An investigation on the effect of changing sulfur ratio and annealing on the physical properties of Cu_2ZnSnS_4 thin film

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دانشگاه دامغان

Introduction

In this research, we investigate the effect of changing the sulfur ratio and the annealing on the properties of CZTS thin film manufactured by the spray pyrolysis method (SPM). According to Kosyak et al [1], the V_s^{2+} is dominating in the CZTS thin films especially in the one zone annealing and Kumar et al [2] showed that $V_{S,\ Se}$ are donors defects which is not good for p-type CZTS. Adelifard research [3] showed that there is a high chance of vaporing Sulfur in the spray method because of its high temperature. Investigation on the SnS_2 manufactured by SPM by Arulanantham et al [4] suggest that increasing in sulfur can improve electrical properties as well as change in the band gaps also Courel et al [5] showed annealing CZTS in the presence of sulfur can improve many properties of it but these methods need expensive staff and special conditions. In this research, we investigate changing the S/M ratio in the solution made for spray and annealing in the open air as a replacement for the earlier expensive methods.

Method

Three solutions with S/M=1, 2, and 3 prepared in 50 cc deionized water and sprayed on the 360 oC glass with the nozzle distance keep constant at 30 cm and the constant rate of 7 cc/min, and then half of the samples were annealed at 350 oC in the open air for an hour. For investigating the electrical properties the 4-probe (Van der Pauw) and Seebeck method were used and for the optical properties, we used a Unico spectrometer in the range of 400-1100 nm.

Results

In the following electrical and optical properties for different S/M before and after annealing presented.

