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Effect of Copper Concentration on Optical Band Gap of Spin Coated Cu_2ZnSnS_4 Thin Films for Photovoltaic Application

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ABSTRACT

Spin coating method was used to grow copper zinc tin sulphide (CZTS) thin films on fluorine doped tin oxide (FTO) substrates. Copper nitrate, zinc nitrate, tin chloride, and thiourea were the sources of Cu, Zn, Sn, and S, respectively. Ammonia was used as pH adjuster and triethanolamine (TEA) served as a complex agent. The precursor solution was formed by varying the concentration of copper from 0.05 M to 0.5 M while keeping the concentrations of other constituents constant. The effect of copper concentration was studied on transmittance, absorbance, reflectance and band gap of the films. The result shows that the film deposited at 0.05 M of copper exhibits highest transmittance and lowest reflectance in the visible region of electromagnetic spectrum and the band gap of the film at 0.2 M of copper was 3.22 eV while the band gap of the film at 0.05 M was 3.80 eV. The film can be used as a buffer layer in heterojunction thin film solar cells.

INTRODUCTION

Solar energy is most reliable among the alternative energy sources because its energy is fueled by sun and the sun releases a huge quantity of energy manifested as heat and radiation at no cost (Sharma, Jain, & Sharma, 2015). The sun expected life is still between 5000 and 10,000 billion years for the climate system with a with a radius of around 7.0 x 10^7km, it makes up approximately 98.6% of the solar system's mass (Luceño-sanchez, Diez-Pascual, & Capilllia, 2019).

A photovoltaic device consists of a p-n junction where the light-absorbing layer has a specific band gap. When photons with energy equal to or greater than this band gap strike the device, they excite electrons from the valence band to the conduction band within the absorbing material. This excitation creates electron-hole pairs. The built-in electric field at the p-n junction then separates these charge carriers, driving electrons toward the n-type side and holes toward the p-type side, generating a current that can be harnessed as electrical energy. (Chander, Krishna, & Srikanth, 2015; Fluieraru et al., 2019)

Copper zinc tin sulphide (CZTS) quaternary semiconductor substance has developed as one of the hopeful materials for photovoltaics applications. Every constituent element in CZTS is earth-abundant and environmentally friendly (Ali, Hussein, & Khudhur, 2024; Boutebakh, Zeggar, Attaf, & Aida, 2017; Isah et al., 2013; Mohammed et al., 2021). Different methods have been documented to deposit the films of CZTS by many researchers. The methods include thermal (Isah et al., 2013; Zakaria et al., 2019), sputtering (Cui, Liu, Sun, Liu, & Yan, 2017; Olgar, Klaer, Mainz, Ozyuzer, & Unold, 2017; Yang, Zhang, Li, Hao, & Song, 2018), electrodeposition (Paraye, Manivannan, & Victoria, 2020) spray pyrolysis (Boutebakh et al., 2017; Diwate, Mohite, Shinde, Rondiya, & Pawbake, 2017), chemical bath deposition (Hamzah, Jabbar, & Mesan, 2017), spin coating (Fan et al., 2018; Islam et al., 2015; Kumar et al., 2016; Swami, Kumar, & Dutta, 2013) The spin coating method is the most straightforward, economical, and suitable for large-area deposition. In this study, spin coating method is used to deposit the films of CZTS and effect of copper concentration on the optical properties of the films is investigated.

MATERIALS AND METHODS

Copper nitrate ($Cu(NO_3)_2$) served as source of copper ion and its concentration was varied from 0.05 M to 0.5 M, 0.2 M of zinc nitrate was used as source of zinc ion, 0.2 M of tin nitrate used as the tin source, 0.8 M of thiourea served as source of sulphur, fluorine doped tin oxide

(FTO) was used as the substrates and methanol served as solvent. Six (6) different precursor solutions were prepared by mixing 10 ml of copper ion with 10 ml each of Zn, Sn and thiourea solutions under continuous stirring, 2 ml of triethanolamine (TEA) was added to serve as an agent of complexing. The precursor solution was stirred for 2 hours at room temperature. The solutions of aqueous ammonia added to it and the final pH of the resulting solution was about 12. A 5ml syringe was used to drop the precursor solution onto center of five (5) FTO substrates which had been clean ultrasonically with acetone and mounted on a spin coater (WS650MZ- 23NPP, Laurell Technology). And, the spin coater was allowed to spin for 25 seconds at 500 revolutions per minute. After which the substrate coated with the film, it was removed from the coater, and annealed at 100°C in an oven (UNISCOPE SM 9053, Surge Friend Medical, England). This was repeated at varying copper concentrations. Avantex UV visible spectrophotometer was used to measure the thin films' optical transmittance in the wavelength range of 239.534 nm to 999.495 nm.

