Fabrication of Cu_4SnS_4 Thin Films: A Review

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***Abstract*-Ternary compounds such as Cu_4SnS_4 thin films can be deposited onto glass substrates by various deposition methods: electrodeposition, chemical bath deposition, successive ionic layer adsorption and reaction, and evaporation techniques. Cu_4SnS_4 films could be used in solar cell applications because of their suitable band gap and large absorption coefficient. This paper reviews previous researches on Cu_4SnS_4 thin films. X-ray diffraction showed that the obtained films are orthorhombic in structure and polycrystalline in nature. Cu_4SnS_4 films exhibited p-type electrical conductivity and indicated band gap values in the range of 0.93 to 1.84eV.**

Keywords-copper tin sulfide; thin films; solar cells; band gap; semiconductor

I. INTRODUCTION

The preparation and characterization of binary [1-6], ternary [7-10], quaternary [11-13] and pentanary thin films [14-18] have been reported. In general, these films are produced using various physical and chemical deposition techniques [19], each having its own advantages and limitations. The choice of deposition method depends strongly on the desired product, material cost, operational cost, and material's properties. In recent years, many scientists researched on new ternary semiconductor materials for their applications in supercapacitor [20], sensors, solar cell [21], and optoelectronic devices. The Cu-Sn-S compounds have attracted great attention due to their excellent morphological, electrical, and optical properties [22, 23]. These materials are non-toxic [24], cheap, and derive from earth abundant elements [25]. This paper examines various deposition techniques used on the production of Cu_4SnS_4 thin films, investigating their results. Moreover, the photovoltaic parameters of Cu_4SnS_4 films used as absorber material in solar cell applications are presented.

II. LITERATURE REVIEW

A. Structural Analysis of Thin Films

The deposition rate and thickness of evaporated Cu_4SnS_4 films have been studied at the substrate temperature of 400°C using X-Ray Diffraction (XRD). The films with orthorhombic phase were observed showing polycrystalline structure. Many XRD diffraction peaks were observed corresponding to the (311), (121), (102), (112), (411), (022), (511), (222), (502), (512), (403) and (503) planes [26]. XRD patterns confirmed that the major peak corresponded to the (311) plane, as its intensity increased when the film's thickness increased from 0.25μm to 1μm. Lattice parameters were measured as a=13.52Å, b=7.67Å and c=6.43Å. Debye-Scherrer formula was used to calculate the crystallite size. Smaller crystallites sized 39nm were observed in thinner films (0.25μm), because of the strong interaction between the substrate and the vapored atoms [26]. Larger crystallites sized 76nm could be found in thicker films (1μm) due to columnar grain growth in the films. Raman analysis was in aggreement with the XRD results. Raman line was detected in $317cm^{-1}$, indicating the 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 were synthesized through mechanochemical and doctor blade processes under different temperatures. XRD patterns showed that diffraction peaks were weak at 28.6°, 33.1°, 47.7° and 56.5° in as-deposited films. However, sharp diffraction peaks were detected in films annealed at 350–450°C. Researchers found that Cu_2S peaks appeared at 500°C, indicating the evaporation of tin and sulfur atoms or decomposition of the Cu-Sn-S compounds [27]. The Successive Ionic Layer Adsorption and Reaction (SILAR) method was used to produce Cu_4SnS_4 films. Deposition was carried out in 60 cycles in $SnCl_2$, $CuCl_2$, and Na_2S solutions [28]. XRD patterns showed the presence of Cu_2S and SnS_2 in deposited films. The formation of orthorhombic phased Cu_4SnS_4 films was observed in annealed under H_2S atmosphere procedure. Raman spectrum showed a peak at $312cm^{-1}$ confirming the existence of Cu_4SnS_4 films. Nanostructured Cu_4SnS_4 films were produced by annealing chemical bath deposited SnS–CuS stacks at 823K in a graphite box under various N_2+S_2 pressures [29]. Orthorhombic phase and crystallize size increased (200nm to 260nm) as pressure increased. XRD data confirmed that a mixture of orthorhombic and a dominant monoclinic phase was observed when the films were prepared at 101.3kPa. Raman spectrum analysis supported this finding. A single peak at $322cm^{-1}$, corresponding to Cu_4SnS_4, and three peaks at $290cm^{-1}$, $351cm^{-1}$ (corresponding to monoclinic), $318cm^{-1}$ (corresponding to Cu_4SnS_4) were found for films synthesized at 1.3-66.7kPa, and 101.3kPa, respectively.

