *e*V for 4 layers. The band gap values that were in agreement to the values found in the literature associated a kesterite CZTS, with band gap between 1 eV and 1.5 eV [23] [30–36].

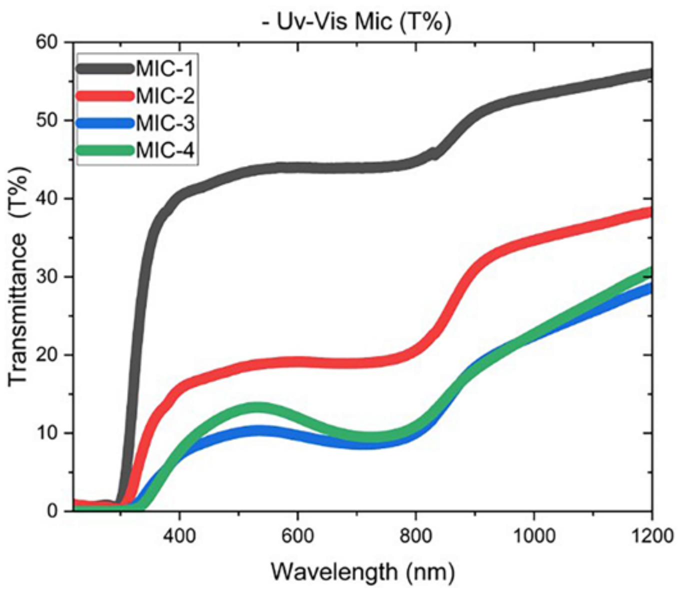

Figure 4: Transmittance values for the layers.

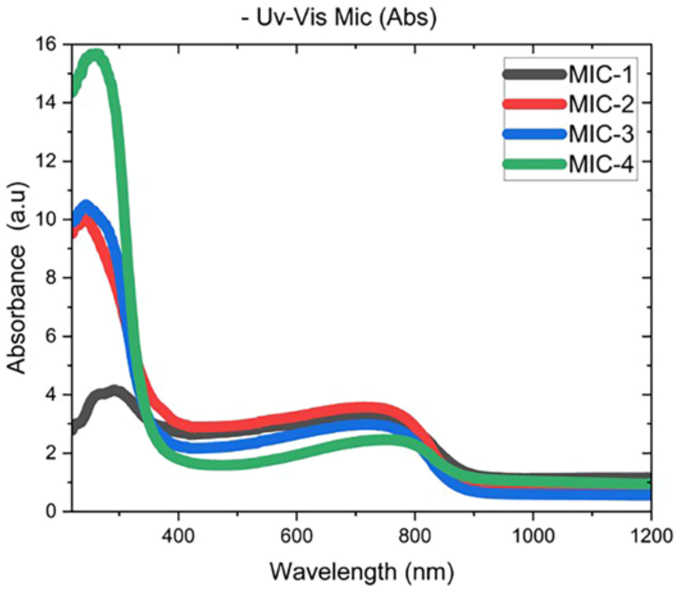

Figure 5: Absorbance plot for the layers.

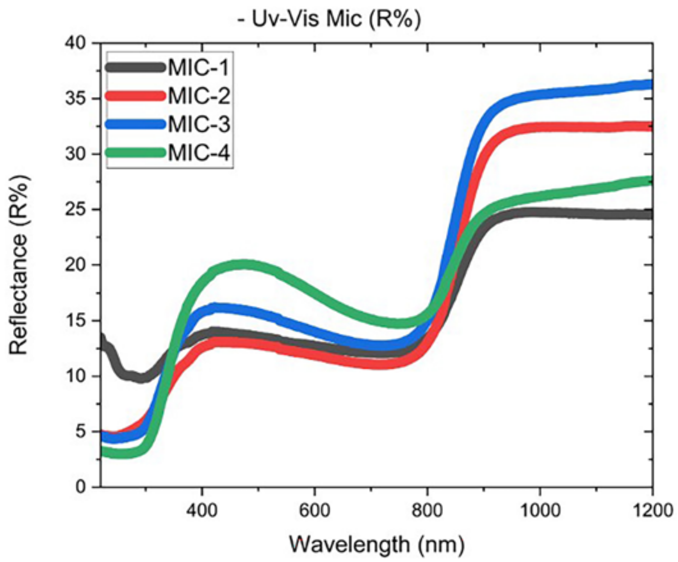

Figure 6: Reflectance plots for the layers.

