Annealing Effect on the Properties of Co-evaporated Cu4SnS4 Films

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Abstract:- One of the potential absorber layers for thin film heterojunction solar cell manufacture is copper tin sulphide (Cu_4SnS_4). In the current work, Cu_4SnS_4 thin films were grown on glass substrates through co-evaporation at a substrate temperature of 300 °C. The as-grown films were annealed in vacuum at temperatures (Ta) ranging from 100 to 400 °C, and the effects of annealing on the properties of Cu_4SnS_4 films were investigated. The composition study revealed that at higher annealing temperatures, the layers were Cu-rich. The annealed layers were polycrystalline in nature and had an orthorhombic crystal structure, with the (311) peak being the predominant orientation, according to X-ray diffraction (XRD) patterns. The layers that were annealed at 300 °C had better crystalline properties. In the annealing heat range studied, the optical transmittance of the films was 50%. The energy band gap of the annealed films ranged from 1.6 to 1.93 eV as T_a changed. As the annealing temperature increased, the electrical resistance of the layers decreased. These findings were presented and discussed in depth.

Keywords:- *Cu4sns4 Films, Co-Evaporation, Annealing Effect, Thin Films, X-Ray Techniques.*

I. INTRODUCTION

Chalcopyrite compounds, notably $CuIn_xGa_{1-x}Se_2$, have played an important role in the development of polycrystalline thin film solar cells in recent years due to their appropriate characteristics. If solar cell technology is to become more cost-effective, the absorber material used in photovoltaic systems must be cheap, non-toxic, and plentiful. Furthermore, for high conversion efficiency, the material should have an ideal energy band gap as well as appropriate electrical properties. In this respect, copper tin sulphide (Cu_4SnS_4) has been identified as a viable option for many device applications [1, 2], particularly as an absorber material in solar cells [3]. It has more plentiful and less hazardous elements than many other semiconductors. Previously, we investigated the effect of substrate temperature on the physical properties of co-evaporated Cu_4SnS_4 films. The films possessed an electrical resistivity of $3.14x10^4$ cm and an optical band gap of 1.94 eV at a substrate temperature of 300 °C. To increase device performance, a good absorber layer with low electrical resistance is necessary. The incorporation of suitable dopants or the production of additional metal atoms [4] by post-deposition annealing or chemical treatment is an effective strategy for producing low-electric-resistance films. As a result, the current study aimed to look into the influence of annealing on the physical properties of co-evaporated Cu_4SnS_4 thin films.

- *Experimental*

Thermal co-evaporation was used to deposit Cu_4SnS_4 films on Corning 7059 glass substrates. The raw materials for evaporation from a tantalum boat were 5N pure CuS and SnS. The depositions were performed at 10^5 Torr utilising a box-type Hind HiVac system. Other deposition parameters, such as substrate temperature (Ts) and distance between source and substrates, remained constant at Ts = 300 °C and 20 cm, respectively.

The as-deposited Cu_4SnS_4 films were annealed at different temperatures that vary in range, 100 to 400 °C for 1 hour in vacuum (10^5 Torr).

The elemental composition and surface morphology of the annealed Cu_4SnS_4 films were examined using scanning electron microscope (SEM) (model: Zeiss EVO MA 15) attached with the energy dispersive X-ray analyser (EDAX)system (model: INCA Penta FET X3). The structural properties of the layers were studied by X-ray diffractometer (XRD) (model: Seifert 3003TT). The optical transmittance spectra of the films were recorded as a function of wavelength using a Perkin Elemer Lambda - 950 UV-Vis-NIR spectrophotometer in the wavelength range, 500 - 2500 nm.

II. RESULTS AND DISCUSSION

Visual examination of the annealed films at different temperatures demonstrated that the layers were uniform and devoid of pinholes. The scratch tape test revealed that the annealed films were also well adherent to the surface of the substrate. The EDAX spectrum of a typical Cu_4SnS_4 film annealed at a temperature of 300 °C is shown in Fig. 1 (a). The spectra showed peaks corresponding to Cu, Sn and S. The compositions of different elements present in the film are found to be 49.8 at. %, 29.6 at. % and 20.5 at. %, for Cu, Sn and S for a typical film annealed at 300 °C respectively.

At lower annealing temperatures, the sulphur composition was slightly high and as the annealing temperature is increased a deficiency of sulphur was observed, making the film Cu- rich.This is mostly due to the re-evaporation of 'S' from the film surface at high annealing temperatures due to the high vapour pressures present at such temperatures. All the as-deposited and annealed films exhibited polycrystalline nature with an orthorhombic crystal structure. The XRD spectra of Cu4SnS4 films annealed at dissimilar temperatures are exposed in Fig.1(b)