The absorbance (A) was calculated from the percentage transmittance (T) using Equation1

$$A = 2 - logT \qquad (1)$$

The reflectance (R) was obtained using Equation 2.

$$A + T + R = 1 \qquad (2)$$

The absorbance coefficients (α) of the films were calculated using Equation.

$$\alpha = \frac{2.303A}{t} \qquad (3)$$

Where A is the absorbance and t = 120.6 nm which is the thickness of the films

The photon energy (E) was calculated in eV using Equation 4.

$$E = \frac{1243}{\lambda} \qquad (4)$$

Connection between absorbance coefficient (α) and incident photon energy (hv) is shown in Equation 5.

$$\alpha h\text{v} = A\sqrt{hv - E_g} \qquad (5)$$

RESULTS AND DISCUSSION

The transmittance of the film is presented in Fig 1. which shows that the transmittance rises as the wavelength increases in the visible region of electromagnetic spectrum and this agrees with (Bakr, & Mahdi, 2016) .However, the films coated at 0.05M concentration of Cu has the least transmittance of 96.7 % at wavelength of 401.16 nm and maximum transmittance of 100 % at 513.92 nm, the films deposited at 0.1 M has minimum transmittance of 44.12% at wavelength 402.37 nm and maximum transmittance of 65.29% at wavelength 695.88 nm, the films at 0.2 M copper transmitted visible electromagnetic radiation between 35.80 and 72.53 % at wavelength 401. 74 and 698.19 nm, respectively. The transmittance was between 44.12 and 78.95%, measured between 402.37 and 697.62 nm for the film at 0.4M copper. The measured transmittance at wavelengths between 401.15 and 699.91 was between 63.9 and 85. 16% for the films of CZTS spin coated at 0.5 M concentration of copper. The transmittances of the films at varying Cu concentrations were high in the visible part of electromagnetic radiation. The higher transmittance in visible region may be attributed to no stoichiometry between the variation of copper and other constituent elements in the films. However, a similar higher transmittance of 80% within the electromagnetic spectrum's visible area was recorded by Touati, Ben Rabeh, & Kanzari, (2014)

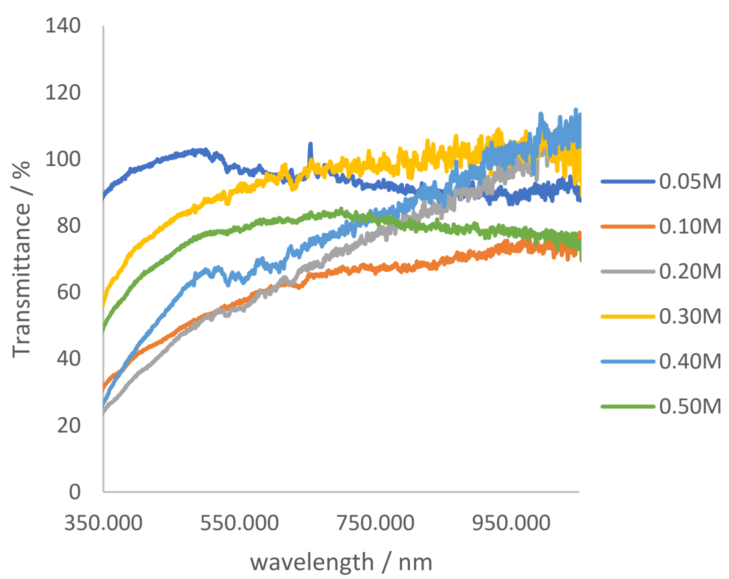

Figure 1: Transmission Spectral For CZTS for Varying Copper Concentration

Also, Fig. 2 shows the absorbance of CZTS at various concentrations of copper decreases as the wavelength increases for all the films, which is in line with (Deokate, Adsool, Shinde, Pawar, & Lokhande, 2014; Turgut & Keskenler, 2017). The maximum and minimum absorption was measured between 400 and 700 nm, and the average absorption was calculated. The CZTS films at the copper concentration of 0.05, 0.10, 0.20, 0, 30, 0.40 and 0.50 M had respective average absorptions of 2.05, 26.65, 29.60, 10.15, 7.30 and 23.15 %. This shows that the film coated at 0.05 M of Cu had the lowest absorbance and the film deposited at 0.2 M had the highest absorbance. CZTS films are normally used as absorber layers, so it is expected to have higher absorption in visible part of electromagnetic spectrum.