3.4. FTIR analysis

FTIR is Infrared Spectroscopy, this analysis has a more detailed track on infrared, above 500 to 4000 wavenumber. The peaks observed for all layers are around 500; 1000; 1500; 2300 and 3500 cm^{-1} , for absorbance (Figure 8). This reinforces the results from the UV-Vis analysis, that is, the peaks were more prominent in the ultraviolet range of the spectrum. The increase from 1 layer to 2 layers also increased the absorbance. However, there was a decrease in absorbance from 3 to 4 layers, which suggests loss of the material quality, at 4 layers.

Figure 9 has the transmittance of the layers from 1 to 4 layers. The highest transmittance observed was around 75% for 1 layer of deposited material. As expected, as more layers are added on top of each other, the transmittance reduces, reaching the lowest value at around 20% transmittance for the 3 layers. The transmittance percentage reached the lowest points, dropping at around 3500 cm^{-1}. The vibrational band around 560 corresponds to the S-S bond; around 1600 is the C-C; around 1200 is the C-O and O-H is about 3500 cm^{-1} [37].

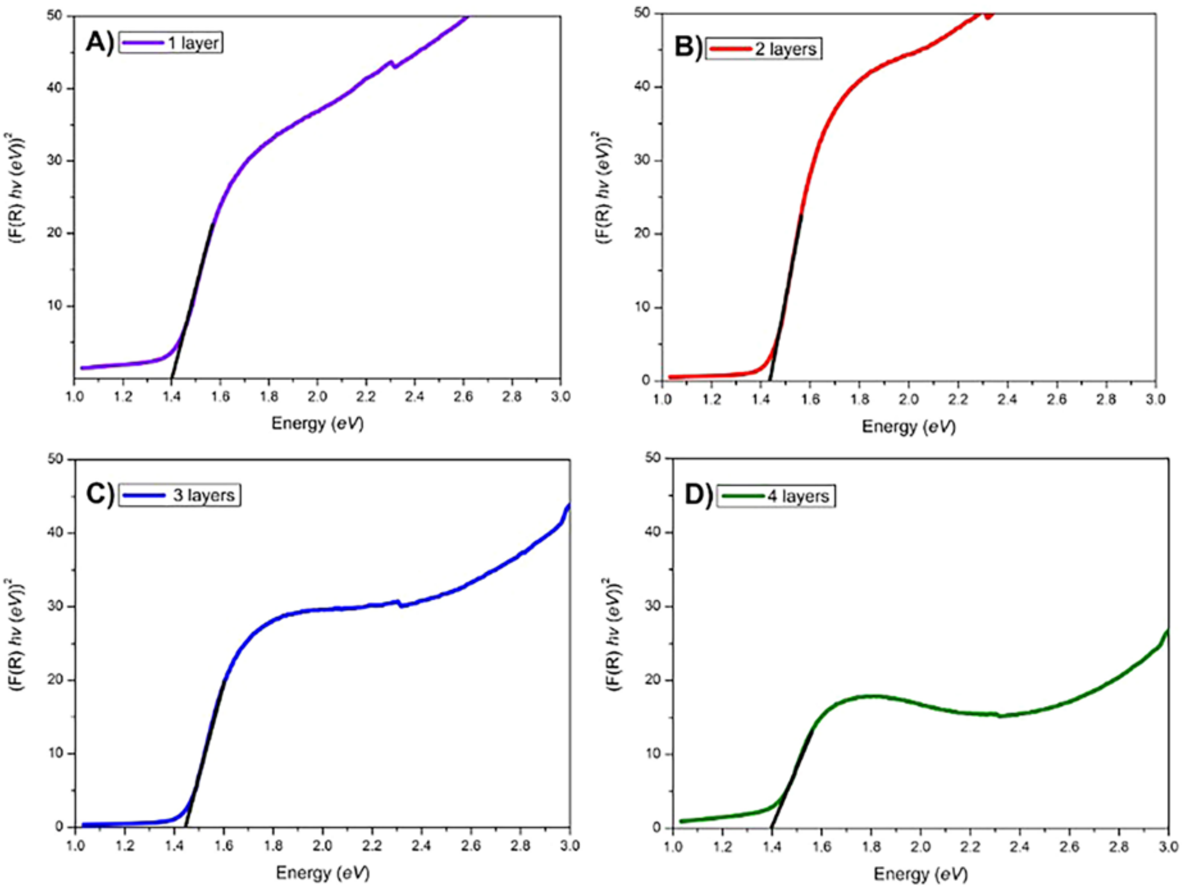

Figure 7: Directed band gap values for (A) 1 layer (B) 2 layers (C) 3 layers (D) 4 layers.

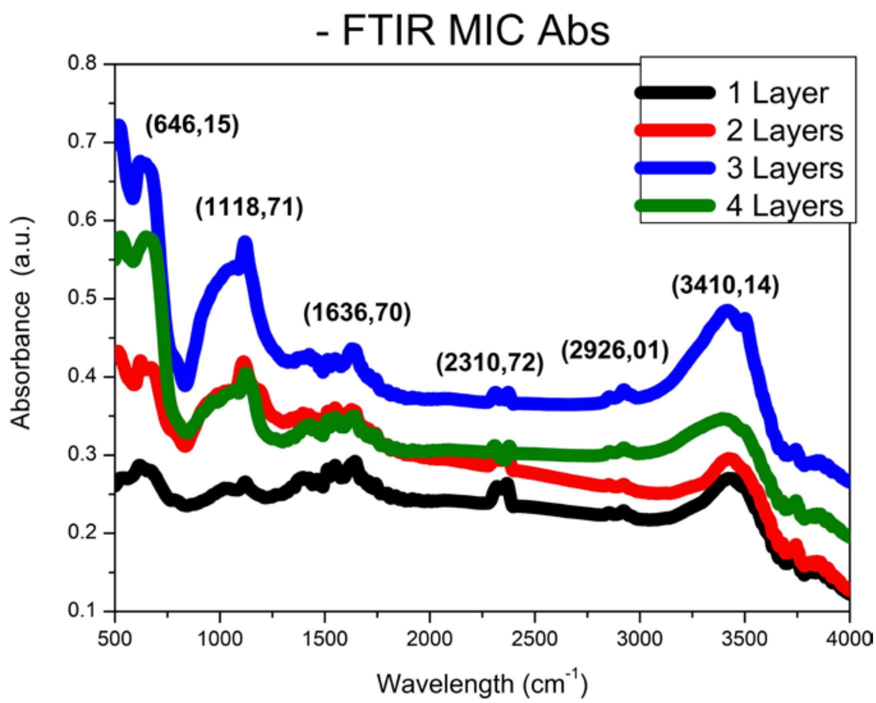

Figure 8: FTIR absorbance plots.