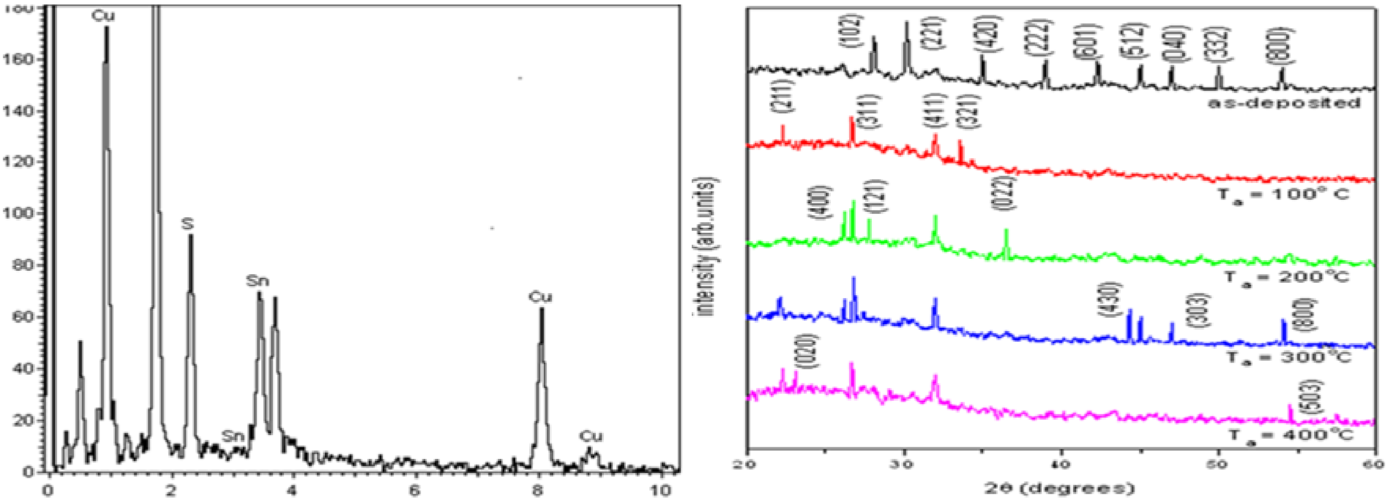

Fig.1 (A) EDAX Spectra For The Film Annealed At 300°c.

- *Xrd Spectra of Cu4sns4 Thin Films Annealed At Different Temperatures.*

The as-deposited films showed(221) plane as the dominant orientation whereas the annealed films indicated (311) plane as the preferred orientation. Generally in polycrystalline thin films, the predominant orientation mainly depends on the deposition process and processing parameters. The observed orientation changes might have occurred due to surface diffusion and migration of grain boundaries during the coalescence of nuclei where the smaller nuclei rotates easily on coalescence that induces the change in the orientation of different grains [5]. The lowest surface energy, grain boundary energy, and surface atom diffusion all contribute to a material's stable polycrystalline state.

Although both techniques produced orthorhombic crystal structures, Anuar et al. [6] reported the presence of (221) orientation for electrodeposited Cu4SnS4 films and Nair et al. [7] reported the presence of (311) plane as the preferred orientation for chemical bath deposition films. This illustrates that the presence of the dominant plane in Cu4SnS4 films is highly dependent on the manner and conditions under which the layers are manufactured. The evaluated lattice parameters were a=13.517, b=7.680, and c=6.478.The influence of annealing temperature on the lattice parameters a, b, and c is shown to be negligible. The calculated d-spacing and lattice parameters are quite close to those in the standard JCPDS data file (Card no. 29-0584). Using the Debye-Scherrer formula [8,] the crystallite size of the annealed layers was determined to be 50 nm for the layers annealed at 300 °C. The crystallite size increased as Ta increased, owing mostly to the coalescence of smaller nuclei or adjacent grains, which was aided by sufficient thermal energy, a frequent phenomenon reported in thin film growth. The grain size was significantly improved by annealing the layers at 300 °C.

SEM analysis of the experimental films reveals that the surface topology of the films is temperature dependent. Figure 2 shows SEM micrographs of the as-deposited and annealed Cu4SnS4 films. The images show needle-like grains that are closely packed. Furthermore, annealed layers have larger grain sizes than as-deposited films. However, when the annealing temperature (Ta) rises, the grain density rises, resulting in a densely packed network. This is supported by the XRD analysis.

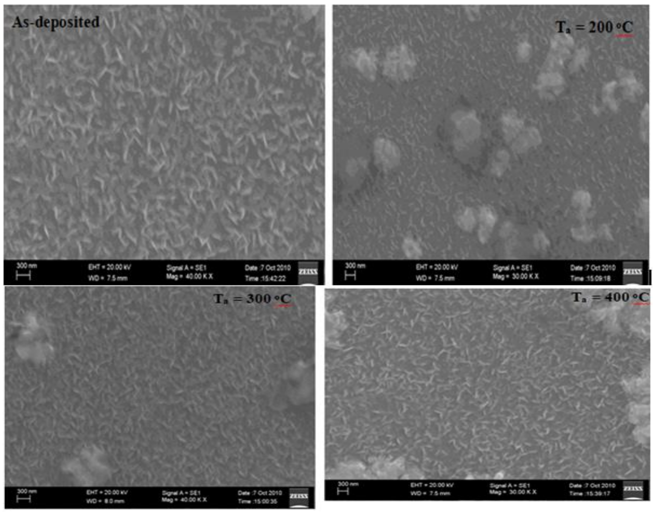

Fig.2 SEM Pictures For Annealed Cu4SnS4 Thin Films.

