The Effect of Chemical Treatment on TL Glow Curves of CdS/ZnS Thin Films Deposited by Vacuum Deposition Method

N. Dahbi, D-E. Arafah

***Abstract*—**The effect of chemical treatment in $CdCl_2$ and thermal annealing in 400°C, on the defect structures of potentially useful ZnS\CdS solar cell thin films deposited onto quartz substrate and prepared by vacuum deposition method was studied using the Thermoluminesence (TL) techniques. A series of electron and hole traps are found in the various deposited samples studied. After annealing, however, it was observed that the intensity and activation energy of TL signal increases with loss of the low temperature electron traps.

***Keywords*—**CdS, chemical treatment, heat treatment, Thermoluminescence, trapping parameters, thin film, vacuum deposition, ZnS

I. Introduction

In recent years, group II–VI compounds (e.g., CdS, ZnS, CdSe, ZnSe) have been often used for the preparation of light emitting diodes because of their good luminescence properties [1]. Cadmium Sulfide (CdS) and Zinc Sulfide (ZnS) are attracting much attention for efficient use in the fabrication of solar cells and other optoelectronic properties [2]. CdS, which is an n –type direct band gap semiconductor with room temperature gap energy of 2.42 eV, It is highly absorbing for wave lengths below 520 nm, as 0.1 nm of CdS film absorb 36% of incident radiation with energy higher to 2.42 eV [3]. Zinc sulfide (ZnS) on the other hand, has a wide direct band gap (3.7eV) so the combination of the two films produce an $Cd_{1-x}Zn_xS$ thin film which has properties between those of ZnS and CdS, it has a larger energy gap than CdS, thus becoming transparent to practically all wavelengths of solar spectrum [4] which makes the material much more attractive for the fabrication of solar cells, it have been widely used as a broad band gap, window material in hetrojunction photovoltaic solar cells with minimum lattice mismatch in the devices [5].Thermolumnescence experiments are expected to yield useful information on the properties of various types of defects presented within an insulator or semi conductor material. The importance of impurity existence is to give rise to localized energy levels within the forbidden energy gap, and the sensitivity of thermoluminesence in the determination of the distribution of the defect energies is unrivalled, it is capable of detecting as few as 10^{-9} defects level in specimen [6], [7]. It is well known that the TL response of ZnS/CdS films is very sensitive to the structural changes of defects and the presence of shallow and deep trapping levels within the material.Therefore, samples are characterized by TL which gives information about the trapping states defects and clusters present by recording the GL- curve [8]. Electron traps are capable of capturing electrons and holding them for relatively a long period of time. Recombination centers, on the other hand, are levels having the ability to capture holes. The electrons within traps need energy to escape from their levels thus transit to lower energy states. As a result of this recombination of holes with electrons, light is emitted and TL can then be observed [9]. In this work we aim to prepare CdS/ZnS layer thin films by vacuum deposition method, Chemical and thermal activated diffusion can be used to achieve homogeneous $Cd_{1-x}Zn_xS$ thin films that could be characterized by analyzing different Thermoluminescence (TL) Glow-curves to gather information on the energy levels related to the impurities and defects in this thin film.

II. Experimental Details

In the preparation of our CdS/ZnS thin film layer, a 0.07-μm-thick ZnS film was first deposited on Quartz substrate by vacuum deposition with a typical working pressures of 10^{-4} Pa were used during evaporation, this was then dipped in 1% $CdCl_2$ methanol solution for about 30 s to improve the conductivity, then dried with an infrared lamp, and then rinsed in the Deionized water. This was followed by an additional deposition of 0.05-μm CdS thin film; finally the samples were annealed in air at 400 °C for 15min.The system employed for TL-detection was a commercial Pitman TOLEDOO TLD 654 READER, with a research module to control the heating cycle. The glow curves (GL-curves) were obtained from the simultaneously recorded signals of TL-response and temperature; both are functions of time. The Readout system represents all necessary information to obtain the intensity of emitted light versus temperature glow-curve (GL-curve) out on platinum planchet at linear heating rate of 2°C s^{-1}. All the produced samples were irradiated using α-source (2 MeV). Deconvolution of the GL-curves was used to separate the overlapping dosimetric peaks.

