Nanostructured Cu_4sns_4 Thin Films Prepared by using Various Deposition Methods: Review

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Abstract—*Ternary compound such as Cu_4SnS_4 thin film has been deposited onto glass substrate by using various deposition methods. These deposition methods including electro deposition method, chemical bath deposition technique (CBD), successive ionic layer adsorption and reaction (SILAR) method and evaporation technique. The Cu_4SnS_4 films could be used in solar cell applications because of suitable band gap and have large absorption coefficient. X-ray diffraction showed that the obtained films are orthorhombic structure and polycrystalline in nature. These nano structured Cu_4SnS_4 films showed some unique properties such as p-type semiconductor material and band appropriate gap value(0.93 eV to 1.84 eV).*

Keywords—*Copper tin sulfide, thin films, solar cells, band gap, semiconductor*

INTRODUCTION

Preparation and characterization of binary [Gennady et al., 2019; Victoria et al., 2019; Guo et al., 2019; Yong et al., 2019; Jagtap et al., 2019; Lim et al., 2013], ternary [Daniel et al., 2019; Liu et al., 2019; Mohamed et al., 2019; Ning et al., 2019], quaternary [Huang et al., 2013; Lopez et al., 2015; Margarita and Urazov, 2013] and pentanary thin films [Hossain et al., 205; Lin et al., 2016; Lee et al., 2019; Babu et al., 2017; Cui et al., 2020] have been reported by many researchers. Generally, these films were produced by using physical method and chemical deposition technique [Ho and Anand, 2015]. Researchers have highlighted that each deposition method has its own advantages and limitations as well. The choice of deposition method strongly depended on the desired product, material cost, cost of operating and properties of materials.

In recent years, many scientists have attempted to looking for new ternary semiconductor materials for their applications in supercapacitor [Lokhande et al., 2018], sensor, solar cell [David et al., 2010], and optoelectronic devices. The Cu-Sn-S compounds have received great attention [Yuehui et al., 2016] due to excellent morphological, electrical, and optical properties [Nair et al., 2003]. Researchers highlighted that these materials are non-toxic [Naoyuki et al., 2019], cheap materials and earth abundant elements [Chalapathi et al., 2017]. In this work, preparation of Cu_4SnS_4 thin films by using various deposition techniques was reported. Characterization of these films was investigated. The photovoltaic parameters of Cu_4SnS_4 films (as light absorber materials for photovoltaic cell applications) were described.

LITERATURE SURVEY

Structural analysis of thin films

The deposition rate and thickness of evaporated Cu_4SnS_4 films were studied at 400 °C by using X-ray diffraction (XRD) technique. The films with orthorhombic phase was observed and showed polycrystalline structure. Many XRD diffraction peaks were observed and correspond to the (311), (121), (102), (112), (411), (022), (511), (222), (502), (512), (403) and (503) planes [Vani et al., 2013]. XRD patterns confirmed that the major peak corresponded to (311) plane, as its intensity increased when the thickness of the film was increased (0.25 µm to 1 µm. The lattice parameters were measured and found that a=13.52 Å, b=7.67 Å and c=6.43 Å. Debye-Scherrer formula was employed to measure the crystallite size during the experiment. Smaller (39 nm) and larger crystallite size (76 nm) could be observed in thinner films (0.25 µm) and thicker films (1 µm), respectively [Vani et al., 2013]. Raman analysis supported XRD data. Raman line could be detected in 317 cm^{-1}, indicated existence of Cu_4SnS_4 phase. Other binary (such as SnS, CuS, SnS_2, Cu_2S) or ternary compounds (such as Cu_2SnS_3, Cu_3SnS_4) were not detected.

Thin films of Cu_4SnS_4 have been synthesized through mechanochemical and doctor blade processes under different temperatures. XRD patterns showed that diffraction peaks are weak at 28.6°, 33.1°, 47.7 ° and 56.5° in as-deposited films. However, sharp diffraction peaks could be detected in annealed films (350 – 450 °C). Researchers found that Cu_2S peaks appeared at 500 °C, indicating the evaporation of tin and sulfur atom or decomposition of the Cu-Sn-S compounds [Chen et al., 2014].

The successive ionic layer adsorption and reaction (SILAR) deposition technique was employed to produce Cu_4SnS_4 films. Deposition was carried out in 60 cycles in $SnCl_2$, $CuCl_2$, and Na_2S solutions [Hao et al., 2013]. XRD patterns showed the presence of Cu_2S and SnS_2 in as –deposited films. The formation of orthorhombic phase Cu_4SnS_4 films could be observed in annealed films under H_2S atmosphere. Raman spectrum showed peak at 312 cm^{-1} confirmed the existence of Cu_4SnS_4 films.