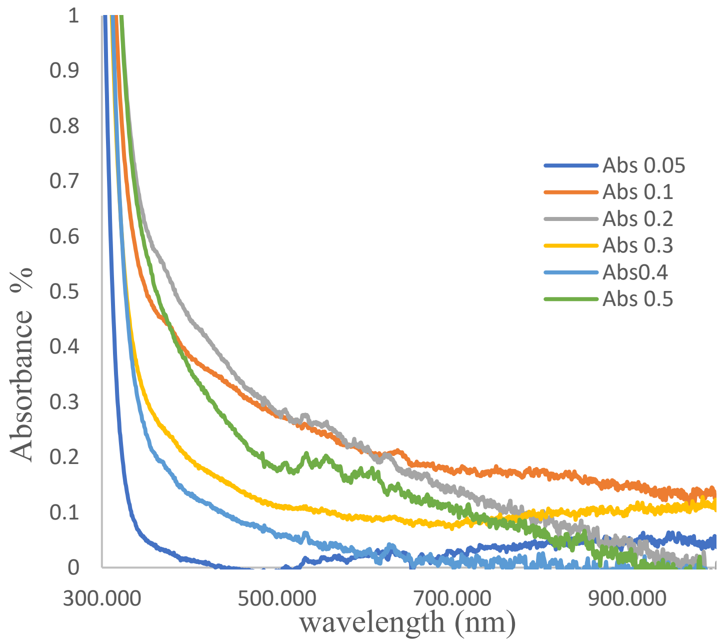

Figure 2: Absorption Spectral For CZTS for Varying Copper Concentration

The reflection of photons of spin coated CZTS thin films at varying copper concentration are obtained from the reflectance spectral of the films as shown in Fig 3.. It is seen that the reflection of the films deposited at 0.05 M and 0.3 M of copper decreased from 0.157% in the UV region at 317.33 nm to 0.00% at 500 nm in the observable part of the electromagnetic spectrum. This was possible because the film had transmitted about 100% of the incident waves. A similar result was observed by (Okoli, 2015) who deposited Magnesium sulphide films at different deposition times and observed low reflectance within the range of 0.067 and 0.186%. Also, the reflectance of CZTS thin films deposited at 0.1 M and 0.2 M concentrations of copper increases gradually in the UV region to the maximum value of 0.21 % at 399.98 nm and started decreasing to minimum value of 0.158 % and 0.137% at 700 nm for film deposited at 0.1M and 0.2 M, respectively. The reflectance of films at 0.4 M was maximum at 0.50% in the UV region and dropped sharply and oscillated between 494.32 and 627.26 nm between 400 and 700 nm and continuously decreased above 700 nm. The observed maximum and minimum reflectance in the visible region between 400 and 700 nm were 0.43 and 0.21 %. Similarly, the films grew at 0.5 M had the least reflectance of 0.05 % in the visible region. Generally, the observed reflectance is less than 1.0%, because it had higher transmittance.