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III. Result and Discussion

Materials having the Thermoluminsence property emit light than can be best described by a “Glow curve”, which may present several glow peaks during a heating process. The intensity can than be correlated to the dose initially absorbed by the material , the trapping energy levels are , however classified as being electron traps or recombination centers .The positions and shapes of the glow curves are related to the various parameters of the trapping state. These parameters are namely :the trapping depth (activation energy) below the conduction band E(eV) ; frequency factor (pre-exponential factor) S_0 (s^{-1}) which has lattice vibrations on the order of 10^8-10^{15} s^{-1} in crystalline solid ; Kienetic order b ; and the number of trapped electrons in traps n_0(cm^{-3}).Typical Glow-Curves (GL-curves) obtained from ZnS\CdS thin films produced using vapor deposition method are shown in Fig.1, before and after the chemical treatment; samples representing the above composition were subjected to controlled linear heating profiles.

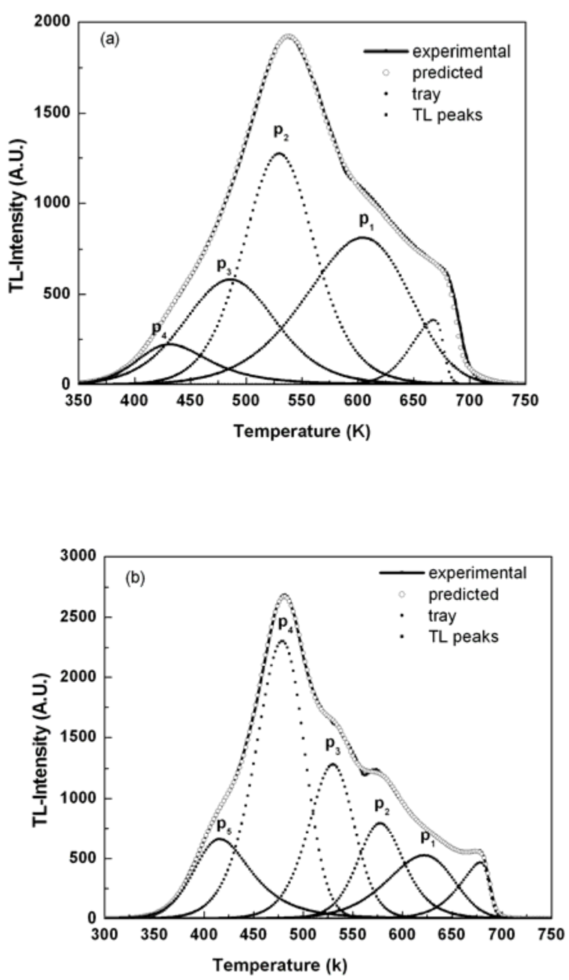

Fig. 1 Total Gl-curve: deconvolution analysis applied to ZnS\CdS thin films: (a) before chemical treatment, (b) after chemical treatment

The GL-curve shown reveals the presence of various states that illustrate the defects present within the material; obviously, several traps are present and occupy different defect states. Close examination of Fig. 1, indicates that the shape and intensity of the GL-curves are drastically changing when a comparison between samples prepared and those after chemical is made. In the as-deposited samples; only four glow peaks are identified, between 441K and 615K; after the application of chemical treatment glow peaks are identified within 416K and 622K their trapping parameters are listed in table. I, the GL-curves indicate a combination of five glow peaks, with their temperature at the center being shifted to higher temperatures by 1%, 8%, the intensity and the activation energy of the peaks has increased too.

