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STRUCTURAL AND OPTICAL PROPERTIES OF Cu_2ZnSnS_4 THIN FILMS GROWN USING A SOL GEL TECHNIQUE

Physics

KEYWORDS: CZTS, sol-gel, XRD, UV-VIS

Tarun Chandel	School of Studies in Physics, Jiwaji University, Gwalior – 474 011 (INDIA)
Vikas Thakur	School of Studies in Physics, Jiwaji University, Gwalior – 474 011 (INDIA)
Poolla Rajaram	School of Studies in Physics, Jiwaji University, Gwalior – 474 011 (INDIA)

ABSTRACT

Thin films of Cu_2ZnSnS_4 (CZTS) were prepared by a sol-gel technique. X-ray diffraction and UV-Visspectrop-hotometry studies were performed to investigate the structural and optical properties of the films. XRD and optical studies confirm the formation of nanocrystalline CZTS thin films. Due to quantum confinement the particle size reduces owing to blue shift.

INTRODUCTION

CZTS possesses huge potential for photovoltaic application due to its optimum energy band gap in the range 1.4-1.6 eV and high absorption coefficient (> 10^4 cm^{-1}) [1-2]. It constitutes non-toxic and readily available elements, which make it is a promising absorber for the use in photovoltaics devices. Solar cells based on CZTS absorber layers have shown conversion efficiencies of upto 8.4% [3]. CZTS thin films can be prepared by various techniques including sputtering [4], electrodeposition [5], chemical bath deposition [6] and spray pyrolysis [7]. In this work we have grown CZTS thin films by a Sol-Gel technique and analyzed them by XRD and UV-Vis spectroscopy.

EXPERIMENTAL

CZTS thin films were prepared using a sol–gel; spin coating process. $CuCl_2$, $ZnCl_2$, $SnCl_2$ and thiourea were used as the raw materials. 2-methoxy ethanol was used to prepare the sols and Monoethanolamine was used as a sol stabilizer. Complex sol of CZTS was prepared by dissolving 0.2M $CuCl_2$, 0.1M $ZnCl_2$, 0.1M $SnCl_2$ and 0.4M thio-urea. Sol was refluxed (while stirring magnetically) at a temperature of 50 °C for 1 hour. After refluxing, the sol was cooled for conversion of sol into gel and spin coated on glass substrates. The spin coating process was carried out using a SPIN NXG M1 (Apex Equipment) spin coater. The films were grown on glass substrates at a constant speed of 3000 rpm. They were dried at a temperature of 100 °C for 5 min after each spin coating step. Two samples were prepared by coating 5 times and 9 times, encoded as '5-L' and '9-L' respectively. After completion of the coating process, annealing of the as grown films was performed for one hour at a temperature of 350 °C in vacuum. The CZTS thin films were characterized using XRD employing Cu-K radiation of wavelength 1.5406 Å for their structural analysis. The optical studies were carried using a double beam UV-VIS spectrophotometer (Shimadzu, model 2450)

RESULT AND DISCUSSIONS

Fig. 1 shows the XRD patterns of CZTS thin films grown using sol-gel technique. The diffraction peaks centered at 2 theta angle equal to 28.5 degree corresponds to the reflection from the (112) plane [6]. The broad shape of the peaks suggests that the films are nanocrystalline in nature. The average crystallite size was calculated using the XRD peak broadening method (Scherrer's equation)

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where, D is the average crystallite size, λ is the wavelength of X-ray, is the full width at half maximum and θ is the diffraction angle. The calculated average crystallite size for 5-L and 9-L were found to be around 4.8 nm and 3.7 nm respectively.