Figure 3(a) depicts the optical transmittance versus wavelength spectra of annealed Cu4SnS4 films. The highest transmittance of the films annealed at 300 °C was 50%. All annealed Cu4SnS4 thin films had absorption coefficients larger than 104 cm^{-1} above the basic absorption. The annealed layers energy band gap was calculated by projecting the linear component of the $(\alpha h\upsilon)^2$ Vs hυ plot onto the energy axis. Figure 3(b) depicts the fluctuation of the energy band gap with annealing temperature at 300 °C.

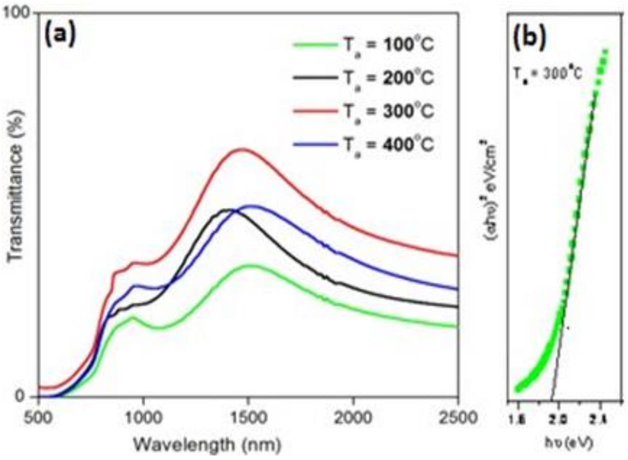

Fig 3 (A) Transmittance Vs Wavelength Spectra Of Cu4SnS4 Thin Films

- *Plot of* $(Ah\upsilon)^2$*Versus Hυ For Film Annealed At 300ºc.*

The power band gap of the as-deposited films was 1.7 eV, which decreased to 1.6 eV after annealing at a heat of 100 ºC. Above this annealing temperature the optical energy band gap of the films raised to 1.93 eV. This change in the energy band gap with annealing temperature might be due to the variation of the degree of crystallinity in the films [9].

All the annealed layers exhibited p-type conductivity. The annealed films' electrical resistivity was measured using a four-probe technique. The resistivity of the films decreased continuously with the raise of annealing temperature from 3.14×10^4 Ωcm to 6.68×10^3 Ωcm, with the decrease being more steep at the beginning up to a temperature of 300 ºC and approximately marginal afterwards. The decline of electrical resistivity with the increase of annealing temperature is due to the excess Cu present in the films since the layers annealed at higher temperature are Cu-rich. Also the lower resistivity could be because of the raise of crystallite size and a reduction in the number of crystal defects present in the layers because of annealing.

III. CONCLUSIONS

Polycrystalline Cu4SnS4 films were deposited by co-evaporation technique. The as-grown layers were annealed in vacuum for 1 hr at different temperatures that vary in the range, 100-400 ºC. The compositional analysis revealed that the annealed layers were rich in Cu. With an increase in annealing temperature, the preferred orientation of the films shifted from the (221) plane to the (311) plane. The films crystallinity rose with annealing temperature up to 300 ºC before declining beyond that. All the layers revealed orthorhombic crystal structure. The layers annealed at 300 ºC showed an optical transmittance of ~ 50 % with an energy band gap of 1.93 eV. As the annealing temperature was raised, the electrical resistance of the films fell from 3.14×10^4 Ωcm to 3.57×10^3 Ω cm.

REFERENCES

[1]. Ichimura M, Takeuchi K, Ono Y, Arai E. Thin Solid Films 2000; 361:98-101.
[2]. El-Nahass MM, Zeyada HM, Aziz MS, El-Ghamaz NA. J Opt Mater 2002; 20:159-170.
[3]. Devika M, Koteswara Reddy N, Ramesh K, Gunasekhar KR, Gopal ESR, Ramakrishna Reddy KT. Semicond Sci Technol 2006;21:1125–1131.
[4]. Mathew M, Jayakrishnan R, Ratheesh Kumar PM, Kartha CS, Vijayakumar KP, Kashiwaba Y, Abe T. J Appl Phys 2006;100:033504-1-8.
[5]. Revathi N, Prathap P, Venkata Subbaiah YP, Ramakrishna Reddy KT. Solid State Sciences 2009;11:1288–1296.
[6]. Anuar K, Ho SM, Tan WT, Atan S, Kuang Z, Haron MJ, Saravanan N. Solid StateSci Technol 2009;17:226-237.
[7]. Nair MTS, Lopez-Mata C, GomezDaza O, Nair PK. Semicond Sci Technol 2003;18:755–759.
[8]. Warren BE. X-ray Diffraction. Dover: New York; 1990.
[9]. Avellaneda D, Nair MTS, Nair PK. J Electrochem Soc 2010; 157:D346-D352.