TABLE I
TRAPPING PARAMETERS OF ZNS/CDS THIN FIML BY COMPUTERIZED TOTAL GLOW CURVE DECONVOLUTION

after chemical treatment in CdCl2

	E (eV)	Tm(K)	b	n_0 (m^{-3})
P_1	1.008	622	1.1	22595.6
P_2	1.75	577.62	2	24761.9
P_3	1.24	529.87	1.43	38451.1
P_4	0.857	478.79	1.22	73560
P_5	0.79	415..92	2.5	26527.1

The use of heat treatment (HT) in the presence of $CdCl_2$ is, however, known to be beneficiary in improving the performance of solar cells; the defects formed can be of different nature depending on the material, but their characteristics are influenced by heat treatments [8]. Figure2 shows the typical Glow-Curves obtained from ZnS\CdS thin films after annealing in 400°C, trapping parameters are listed in table.2.

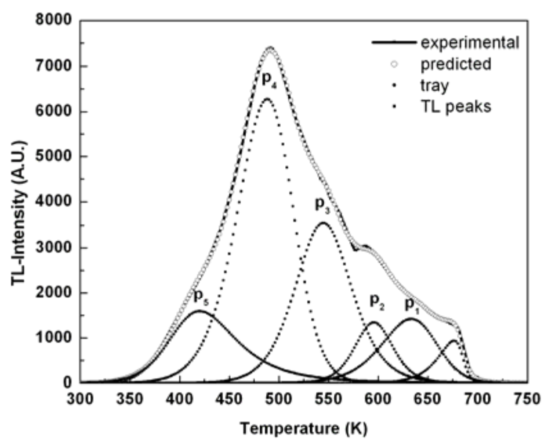

Fig. 2 Deconvoluted TL glow curve of ZnS\CdS thin films after annealing. Separated peaks represent deconvolution procedure using least square method. (See table.II for detailed information)

A closer look indicates that the intensity of various peaks P_1, P_2, P_3, P_4 and P_5 have strongly increased after annealing (better crystallinity) by 125%, 435%, 500%, 2%, and 30% respectively. Amongst the variations noted are those observed on these values; a mixture between first order and general kinetic order is also noted. These findings are consistent with those of Ferekides and his team, who found that HT (Heat treatment) followed treatment with $CdCl_2$ not only affects the CdTe/CdS junction but also enhances the interdiffusion between the semiconductors leading to the formation of a $CdS_{1-x}Te_x$ interfacial layer. The latter is, however, believed to improve current transport in terms of charge carriers as well as affecting the electronic structure of CdTe [10].

TABLE II
TRAPPING PARAMETERS OF ZNS/CDS THIN FIML BY COMPUTERIZED TOTAL GLOW CURVE DECONVOLUTION

ZnS/CdS thin film after annealing in 400 °C				
	E (eV)	Tm(K)	b	n_0 (m^{-3})
P_1	1.39	633.451	1.3	51040.4
P_2	1.17	596.73	1.74	132927
P_3	0.79	544.17	1.3	229774
P_4	0.68	488.3	2.5	74815..3
P_5	2.1	417.63	1.82	33924..5

In general, oxygen impurities are known to be first physically adsorbed at the grain boundaries and on the ZnS surface. On the other hand, oxygen when present at the film surface and at grain boundaries, it acts as luminescent centers [11]-[13]. In addition, the presence of chlorine impurities in the ZnS thin films is trapped at Zn vacancy (V_{Zn})-Cl and (V_{Zn}-Cl) defects. These defects capture free electrons generated after irradiation by highly energetic particles (α-rays) and act as electron traps. In this work, the data obtained from TL glow curves and emission spectra support that V_{Zn}-Cl defects act as traps and O^{-2} impurities act as luminescent centers [14].

IV. Conclusion

We have studied the effect of chemical treatment in $CdCl_2$ and heat treatment at 400°C for 15min on the vacuum deposited ZnS/CdS multilayer, this temperature which is generally the temperature suitable for processing solar cells. It was observed that intensity of TL signal increases markedly after chemical and heat treatments, a series of traps also have been identified in addition to charge transfer and conversion between traps is noted.

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