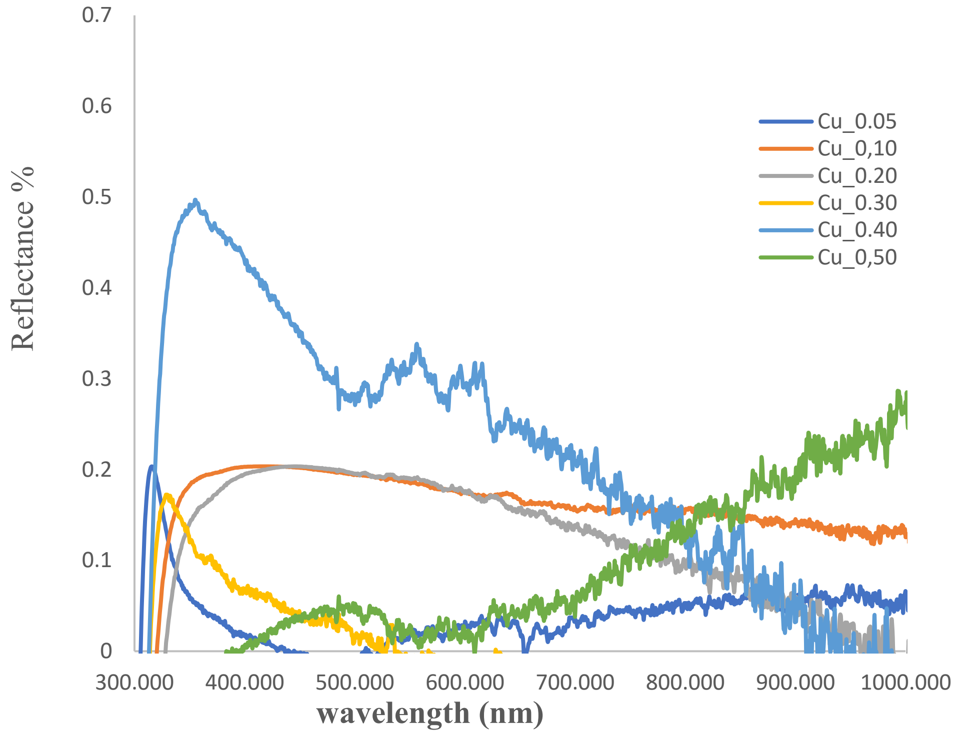

Figure 3: Reflection Spectral For CZTS for Varying Copper Concentration

The optical energy gaps are extrapolated from Fig 4. The band gap for spin-coated CZTS was between 3.22 and 3.80 eV. The film of CZTS deposited at 0.20 M of Cu had the lowest band gap, while the film with 0.05 of copper had the largest band gap. This implies that the film that had maximum transmittance had the lowest band gap and the film with the lowest transmittance had the highest energy gap. The band gap of spin-coated was higher than the ideal band gap of about 1.50 eV for layer of absorber in thin-film solar cells and the reason for this could be the low film thickness of 120. 6 nm and non-stochiometric of the ions that made up the precursor solutions. However, similar higher energy gap of 2.5 eV instead of 1.5 eV was obtained by Abdullahi, Momoh, Moreh, Bayawa and Saidu, (2020) in the deposition of CZTS using the RF sputtering technique and examined the consequence of heat treatments on the characteristics of the films. Also, the energy gap of about 2.9 eV which was higher than the bulk energy gap of 1.5 eV was observed for CdTe thin films by Singh et al. (2004)) reported improvement in the energy gap makes CdTe an ideal material for a photonic application and window component of CdTe homo junction device.

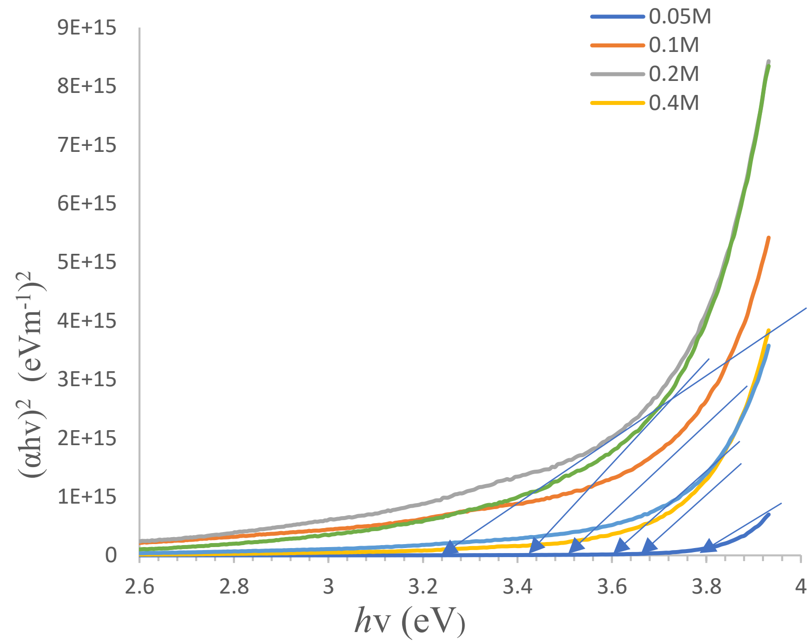

Figure 4: Plot of $(Ahv)^2$ against Photon Energy for CZTS at Various Copper Concentrations

CONCLUSION

The films of copper zinc tin sulphide are deposited onto fluorine doped tin oxide substrates using spin coating technique. The concentration of copper ions was varied and its effect was studied on transmittance, absorbance, reflectance and optical energy gap in visible region of electromagnetic radiation. The investigation shows that the transmittance was high while low reflectance was observed in the visible region of electromagnetic radiations. Also, the bandgap was higher than the bulk bandgap of the film. It is recommended that the film can be used as a buffer layer in heterojunction thin film solar cells. However, future characteristics such as x-ray diffractometry and scanning electron microscopy of the films can be investigated.

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