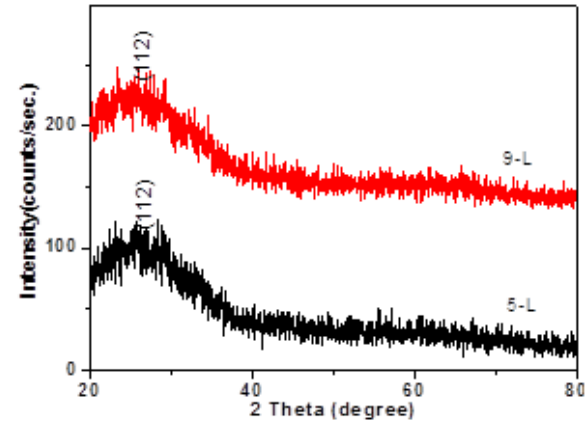


Figure 1: XRD patterns of CZTS nanocrystalline thin films

Fig. 2 shows the transmission spectra of CZTS thin films (5-L and 9-L). The absorption edge is observed around 700 nm. The optical band gap of the samples is determined using the Tauc relationship

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^m$$

Where, α is absorption coefficient, hυ is the photon energy in electron volts, A is a constant, Eg is the optical band gap energy and m is the type of optical transition (m= 2 for indirect transitions and m= ½ for direct transitions).The optical band gap values obtained from the intercept on the X-axis of $(\alpha h\upsilon)2$ versus hυ are 1.96 eV and 1.85 eV for '5-L' and '9-L' respectively (Fig. 3). These values are higher than the reported values for single crystal CZTS (1.5 eV). It can also be seen that the optical gap shifts from 1.85 eV to 1.96 eV as the particle size decreases from nm to nm. This increase in band gap with decrease in particle size is due to quantum confinement and is known as 'blue shift'. It is well known that as the particle size is reduced below the exciton radius of the material, quantum confinement effects begin to show up. The (bandgap in the case of semiconductors) increases with decreasing particle size and further the electron energy levels in the conduction and valence bands change from quasi-continuous to discrete.

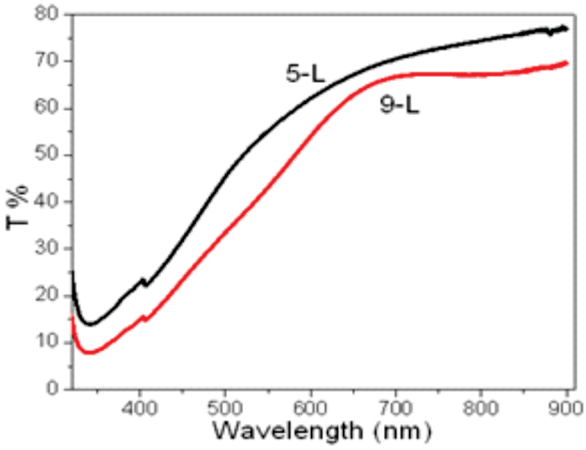


Figure 2: Transmission spectra of CZTS nanocrystalline thin films

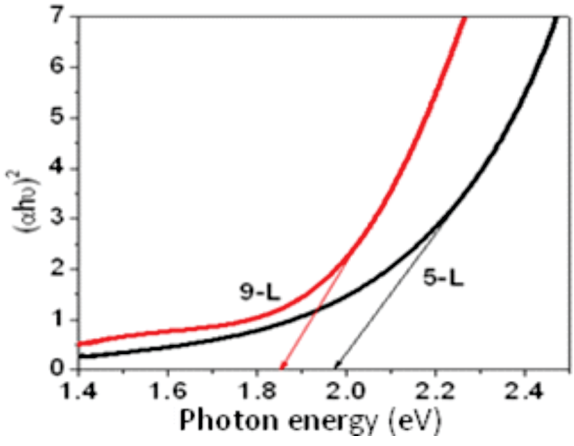


Figure 3: hυ versus (αhυ)2 plot of CZTS nanocrystalline thin films

CONCLUSIONS

Nnanocrystalline CZTS thin films were successfully grown by a sol-gel technique. XRD patterns confirm the growth of single phase CZTS having nanocrystalline nature. Optical studies show the blue shift in bandgap due to the quantum confinement effect.

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