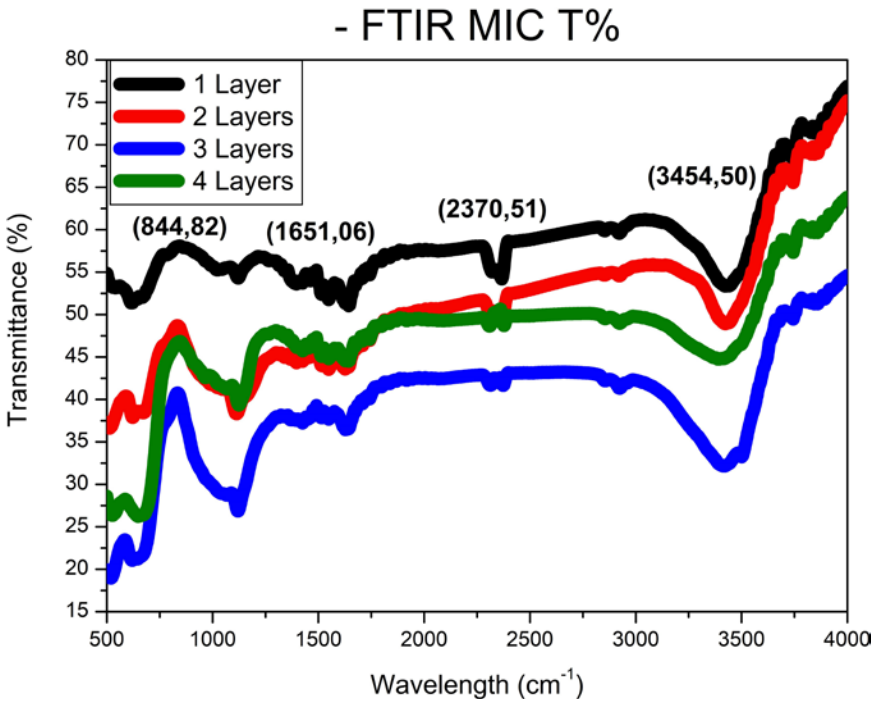

Figure 9: FTIR transmittance plots.

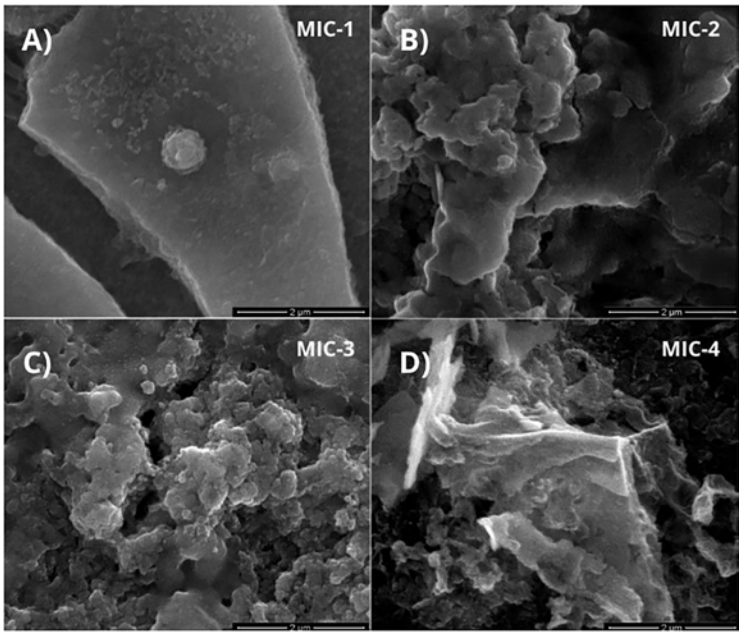

Figure 10: SEM analysis of the (A) 1 layer (B) 2 layers (C) 3 layers (D) 4 layers.

3.5. SEM analyses

Figure 10 shows the SEM analysis of the 1 layer (Figure 10 (A)); 2 layers (Figure 10 (B)); 3 layers (Figure 10 (C)) and 4 layers (Figure 10 (D)). The images show no defined geometry, but it is clear there is a formation of more clusters as the layers add up. At 4 layers, it is possible to observe that the clusters become more disorganized. The images show the growth of the materials as plates, and as the plates are being added up on top of each other, there is a crack observed in the plate's underneath. The formation of the films can help the efficiency in solar cells, since thin films are often used as the photoanode for photovoltaic applications.

4. CONCLUSION

The drop casting method successfully deposited the CZTS films, as observed by the analysis. The UV-Vis noted that the film has absorbance around 350 nm with band gap around 1.10 eV. Transmittance and reflectance reached values around 50 and 40%. This, together with the FTIR analysis proves the potential to be used as an optical device. The CZTS with 2 layers was identified as kesterite. Future work is thermogravimetric analysis of formation CZTS phases on FTO glass, this analysis provides a greater data of the mass loss from the synthesis process and the thickness effects using the precursor solution. Doping of CZTS/Se Solar Cells with metal salts containing Cd, Te or Ag to increase the Photovoltaic (PV) Efficiency, those contaminants increase the electron density because they are of the n-type and others increase the hole density because they are of the p-type.

5. ACKNOWLEDGMENTS

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