The nanostructured Cu_4SnS_4thin films were produced by stack SnS–CuS (by chemical bath déposition annealing route) at 823K in a graphite box under various (N_2+S_2) pressures [Chalapathi et al., 2018]. The films showed orthorhombic phase and crystallize size was increased (200 nm to 260 nm) when the pressure was increased. XRD data confirmed that a mixture of orthorhombic phase and a dominant monoclinic phase could be observed when the films were prepared at 101.3kPa. Raman spectra analysis supported this explanation. Single peak at 322 cm^{-1} (formation of Cu_4SnS_4) and three peaks at 290 cm^{-1}, 351 cm^{-1} (formation of monoclinic phase), 318 cm^{-1} (corresponding to Cu_4SnS_4) could be found for the films synthesized at 1.3-66.7 kPa, and 101.3 kPa, respectively.

Electro deposition method was utilized to prepare Cu_4SnS_4 thin films onto indium doped tin oxide (ITO) glass (as substrate) under various deposition potentials [Kassim et al., 2010]. This deposition method has many advantages such as cheap raw materials, cheap equipment capital, can deposit large area thin film in low temperature. It is seen from XRD patterns that reflecting planes are (221), (420), (312), (512) and (711), could be observed at deposition potential of -0.4 and -0.6 V versus Ag/AgCl. However, only four diffraction peaks could be detected at -0.8 V. The effect of temperature on the electrodeposited Cu_4SnS_4 was studied [Anuar et al., 2008]. XRD data displayed six diffraction peaks when the films were prepared at low temperature such as 25 °C and 35 °C. The major peak corresponding to (221) plane and its intensity increased with the bath temperature from 25 °C to 50 °C.

Morphology Analysis of Thin Films

The morphologies of Cu_4SnS_4 thin films with various thicknesses produced by evaporation method were studied. The scanning electron microscopy (SEM) images indicated various morphologies such as worm like grains, and uniformly distributed in all samples. However, small grain with regular shape and bigger grain with multiple structure were observed in thickness less than 0.5 µm and more than 0.75 µm, respectively [Vani et al., 2013]. The influence of annealing temperature on the thin films was studied. The Cu_4SnS_4 films prepared at low annealing temperature (350 °C- 450 °C) are powder-like, densely packed if compared to 500 °C. The morphologies of SILAR deposited thin films were studied in H_2S atmosphere [Hao et al., 2013]. It was found that as-deposited films exhibited cluster approximately few hundred nanometers. However, annealed films under H_2S atmosphere showed coarse surface and small amount of holes. The nanostructured Cu_4SnS_4 thin films were produced by stack SnS–CuS (by chemical bath déposition annealing route) at 823K under various (N_2+S_2) pressures [Chalapathi et al., 2018]. Field emission scanning electron microscope (FESEM) results exhibited that the (N_2+S_2) pressure can control the morphology of films at 1.3 kPa (large grains with 3-6 micrometers and compact grains), 26.7 kPa to 66.7 kPa (grains size increases up to 6 micrometers), and 101.3 kPa (small grain with 2 micrometers, a few voids presented). The influence of deposition potential on electrodeposited Cu_4SnS_4 films was studied [Kassim et al., 2010]. These films showed incomplete coverage of the surface of substrate (at deposition potential of -0.4 versus Ag/AgCl), compact and smooth surface (at deposition potential of -0.6 versus Ag/AgCl) and not uniform surface (at deposition potential of -0.8 versus Ag/AgCl) based on atomic force microscopy (AFM) images. The Na_2EDTA was used as complexing agent during the chemical bath deposition of Cu_4SnS_4 films [Anuar et al., 2010]. Atomic force microscopy images revealed that the film thickness increased (640 nm to 981 nm) with increasing Na_2EDTA concentration (0.01 M to 0.05 M). However, its thickness was 125 nm when the 0.1M of complexing agent was used.

Compositional Analysis of Thin Films

Energy dispersive X-ray analyser (EDAX) was employed to investigate the compositional of thin films. The obtained evaporated Cu_4SnS_4 films with a thickness of 1 µm indicated the elemental composition was copper (43.35%), tin (15.56%) and sulfur (41.09%), respectively [Vani et al., 2013]. The nanostructured Cu_4SnS_4 thin films were produced by stack SnS–CuS (by chemical bath déposition annealing route) at 823K under various (N_2+S_2) pressures [Chalapathi et al., 2018]. The atomic percentage of sulfur (44.2% to 51.6%) and tin (12.1% to 15.7%) were increased, but copper decreased (43.1% to 32.7%) as the (N_2+S_2) pressure was increased from 1.3 kPa to 101.3 kPa. Chemical bath deposition method was used to prepare Cu_4SnS_4 films under experiment conditions such as at pH 1.5, bath temperature of 50 °C, 120 minutes, and 0.05 M of electrolyte concentration [Tan et al., 2010]. The EDAX analysis indicated the presence of only copper (49.1%), tin (12.6%) and sulfur (38.3%) in sample.