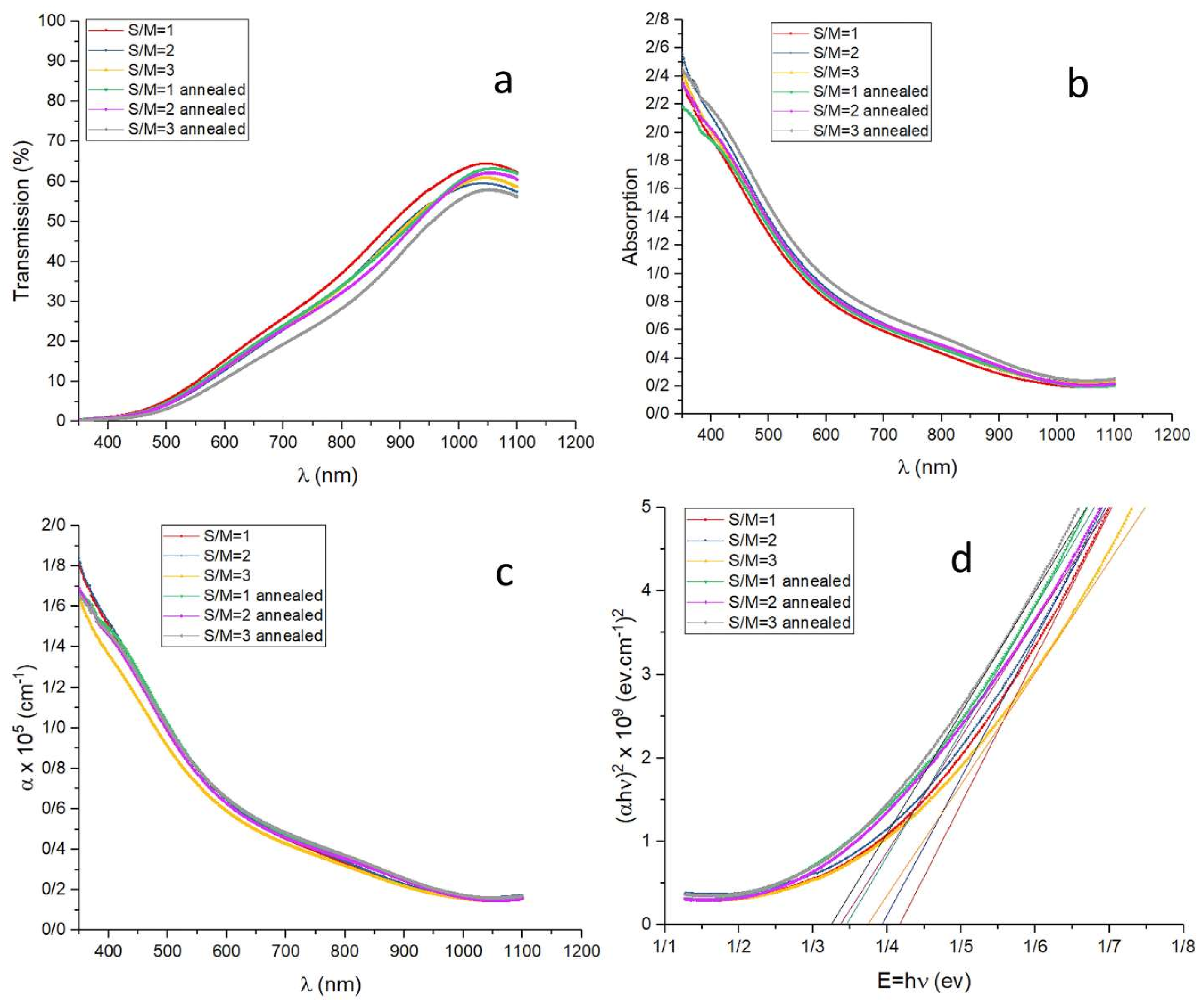

Figure 1

(a) Transmission, (b) absorption, (c) absorption coefficient and (d) bandgap of the layers

Table 1 – bandgap changing		
S/M	Bandgap (eV) As deposited	Bandgap (eV) Annealed
1	1.41	1.34
2	1.39	1.33
3	1.37	1.32

Table 1

Bandgap changing with different S/M for as deposited and annealed samples

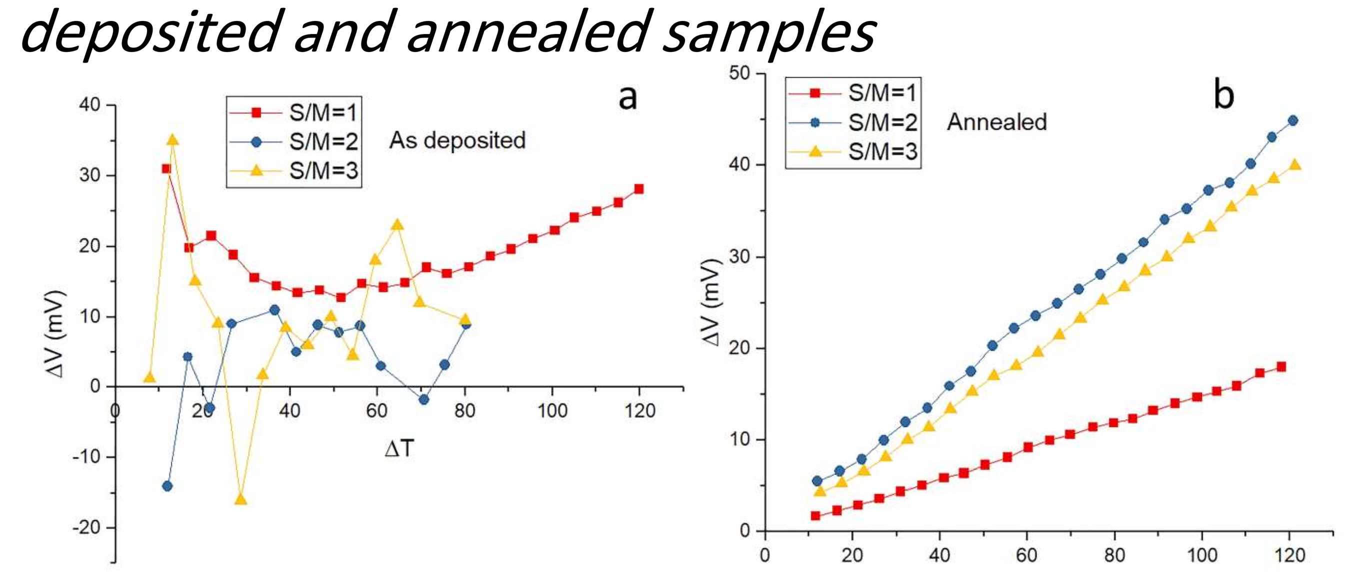

Figure 2

Seebeck effect (a) as deposited and (b) annealed

Table 2 – electrical properties changing				
S/M	$\rho_{As\ deposited}$ (Ω.cm)	$\rho_{Annealed}$ (Ω.cm)	$R_{sh,\ as\ deposited}$ (KΩ/sq)	$R_{sh,\ annealed}$ (KΩ/sq)
1	3.3×10^{-1}	7.1×10^{-4}	1.1×10^{3}	2.3
2	5.4×10^{-1}	5.3×10^{-2}	1.6×10^{3}	1.6×10^{2}
3	4.1×10^{-1}	2.1×10^{-2}	1.2×10^{3}	6.2×10

Table 2

Changing in Electrical properties

Discussion

By increasing the S/M bandgap and Transmission reduced and absorption increased. Also, annealing improved electrical properties and heat carriers. The increased sulfur can reduce the Vs effect and annealing can release the excess of sulfur in them and make the structure better.

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