Electrodeposition was used to prepare Cu_4SnS_4 thin films onto indium doped tin oxide glass substrate under various deposition potentials in [30]. This deposition method has many advantages such as cheap raw materials and equipment, while it can deposit a large area of thin film in low temperature. XRD patterns showed that reflecting planes are (221), (420), (312),

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(512), and (711), while a deposition potential of -0.4 and -0.6V versus Ag/AgCl was observed. However, only four diffraction peaks were detected at -0.8V. The effect of temperature on electrodeposited Cu_4SnS_4 was studied in [31]. XRD analysis showed six diffraction peaks when the films were prepared at low temperatures such as 25 and 35°C. The major peak corresponded to (221) plane, and its intensity increased as bath temperature increased from 25°C to 50°C.

B. Morphology Analysis of Thin Films

The morphology of Cu_4SnS_4 thin films with various thicknesses produced using the evaporation method was also studied. Scanning Electron Microscopy (SEM) images indicated worm like grains uniformly distributed on the substrate surface in all samples. However, small grains with regular shapes and bigger grains with multiple structures were observed in thicknesses less than 0.5μm and more than 0.75μm, respectively [26]. The effect of annealing temperature was also reported. Cu_4SnS_4 films prepared at low annealing temperatures (350-450°C) are powder-like and densely packed compared to films prepared at 500°C. The morphology of SILAR deposited thin films in H_2S atmosphere was studied in [28]. It was found that as-deposited films contained clusters in the size of hundreds of nanometers. However, annealed films under H_2S atmosphere showed coarse surfaces and small amounts of holes. Nanostructured Cu_4SnS_4 films were produced by annealing chemical bath deposited SnS–CuS stacks at 823K in a graphite box under various N_2+S_2 pressures [29]. Field Emission Scanning Electron Microscope (FESEM) results showed that N_2+S_2 pressure can control the morphology of films at 1.3kPa (large grains with 3-6μm and compact grains), 26.7 to 66.7kPa (grains' size increased up to 6μm), and 101.3kPa (small 2μm grains, with a few voids). The influence of deposition potential on electrodeposited Cu_4SnS_4 films was studied in [30]. These films showed incomplete coverage substrate's surface (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 influence of the concentration of Na_2EDTA complexing agent on the chemical bath deposited Cu_4SnS_4 films was studied in [32]. AFM images revealed that film's thickness increased from 640nm to 981nm with increasing Na_2EDTA concentration from 0.01M to 0.05M. However, its thickness was 125nm when 0.1M of complexing agent was used.

C. Compositional Analysis of Thin Films

Energy Dispersive X-ray Analysis (EDAX) has been utilized to study the composition of thin films. The evaporated 1μm thick Cu_4SnS_4 films indicated that the elemental composition was copper at 43.35%, tin at 15.56%, and sulfur at 41.09%, respectively [26]. Nanostructured Cu_4SnS_4 films were produced by annealing chemical bath deposited SnS–CuS stacks at 823K in a graphite box under various N_2+S_2 pressures [29]. As N_2+S_2 pressure increased from 1.3kPa to 101.3kPa the atomic percentage of sulfur and tin increased from 44.2% and 12.1% to 51.6% and 15.7%, respectively, but copper decreased from 43.1% to 32.7%. Chemical bath deposition has been used to prepare Cu_4SnS_4 films under experimental conditions such as: pH 1.5, bath temperature 50°C, for 120 minutes, and 0.05M of electrolyte concentration [33]. The EDAX analysis indicated the presence of only copper (49.1%), tin (12.6%) and sulfur (38.3%) in the sample.

