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Defect Analysis Of CZTS Thin Films Using Photoluminescence Technique

N.Poornima, V.G.Rajeshmon, C.Sudha Kartha, K.P.Vijayakumar

Department of Physics, Cochin University of Science and Technology, Cochin-682022
Corresponding author: kpv@cusat.ac.in

Abstract. Photoluminescence (PL) technique was used to identify defect levels in Copper Zinc Tin Sulphide (CZTS) thin films deposited using Chemical Spray Pyrolysis (CSP). Films were deposited for different Cu:Zn:Sn:S ratios. An emission was observed at 0.8 eV. It was monitored from 15K to room temperature and activation energy was calculated. Excitation power dependent studies were done to analyze the type of transition.

Keywords: Photoluminescence, CZTS, defects.
PACS: 78.55.-m, 81.05.Hd, 68.35.Dv;

INTRODUCTION

The compound semiconductor CZTS is receiving worldwide attention for photovoltaic applications owing to its favorable optoelectronic properties and also the abundance and non-toxicity of its constituent elements [1]. It is essential to have an idea of the band structure of CZTS and the defects in CZTS because they have a profound impact on the device performance. There are reports on first principle calculations of band structure and also defect studies on CZTS [2]. Here we report the identification of defects in spray pyrolysed CZTS thin films prepared for different Cu:Zn:Sn:S ratios.

EXPERIMENTAL TECHNIQUE

CZTS thin films were prepared for Cu:Zn:Sn:S ratios 2:1:1:12, 2.5:1:1:12 and 1:1:1:12 by spraying aqueous solutions of respective salts on to soda lime glass substrates maintained at 350°C and were named A, B and C respectively. For PL studies, these samples were excited with 632.8nm line of He-Ne laser (Melles Griot; output power 15mW) and the PL spectra were recorded with thermoelectrically cooled InGaAs array detector coupled to the computer via custom made software OOIBase32. Excitation power dependent PL measurements were carried out by varying the laser power using neutral density filters. Low temperature PL measurements were performed by mounting the sample in the cold finger of a liquid helium closed cycle cryostat [Janis Research Company Model CCS 202].

RESULTS AND DISCUSSIONS

The room temperature PL spectra of samples A, B and C are shown in Figure 1. An emission centered at ~0.8eV is observed in these samples. The emission was not observed for sample C where the copper concentration was reduced. It could be seen that the emission intensity was higher in sample B and there was a slight shift in peak position with increase in Cu concentration to higher energy (0.81eV).

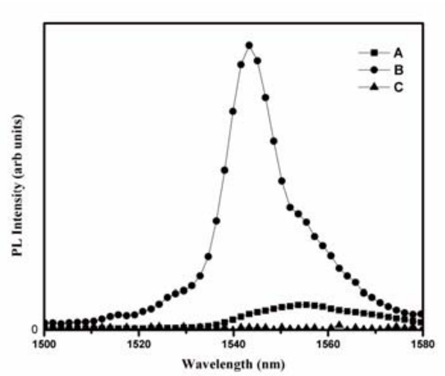

FIGURE 1. Room temperature PL spectrum of samples A, B and C.

In order to calculate the activation energy of the recorded emission, low temperature PL measurements

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were done on these samples. Arrhenius plot (log PLintensity vs 1000/T) of sample A is shown in Figure 2.

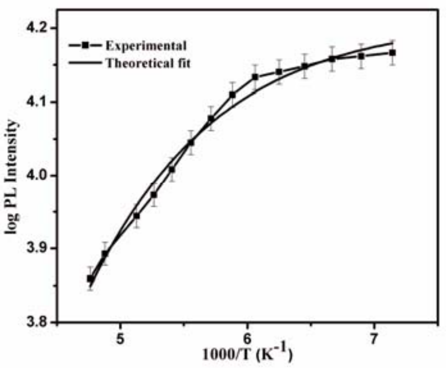

FIGURE 2. Arrhenius plot of sample A.

From the Arrhenius plot, activation energy of ~ 0.1 eV could be obtained. It has already been reported that copper in zinc site [Cu_{Zn}] is the most stable defect with low formation energy in CZTS [3]. Cu_{Zn} is reported to occupy ~0.1eV from the valence band maximum. The activation energy obtained matches closely with reported values. For sample B also we obtained values close to 0.1eV

In order to understand the transition type, excitation power dependent PL measurements were carried out. Figure 3 shows the excitation power dependent PL spectra of sample A.

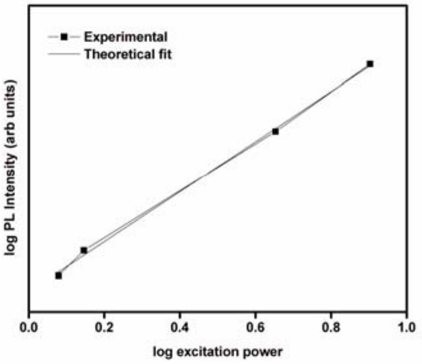

FIGURE 3. Excitation power dependent PL spectrum of sample A.

PL intensity (I) depends on excitation power (P) as $I \alpha P^{\gamma}$ and the value of γ decides the transition type. The transition is donor to acceptor type (DAP) if the value of γ is less than 1. Midgap states have been reported in CZTS thin films due Cu_{Sn}, Cu_{Zn} etc. Oxygen is an unavoidable contaminant in CSP. In sprayed CZTS thin films thus possibility of midgap states due to oxygen cannot be ruled out. In order to check whether it is due to oxygen, films A and B were vacuum annealed and PL was taken. It was interesting to see that the emission was absent. The most probable reason for the disappearance of the emission after vacuum annealing might be the removal of defects due to oxygen. Thus the emission observed at 0.8eV is proposed to be a transition from a mid gap defect due to oxygen to an acceptor created by Cu_{Zn} antisite defect. In order to further confirm the nature of the mid gap defect other studies are in progress.

CONCLUSIONS

The emission centered at 0.8eV observed in PL emission spectra of CZTS film could be identified as due to transition from mid gap defect due to oxygen to an acceptor level created by Cu_{Zn} defect. This was confirmed through PL measurements at different excitation power. The activation energy obtained for Cu_{Zn} defect was ~0.1eV.

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