Optical Analysis of Thin Films

The transmittance of the evaporated Cu_4SnS_4 films with various thicknesses was studied. The presence of direct optical transition could be observed when a steep increase in the transmittance near the fundamental absorption [Vani et al., 2013]. Experimental results revealed that absorption edge was moved towards longer wavelength as the thickness was increased (0.25 µm to 1 µm). They conclude that the decrease of the band gap (1.47 eV to 1.21 Ev), due to the reduce of structural disorder and increase in crystalline size. The influence of annealing temperature on the Cu_4SnS_4 prepared by mechanochemical and doctor blade processes was studied [Chen et al., 2014]. The UV-Visible –IR spectra indicated that absorption intensity reduces at 935 – 1500 nm, but, its intensity increases at wavelength longer than 1500 nm, with the increased annealing temperature from 350 °C to 500 °C. The optical properties of thin films highlighted that Cu_4SnS_4 could be very sensitive to the annealing temperature in terms of band gap measurement. Band gap was 0.55 eV at 350 °C, it reduces with increasing annealing temperature up to 500 °C (1.02 Ev). The Cu_4SnS_4 thin films were synthesized by using successive ionic layer adsorption and reaction method [Hao et al., 2013]. The band gap and optical absorption coefficients are 0.93 eV and 10^4 cm^{-1}, respectively. Deposition potential plays an important during the preparation of thin films. The band gap values of electro deposited Cu_4SnS_4 films at deposition potential of -0.4 V to -0.8 V versus Ag/AgCl are in the range of 1.58 eV to 1.84 eV [Kassim et al., 2010]. Preparation of Cu_4SnS_4 thin films onto substrate (indium tin oxide coated glass) via chemical bath deposition method in the presence and absence of complexing agent [Atan et al., 2010]. The films produced by using complexing agent such as Na_2EDTA showed high absorption characteristics because of more materials successfully deposited onto substrates. The presence of complexing agent during the deposition process produced better quality of films.

Electrical Analysis of Thin Films

Evaporated Cu_4SnS_4 thin films showed p-type electrical conductivity based on the hot probe test. The resistivity (5.8 X 10^2Ωcm to 2.5 X 10^2 Ωcm) and the mobility of the films (12 $cm^2V^{-1}s^{-1}$ to 7 $cm^2V^{-1}s^{-1}$) decreased, however, the carrier concentration of the thin films increased (9 X 10^{14} cm^{-3} to 3.6 X 10^{15} cm^{-3}) with the increase of film thickness (0.25 µm to 1 µm) [Vani et al., 2013]. On the other hand, researchers have reported that the electrical resistivity decreased as the temperature was increased, showing the semiconducting properties [Amitava et al., 2017]. The p-type behaviors in Cu_4SnS_4 films could be supported by large positive Seebeck coefficients [Amitava et al., 2017]. The Seebeck coefficients increased when the temperature was increased during the experiment. Electrical properties of successive ionic layer adsorption and reaction (SILAR) deposited thin films were investigated. The electrical conductivity increased when the temperature was increased from room temperature (3.6 $\Omega^{-1}cm^{-1}$) to 475 K [Hao et al., 2013]. The activation energy values were 0.009 eV and 0.06 eV in the temperature region less than 343 K, and more than 343K, respectively. The nanostructured Cu_4SnS_4 thin films were produced by stack SnS–CuS (by chemical bath déposition annealing route) at 823K under various (N_2+S_2) pressures [Chalapathi et al., 2018]. Resistivity, mobility and carrier concentration of these films were found to be in the range of 0.41 to 0.52 Ωcm, 69.5 to 150 cm^2/Vs, and 1.96 x10^{17} to 1.25 x 10^{18} cm^{-3}, respectively.

Photovoltaic Characteristics Analysis of Thin Films

Solar cell was fabricated by using Mo/Cu_4SnS_4/In_2S_3/TiO_2/fluorine doped tin oxide glass. Short circuit current (17.44 to 29.24 mA/cm^2), open circuit voltage (0.21 to 0.3 V) and power conversion efficiency (0.91 % to 2.34 %) increased when the temperature was increased from 350 ° C to 375 °Cduring the experiment. However, these values decreased [Chen et al. 2014] as the temperature was increased to 500 °C (short circuit current=1.12 mA/cm^2, open circuit voltage=0.03V, fill factor =0.26, power conversion efficiency= 0.009%).

CONCLUSIONS

Cu_4SnS_4 thin films have been prepared by using various deposition methods under different experimental conditions. Physical properties of films were characterized via X-ray diffraction, atomic force microscopy, scanning electron microscopy, UV-Visible spectrophotometer, energy dispersive x-ray analyzer, Raman spectroscopy technique. The formation of Cu4SnS4 phase has been confirmed by using X-ray diffraction. The highest power conversion efficiency of obtain films was 2.34%.

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