D. Optical Analysis of Thin Films

The transmittance of the evaporated Cu_4SnS_4 films with various thicknesses has been also studied. The presence of direct optical transition was observed with a steep increase in the transmittance near the fundamental absorption [26]. Experimental results revealed that absorption edge moved towards longer wavelength as the film thickness increased from 0.25μm to 1μm. The band gap decrease of thin films from 1.47eV to 1.21eV with the increase in film thickness was caused by the reduction of structural disorder and the increase in the crystalline size. The influence of annealing temperature on the Cu_4SnS_4 prepared by mechanochemical and doctor blade processes was studied in [27]. The UV-Visible-IR spectra indicated that absorption intensity reduced at 935–1500nm, but, its intensity increased at wavelengths longer than 1500nm as annealing temperature increased 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. Cu_4SnS_4 thin films synthesized by using SILAR method in [28] had band gap and optical absorption coefficients at 0.93eV and 10^4cm^{-1}, respectively. Deposition potential plays an important role during the preparation of thin films. The band gap values of electrodeposited Cu_4SnS_4 films at deposition potential of -0.4 to -0.8V versus Ag/AgCl were in the range of 1.58 to 1.84eV [30]. Preparation of Cu_4SnS_4 thin films onto indium tin oxide (ITO) coated glass via chemical bath deposition method in the presence and absence of complexing agent was described in [34]. The films produced by using complexing agent such as Na_2EDTA showed high absorption characteristics, as more materials were successfully deposited onto substrates. The presence of complexing agent during the deposition process produced better quality of films.

E. Electrical Analysis of Thin Films

Evaporated Cu_4SnS_4 thin films show p-type electrical conductivity based on the hot probe test. The increase of film thickness decreased resistivity and mobility of the films from $5.8\times10^2\Omega cm$ to $2.5\times10^2\Omega cm$ and $12cm^2V^{-1}s^{-1}$to$7cm^2V^{-1}s^{-1}$ respectively, while their carrier concentration increased from $9\times10^{14}cm^{-3}$ to $3.6\times10^{15}cm^{-3}$ [26]. On the other hand, electrical resistivity decreased as the temperature increased, showing their semiconducting properties [35]. The p-type behaviors in Cu_4SnS_4 films are supported by large positive Seebeck coefficients, indicating that major carriers are predominantly holes possibly arising from copper deficiency [35]. Seebeck coefficients increased as temperature increased during the experiment. Electrical properties of SILAR deposited thin films were also investigated, and electrical conductivity increased as temperature increased from room temperature to 475K [28]. Activation energy values were 0.009eV and 0.06eV in the temperature regions less and more than 343K, respectively. In nanostructured Cu_4SnS_4 films produced by annealing chemical bath deposited SnS–CuS stacks at 823K in a graphite box under various N_2+S_2 pressures, resistivity, mobility and carrier concentration were found to be in the range of 0.41 to

$0.52\Omega cm$, 69.5 to $150 cm^2/Vs$, and 1.96×10^{17} to $1.25\times10^{18} cm^{-3}$, respectively [29].

F. Photovoltaic Characteristics Analysis of Thin Films

Solar cells have been fabricated by using $Mo/Cu_4SnS_4/In_2S_3/TiO_2$/fluorine doped tin oxide glass in [27]. As temperature increased from 350°C to 375°C, short circuit current, open circuit voltage, and power conversion efficiency increased from 17.44 to $29.24 mA/cm^2$, from 0.21 to 0.3V, and from 0.91% to 2.34% respectively. However, these values decreased as temperature increased to 500°C. At this annealing temperature, short circuit current, open circuit voltage, fill factor and power conversion efficiencies were $1.12 mA/cm^2$, 0.03V, 0.26, and 0.009% respectively [27]. On the other hand, the photovoltaic performance of Cu_4SnS_4 thin films was studied in [36] achieving a power conversion efficiency of 2.4%.

III. Conclusions

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

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